

Université de Lille – Faculté des Sciences et Technologies

École Doctorale Sciences de la Matière, du Rayonnement et de l'Environnement

Thèse de Doctorat

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Soutenance le **18 décembre 2025**

Magmatisme cénozoïque de l'arc équatorien : chronologie, géochimie et dynamique d'une croûte en évolution

En vue de l'obtention du grade de Docteur de l'Université de Lille

Spécialité : Géosciences, Écologie, Paléontologie, Océanographie

Discipline : Sciences de la Terre et de l'Univers

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Ph.D. course in Earth

Sciences Series XXXVIII

Cenozoic magmatism of the Ecuadorian arc: chronology, geochemistry, and dynamics of an evolving crust

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ABSTRACT

Magmatic arcs are primary sites of continental crust formation and recycling, where the interplay between mantle inputs, crustal architecture, and subduction dynamics controls their evolution and ultimate contribution to continental growth. The Cenozoic magmatic arc of Ecuador provides a natural laboratory to explore these processes. It preserves an almost continuous magmatic record developed across contrasting basement domains, oceanic and continental, that result of the accretion of oceanic lithosphere at the continental margin.

To reconstruct this history, a multiproxy approach integrating zircon U–Pb geochronology, Hf–O isotopes, and trace-element geochemistry, along whole-rock compositions, was applied. Zircon dating established a refined temporal framework, while isotopic and trace-element proxies constrained magma sources, the balance between juvenile and recycled crustal inputs, and the pressure–depth conditions of differentiation.

New data reveal a long-lived magmatic record extending from ~65 to 6 Ma in the south, and from ~41 to 6 Ma along the Western Cordillera (northern and central segments). During the Paleocene–Eocene, magmatism was restricted to the south, where the San Lucas Batholith (65–49 Ma) records mantle-derived melts variably enriched through assimilation of thickened continental crust inherited from Late Cretaceous accretion. Contemporaneous detrital zircon evidence from the forearc indicates more juvenile activity farther north. Between 45 and 15 Ma, magmatism in the Western Cordillera developed over an oceanic-type basement, yielding highly juvenile zircon $\epsilon\text{Hf}_{(t)}$ values that gradually evolved toward slightly enriched sources, likely reflecting minor sediment, or enriched oceanic-crustal input. In contrast, the southern segment displays pronounced isotopic contrasts across the Las Aradas Fault, juvenile, mantle-like magmas emplaced westward into thin, oceanic-affinity crust (e.g., Celica–Lancones basin), and enriched Hf–O signatures eastward, indicating mantle sources modified by sediment assimilation.

After ~15 Ma, the Western Cordillera records a shift toward enriched Hf–O isotopic compositions and trace-element patterns indicative of deepening magma differentiation within the garnet stability field. Adakite-like signatures appear diachronously (~14 Ma in the north, inbetween ~20–11 Ma in the center), likely associated with crustal thickening and enhanced compression triggered by the arrival of the young, buoyant Nazca Plate. In the southern segment, Late Miocene intrusions (13–6 Ma) show also enriched signatures, consistent with magma generation under thicker crust and deeper melting conditions. Crustal thickness

estimates range from ~30 km in thinned domains (45–15 Ma) to >60 km during Miocene compression, matching present-day geophysical constraints.

Collectively, these results show that the Ecuadorian Cenozoic arc evolved as a segment-partitioned system within a transitional subduction setting developed on hybrid continental–oceanic crust. Its magmatic evolution was governed by the interplay between mantle inputs, inherited basement heterogeneity, and crustal thickening. Isotopic signatures primarily reflect source characteristics established at depth, while crustal thickness exerted a first-order control on differentiation. This framework not only refines the temporal and petrogenetic evolution of the arc and establishes a basis for developing segment-specific tectono-magmatic models, but also contributes to advancing our understanding of the evolution of magmatism in complex subduction systems.

RESUME

Les arcs magmatiques constituent des sites essentiels de formation et de recyclage de la croûte continentale, où l'interaction entre les apports mantelliques, l'architecture crustale et la dynamique de subduction contrôle leur évolution et leur contribution finale à la croissance continentale. L'arc magmatique cénozoïque de l'Équateur offre un laboratoire naturel pour explorer ces processus. Il préserve un enregistrement magmatique presque continu, développé sur des domaines de socle contrastés – océaniques et continentaux – résultant de l'accrétion de lithosphère océanique le long de la marge continentale.

Pour reconstituer cette histoire, une approche multiproxy intégrant la géochronologie U–Pb sur zircon, les isotopes Hf–O et la géochimie des éléments traces, complétée par des analyses de roche totale, a été appliquée. Les datations sur zircon ont permis d'établir un cadre temporel raffiné, tandis que les proxys isotopiques et géochimiques ont contraint les sources magmatiques, l'équilibre entre apports juvéniles et recyclés, ainsi que les conditions de pression et de profondeur de différenciation.

Les nouvelles données révèlent un enregistrement magmatique de longue durée, s'étendant de ~65 à 6 Ma dans le sud, et de ~41 à 6 Ma le long de la Cordillère Occidentale (segments nord et central). Durant le Paléocène–Éocène, le magmatisme était limité au sud, où le batholite de San Lucas (65–49 Ma) témoigne de magmas d'origine mantellique enrichis par assimilation d'une croûte continentale épaissie héritée de l'accrétion du Crétacé supérieur. Parallèlement, les zircons détritiques du bassin d'avant-arc indiquent une activité plus juvénile vers le nord. Entre 45 et 15 Ma, le magmatisme de la Cordillère Occidentale s'est développé sur un socle de type océanique, présentant des valeurs de zircon $\varepsilon_{\text{Hf}}(t)$ très juvéniles évoluant progressivement vers des sources légèrement enrichies, traduisant probablement un apport mineur de sédiments ou de croûte océanique enrichie. En revanche, le segment sud présente de forts contrastes isotopiques à travers la faille de Las Aradas : à l'ouest, des magmas juvéniles à signature mantellique se sont mis en place dans une croûte amincie d'affinité océanique (bassin Celica–Lancones) ; à l'est, des signatures Hf–O enrichies indiquent des sources mantelliques modifiées par assimilation sédimentaire.

Après ~15 Ma, la Cordillère Occidentale enregistre une transition vers des compositions isotopiques Hf–O enrichies et des tendances géochimiques indiquant une différenciation magmatique plus profonde dans le champ de stabilité du grenat. Des signatures de type adakite apparaissent de manière diachrone (~14 Ma au nord, entre ~20 et 11 Ma au centre),

probablement associées à un épaississement crustal et à une compression accrue liée à l'arrivée de la jeune plaque Nazca, plus flottante. Dans le segment sud, les intrusions du Miocène supérieur (13–6 Ma) montrent également des signatures enrichies, compatibles avec une genèse magmatique sous une croûte plus épaisse et à des conditions de fusion plus profondes. Les estimations d'épaisseur crustale varient d'environ 30 km dans les domaines amincis (45–15 Ma) à plus de 60 km durant la compression miocène, en accord avec les contraintes géophysiques actuelles.

Dans l'ensemble, ces résultats montrent que l'arc cénozoïque équatorien a évolué comme un système segmenté au sein d'un contexte de subduction transitionnelle développé sur une croûte hybride continentale–océanique. Son évolution magmatique a été gouvernée par l'interaction entre les apports mantelliques, l'hétérogénéité du socle hérité et l'épaississement crustal. Les signatures isotopiques reflètent principalement les caractéristiques des sources profondes, tandis que l'épaisseur crustale a exercé un contrôle de premier ordre sur la différenciation. Ce cadre affine l'évolution temporelle et pétrogénétique de l'arc, établit une base pour le développement de modèles tectono-magmatique spécifiques à chaque segment, et contribue à faire progresser notre compréhension de l'évolution du magmatisme dans les systèmes de subduction complexes.

RIASSUNTO

Gli archi magmatici rappresentano i principali siti di formazione e riciclo della crosta continentale, dove l'interazione tra gli apporti mantellari, l'architettura crostale e la dinamica della subduzione ne controlla l'evoluzione e il contributo finale alla crescita continentale. L'arco magmatico cenozoico dell'Ecuador costituisce un laboratorio naturale per esplorare questi processi. Esso conserva un registro magmatico quasi continuo, sviluppato su domini di basamento contrastanti – oceanico e continentale – risultanti dall'accrescimento di litosfera oceanica lungo il margine continentale.

Per ricostruire questa storia, è stato applicato un approccio multiproxy che integra la geocronologia U–Pb su zircone, gli isotopi Hf–O e la geochemica degli elementi in traccia, insieme alle composizioni di roccia totale. Le datazioni su zircone hanno permesso di stabilire un quadro temporale raffinato, mentre i proxy isotopici e geochemici hanno vincolato le sorgenti magmatiche, l'equilibrio tra apporti crostali giovanili e riciclati, e le condizioni di pressione–profondità della differenziazione.

I nuovi dati rivelano un lungo registro magmatico che si estende da ~65 a 6 Ma nel sud e da ~41 a 6 Ma lungo la Cordigliera Occidentale (segmenti settentrionale e centrale). Durante il Paleocene–Eocene, il magmatismo era limitato al sud, dove il batolite di San Lucas (65–49 Ma) mostra magmi di origine mantellare arricchiti per assimilazione di una crosta continentale ispessita, ereditata dall'accrescimento del Cretaceo superiore. Contestualmente, zirconi detritici provenienti dal settore di avanfossa indicano un'attività più giovanile verso nord. Tra 45 e 15 Ma, il magmatismo della Cordigliera Occidentale si sviluppò su un basamento di tipo oceanico, con valori di zircone $\varepsilon_{\text{Hf}}(t)$ altamente giovanili che evolvono progressivamente verso sorgenti leggermente arricchite, probabilmente a causa di un modesto apporto di sedimenti o di crosta oceanica arricchita. Al contrario, il segmento meridionale mostra forti contrasti isotopici lungo la faglia di Las Aradas: a ovest, magmi giovanili di tipo mantellare si sono intrusi in una crosta sottile di affinità oceanica (bacino Celica–Lancones); a est, firme Hf–O arricchite indicano sorgenti mantellari modificate da assimilazione sedimentaria.

Dopo ~15 Ma, la Cordigliera Occidentale registra un'evoluzione verso composizioni isotopiche Hf–O arricchite e schemi geochemici indicativi di una differenziazione magmatica più profonda, all'interno del campo di stabilità del granato. Firme di tipo adakitico compaiono in modo diacrono (~14 Ma a nord, tra ~20 e 11 Ma al centro), probabilmente associate all'ispessimento crostale e alla maggiore compressione indotta dall'arrivo della giovane e più

galleggiante placca di Nazca. Nel segmento meridionale, intrusioni del Miocene superiore (13–6 Ma) mostrano anch'esse firme arricchite, coerenti con una generazione magmatica sotto una crosta più spessa e condizioni di fusione più profonde. Le stime di spessore crostale variano da circa 30 km nei domini assottigliati (45–15 Ma) a oltre 60 km durante la compressione miocenica, in accordo con i modelli geofisici attuali.

Nel complesso, questi risultati mostrano che l'arco cenozoico dell'Ecuador si è evoluto come un sistema segmentato in un contesto di subduzione transizionale sviluppato su una crosta ibrida continentale–oceanica. La sua evoluzione magmatica è stata governata dall'interazione tra apporti mantellari, eterogeneità del basamento ereditato e ispessimento crostale. Le firme isotopiche riflettono principalmente le caratteristiche delle sorgenti profonde, mentre lo spessore crostale ha esercitato un controllo di primo ordine sulla differenziazione. Questo quadro non solo affina l'evoluzione temporale e petrogenetica dell'arco e fornisce una base per lo sviluppo di modelli tettono-magmatici specifici per ciascun segmento, ma contribuisce anche ad avanzare la nostra comprensione dell'evoluzione del magmatismo nei sistemi di subduzione complessi.

ACKNOWLEDGMENTS

After three years, this stage finally comes to an end, and it cannot be closed without first expressing my gratitude to all those who, in one way or another, were part of this journey. I hope not to overlook anyone, but rest assured that I carry you all in mind.

My deepest gratitude goes to my thesis advisor, César Witt, for his guidance, teaching, and constant support throughout the PhD. Thank you for your patience since that first, somewhat disastrous draft, for the friendship, the field anecdotes, the beers, the “ricards” why not, and above all for helping me to discover the world of research in a more meaningful way. I am also grateful for the opportunity to continue exploring the hidden corners of Ecuador through field campaigns, always filled with stories, good food, and, of course, samples. At the University of Lille, I also wish to thank Olivier Averbuch and Frank Chanier for their scientific contributions and insightful discussions, which greatly enriched the chapters presented here. Finally, at the University of Padova, I am deeply grateful to my co-supervisor, Massimiliano Zattin, for being part of this project and for his invaluable guidance and teaching in thermochronology.

I would also like to express my heartfelt gratitude to Monique Seyler, Olivier Bruguier, Marc Pujol, Osman Poma, María José Hernández, Delphine Bosch, Valérie Bosse, François Guillot and Nordine Bouden. Their expertise and knowledge were essential both for the acquisition and interpretation of data through the different methodologies applied in this project, as well as for the invaluable discussions that helped refine this work. I am also grateful to Sandra Procel for her support and assistance at the Escuela Politécnica Nacional in Quito.

My appreciation also goes to the University of Lille, the *École Doctorale Sciences de la Matière, du Rayonnement et de l'Environnement (ED SMRE)*, the Laboratory of Oceanology and Geosciences (LOG), IREPSE, and the Graduate Program for providing the academic, financial, and technological resources necessary for the development of this doctoral research.

I am grateful to all the people I met and shared time with in SN5, and to those who offered invaluable help, especially Sandra and Alexandre. To Monique Gentric, thank you for your constant positive energy, for bringing joy to all of us, and especially for your tireless support of doctoral students, without your guidance through bureaucracy, we would surely have been lost. My heartfelt thanks also go to my friends with whom I shared countless moments, Imene, Rachid, Mathilde, Zhenyu, Noé, Bouba, Fang-Yi, Fabien, Gaia, Claire and Wilman, for making life in Lille warmer than the weather itself.

I am equally grateful to my friends in Padova, Ricardo, Patrick, and Xiaoqin, who, over a spritz or a gelato, made my time in Italy much more enjoyable. My sincerest thanks also go to Caro, with whom I began this project; through ups and downs, we made it to the end, what a pleasure it has been to share this path with you, *ma fren*. To my friends at the residence, with whom I connected through exercise and daily life in Lille, thank you, especially Azu, for the desserts and the wonderful conversations.

Finally, my deepest gratitude goes to Louise and Teo, my family in France. Thank you for the countless stories, festivals, late nights, pétanque tournaments, and for your energy, which has been a fundamental part of completing this thesis.

On a personal level, I wish to acknowledge the unconditional support of my family. You have been my driving force since the very first day. Thank you for your understanding, encouragement, and trust during both the good and the difficult times, you gave me the strength to carry on and complete this project. You were my daily motivation. I love you all.

The final lines of this acknowledgment are dedicated to you, Tamara. Thank you for your support in every moment, both good and bad, and for showing me how to find the light in each day. Your presence fills me with peace and gives me the energy to keep moving forward. We have crossed this finish line together. I love you.

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CHAPTER 1: Introduction

1.1 Overview of Magmatism in Convergent Margins

Active convergent margins are fundamental components of Earth's tectonic system, defined by the subduction of an oceanic plate beneath a continental or oceanic plate (Wilson, 2007). These margins are responsible for a significant proportion of the Earth's magmatism, the formation of mountain ranges, and the generation and recycling of continental crust (Ducea et al., 2015; Stern, 2002). They also host a significant part of global seismic and volcanic activity, making them critical regions for understanding both geodynamic evolution and natural hazards (Stern et al., 2016). Moreover, convergent margins are of considerable economic interest, as they are commonly associated with the formation of metallogenic belts rich in copper, gold, and other valuable resources derived from magmatic–hydrothermal processes (Richards, 2011). Magmatic arcs constitute the surface expression of the interaction between the subducting slab, the overlying mantle wedge, and the upper crust, which collectively controls their genesis and evolution.

Magmatic arcs are broadly classified according to the nature of the crust upon which they are built: island arcs, developed on oceanic crust (e.g., the Caribbean, Aleutian, Kamchatka, Japanese, and Mariana arcs), and continental arcs, principally formed on continental crust (e.g., the Andes, the Central American Volcanic Belt, the Mexican Volcanic Belt, and the Cascades) (Gill, 2009; Wilson, 2007; Winter, 2014).

Continental arcs, also referred to as Andean- or Cordilleran-type arcs, develop on continental crust, but may also form on accreted transitional crust, consisting of fragments of oceanic crust that have become incorporated into the active continental margin., as exemplified by the Andean Arc (Ducea et al., 2015a). They play a fundamental role in the evolution of the continental crust, as they are key sites of crustal generation, differentiation, and recycling (Tatsumi, 2005). Compared with island arcs, continental arcs are characterized by thicker crust, heterogeneous basement lithologies, and longer-lived tectono-magmatic histories, factors that promote more complex interactions between mantle-derived magmas, slab-derived fluids, and the overlying crust (DeCelles et al., 2009; Paterson and Ducea, 2015; Pearce and Peate, 1995). These conditions enable processes such as crustal assimilation, deep crustal magma storage and differentiation, and compositional evolution linked to progressive crustal thickening,

processes that are critical for understanding continental crust growth and reworking through geological time (Chapman et al., 2015; Kay et al., 2005; Profeta et al., 2015).

1.2 Controls on magma composition

Magma is a mixture of molten or partially molten silicate material, crystals, and volatiles, that forms through partial melting in response to variations in pressure, temperature, and volatile content within the mantle and crust, representing the main agent of chemical differentiation within the Earth (Gill, 1981; Wilson, 2007; Winter, 2014). The chemical composition of arcs at convergent margins reflects the interplay between tectonic and magmatic processes, including melting, assimilation, and differentiation within the arc crust, operating at multiple spatial and temporal scales (Stern, 2002; Tatsumi, 2005; Wilson, 2007). Both the physical (e.g., mantle flow, magma ascent) and chemical (e.g., slab dehydration, mantle metasomatism, crust assimilation) processes associated with subduction, together with the tectonic evolution of the upper plate, exert first-order controls on the nature of the magmas generated, their sources, and their subsequent differentiation paths (Ducea et al., 2015a; Hawkesworth et al., 1993; Pearce and Peate, 1995).

Arc magmatism is influenced by two primary sets of tectonic factors: external parameters related to processes occurring outside the arc itself and internal factors linked to the evolution of the overriding plate (e.g., Horton, 2018; Jara et al., 2021; Paterson and Ducea, 2015). External factors include changes in plate-tectonic motions such as variations in slab dip, convergence angle, and the degree of interplate coupling, all of which can modify subduction dynamics and trigger processes like subduction erosion (e.g., Chapman et al., 2013; Lallemand et al., 2005; Savignano et al., 2016). For instance, a decrease in slab dip or a shallower subduction angle tends to broaden the arc-trench gap and shift magmatic activity landward, as the locus of fluid release from the slab migrates beneath thicker crustal sections (e.g., Manea et al., 2017; Syracuse and Abers, 2006). Conversely, a steeper slab promotes more localized magmatism closer to the trench and enhances mantle wedge melting efficiency. Changes in convergence rate and plate coupling can also influence the thermal structure of the subduction system, controlling the degree of mantle wedge hydration and melt generation (e.g., Lallemand et al., 2005).

In contrast, internal factors are related to the geodynamic evolution of the upper plate, including upper-plate thickening, thrust belt shortening and delamination. These processes

modulate magma storage, differentiation, and ascent through the crust (DeCelles et al., 2009; Ducea et al., 2015a; Horton, 2018). For example, crustal thickening increases the pressure gradient and promotes extensive magma differentiation and crustal assimilation, leading to more evolved magmatic compositions (DeCelles et al., 2009; Ducea et al., 2015a). Similarly, delamination or removal of dense lithospheric roots can induce asthenospheric upwelling, enhancing magma generation, and rejuvenating magmatism within previously thickened arcs (e.g., Ducea, 2011; Kay and Kay, 1993).

Overall, the interplay between these external and internal parameters, which remains a subject of ongoing debate, governs not only the spatial and temporal distribution of magmatism but also the chemical and isotopic evolution of arc systems through time. Based on mineral geochemistry, particularly zircon records, several studies propose that long-term cyclic trends in zircon compositions reflect predominantly internal crustal processes, with little relation to external tectonic forcing (e.g., Farner and Lee, 2017; Genge et al., 2025; Kirsch et al., 2016; K. Liu et al., 2024). In contrast, other investigations attribute short-term geochemical variations to external controls, particularly slab dynamics (e.g., Chapman et al., 2013; Chapman et al., 2015). Furthermore, recent studies suggest that slab dynamics dominate during extensional periods, whereas both external and internal processes exert significant influence during compressional stages (Jara et al., 2021)

At the magma source level, slab dehydration plays a main role. As the oceanic lithosphere subducts, progressive metamorphism from blueschist to eclogite facies releases aqueous fluids rich in H₂O, Cl, and other volatiles (Hacker et al., 2003; Stern, 2002; Tatsumi, 2005). These fluids percolate into the overlying peridotitic mantle wedge, lowering its solidus and generating calc-alkaline basaltic magmas (Ducea et al., 2015a; Pearce and Peate, 1995; Tatsumi, 2005). The chemical composition of the resulting magmas depends on the relative contributions of slab-derived fluids, melts from subducted sediments or altered oceanic crust, and the mantle wedge itself (Pearce and Peate, 1995; Ulmer, 2001). Fluid-dominated inputs produce the typically arc signature, moderate enrichment in large-ion lithophile elements (LILE: Rb, Ba, K) and depletion in high-field-strength elements (HFSE: Nb, Ta, Ti) (Elliott, 2004; Gill, 2009; Spandler & Pirard, 2013). In contrast, a greater contribution from melts generated by partial melting of the subducted oceanic crust or sediments produces higher concentrations of fluid-immobile elements such as LREE, HFSE (e.g., La, Ce, Nb), and some LILE (e.g., Be and Th) (Pearce and Peate, 1995; Plank and Langmuir, 1998). Such slab-derived melts are commonly associated with adakitic compositions as originally defined by Defant and Drummond (1990), although similar geochemical signatures may also result from other

processes, such as fractional crystallization of garnet-bearing assemblages from mafic magmas (e.g., Macpherson et al., 2006).

Once generated, mantle-derived magmas ascend into the crust, where upper-plate architecture and tectonic regime become critical in controlling their evolution. Thickened crust promotes magma ponding at deep levels, allowing prolonged differentiation under high-pressure conditions, while extensional settings favour rapid ascent and limited crustal assimilation (Annen, 2009; Annen et al., 2006; Chapman et al., 2015; Profeta et al., 2015). Differentiation processes like assimilation–fractional crystallization (AFC) and magma mixing processes superimpose additional chemical signatures (Annen et al., 2006; DePaolo, 1981; Hildreth and Moorbath, 1988), modulating isotopic ratios (e.g., Sr–Nd–Pb–Hf) and trace element systematics inherited from the mantle source.

1.3 Geological Framework

The Andes represent the largest active orogenic system in the world, resulting from the Mesozoic–Cenozoic subduction of Pacific oceanic plates beneath the South American margin. Based on structural features and volcanic segmentation, the Andes are usually divided into three main morpho-structural domains: the Northern (12°N–4°S), Central (4°–46°S), and Southern Andes (46°–55°S; Fig.1; Ramos, 1999, 2009). At the southern end of the Northern Andes, Ecuador preserves a long and complex subduction history that has been marked by several processes, including oceanic accretions, and ridge subductions, which have been major players in the geodynamic regime of the region and that collectively shaped the lithospheric architecture on which the Cenozoic magmatic arc was constructed (Kerr et al., 2002; Vallejo et al., 2009; Michaud et al., 2009).

The Northern Andes, encompassing Venezuela, Colombia and Ecuador (Winter, 2014), are distinguished by the presence of oceanic rocks forming the basement of the forearc basins and the Western cordillera of both Ecuador and Colombia (Aizprua et al., 2020; Hernández et al., 2020; McCourt et al., 1984; Villagómez et al., 2011). This oceanic basement reflects a complex history of accretionary events interpreted either as a single Late Cretaceous event (75–65 Ma; Luzieux et al., 2006; Vallejo et al., 2009) or as multiple accretionary episodes extending into the Eocene (Hughes and Pilatasig, 2002; Jaillard, 2022; Jaillard et al., 2009; Kerr et al., 2002). These accreted terranes consist of allochthonous mafic sequences with oceanic plateau affinities (~92–88 Ma) and arc-related rocks (85–72 Ma) generated by subduction beneath the plateau prior to accretion (e.g., Seyler et al., 2021; Vallejo et al., 2009; Whattam & Stern, 2015).

In Ecuador, most of the boundary between this oceanic basement and the continental paleo-margin is defined by the Calacali–Pujilí–Pallatanga fault system (CPP; Fig. 1.2, Hughes & Pilatásig, 2002), which continues northward into Colombia as the Romeral fault system (e.g., Chicangana, 2005; Vinasco, 2019).



Figure 1.1 Geodynamic setting of the South American convergence system. The map shows the division and extent of the Northern, Central, and Southern Andes, as well as the distribution of flat-slab segments along the Andean margin (Bucaramanga, Peruvian, and Pampean). The main tectonic plates are highlighted (Nazca, Cocos, Caribbean, South American, Antarctic, and Scotia plates), together with key bathymetric features such as the Nazca and Iquique ridges. Data sources include a Digital Elevation Model (ESRI) and bathymetric data (GEBCO). Also indicated are Quaternary volcanoes and the limit of the Andean region (after Ramos, 1999)

The continental basement in Ecuador is exposed in two major geological domains: the Eastern Cordillera and the Amotape terrane. The Eastern Cordillera consists mainly of Paleozoic metamorphic rocks intruded by Triassic granitoids (Spikings et al., 2015; Witt et al., 2017), whereas the Amotape terrane constitutes a distinct major crustal block bounded to the south by the Celica–Lancones Basin and composed of metamorphic rocks intruded by Triassic plutons (Aspden et al., 1995; Bosch et al., 2002; Riel et al., 2013; Sandoval-Espinel et al., 2025). The geological affinity of the Amotape block remains debated: it has been interpreted

either as an allochthonous fragment accreted to the continental margin during the late Paleozoic to early Mesozoic (Mourier et al., 1988; Ramos, 2009; Winter et al., 2010), or as the southern continuation of the Eastern Cordillera and the Peruvian Olmos terrane (Aspden et al., 1992; Witt et al., 2017). Recent detrital zircon ϵHf_t from southern Ecuador and northern Peru provide further constraints, showing very negative values (-20 to -40), consistent with melting of ancient cratonic sources rather than juvenile oceanic material (Sandoval-Espinel et al., 2026). These isotopic signatures closely resemble those from northeastern South America (Hueck et al., 2022; Milhomem Neto and Lafon, 2019), reinforcing the continental character of this region in contrast to the accreted oceanic terranes farther north.

The Cretaceous tectono-magmatic evolution in Ecuador was marked by significant changes in subduction geometry and magmatic styles. Early Cretaceous magmatism coincided with a major change in subduction direction from ESE to NNE and with slab steepening that promoted an extensional regime, facilitating the formation of lower crustal domains with oceanic affinities (Gabriele, 2002; Riel et al., 2014). This early Cretaceous magmatism was primarily mantle-derived and evolved at upper to middle crustal levels (Sandoval-Espinel et al. 2026). During the Middle Cretaceous, magmatism migrated westward and was coeval with the opening of the Celica–Lancones Basin in southern Ecuador, a rifted arc system driven by back-arc spreading, possibly triggered by a slab rollback process (Jaillard et al., 1999; Sandoval-Espinel et al. 2026; Winter et al., 2010). By the Late Cretaceous, magmatic activity took place under a compressional regime, and its compositional features reflect the contribution of sources with oceanic affinities (Sandoval-Espinel et al., 2026).

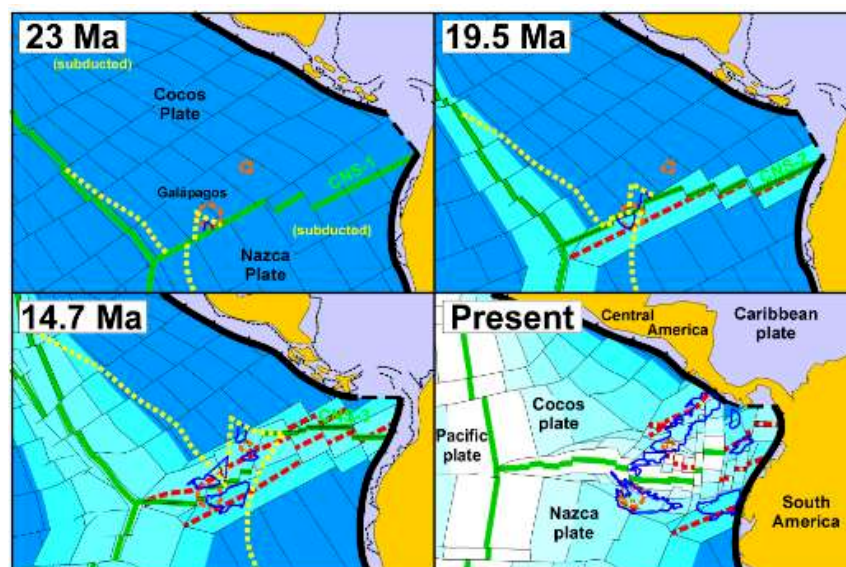


Figure 1.2 Paleogeographic reconstruction showing the plate-tectonic evolution of the Cocos and Nazca plates through time. Modified after Meschede and Barckhausen (2001).

Following the Cretaceous arc, a distinct Cenozoic magmatic arc began to develop around 60 Ma, as evidenced by Paleocene intrusions such as the San Lucas Batholith in southern Ecuador and the widespread occurrence of magmatic zircons in the detrital record (George et al., 2021; Witt et al., 2023). The Cenozoic evolution of the Ecuadorian margin records the progressive eastward subduction of the Farallon plate and, following its

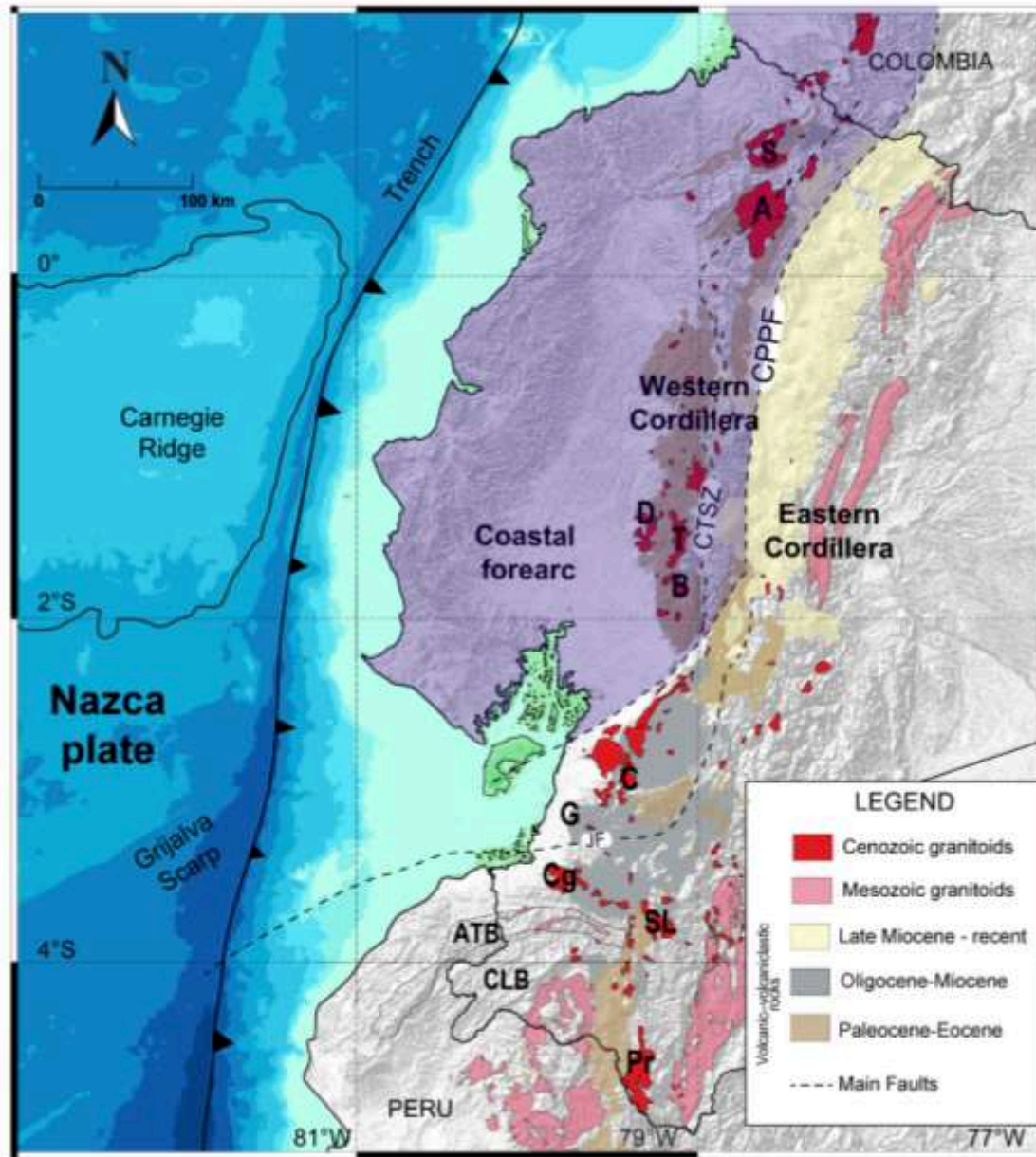


Figure 1.3 Geodynamic sketch of Ecuador highlighting the location of the Cenozoic arc. Major intrusive bodies are labeled as follows: S–Santiago, A–Apuela, D–Domo, T–Telimbela, B–Balzapamba, C–Chaucha, G–Gaby, Cg–Cangrejos, SL–San Lucas, and Pr–Portachuela. Also shown are the ATB–Amotape Tahuin Block, the CLB–Celica Lancones Basin, CPPF–Calacali Pallatanga Pujili fault, CTSZ–Chimbo Toachi Shear Zone, JF–Jubones fault. Oceanic accreted terranes are shown in blue. Data sources include a Digital Elevation Model (ESRI) and bathymetric data (GEBCO). Geology of Ecuador and northern Peru modified from Egüez et al. (2017) and INGEMMET.

fragmentation in the early Miocene (~23 Ma; Lonsdale, 2005; Meschede & Barckhausen, 2001), the subsequent subduction of the Nazca plate beneath the South America. The subduction of the Carnegie Ridge represents another major tectonic feature, with proposed initiation subduction ages ranging from ~2 to 15 Ma, and the best estimates around 5-6 Ma (Gutscher et al., 1999; Hernández et al., 2020; Michaud et al., 2009; Spikings et al., 2010).

In addition to the inherent complexities introduced by the accretion of multiple oceanic terranes and the subsequent fragmentation of the subducting plates; the Cenozoic tectonic evolution of the region was further shaped by alternating stress regimes. Periods of progressive crustal thickening and arc maturation, which favoured the generation of intermediate to silicic magmas with distinct geochemical signatures typically associated with compressional settings, are thought to be intermittently disrupted by episodes of tectonic extension (Chiaradia, 2009; George et al., 2021; Schütte, Chiaradia, et al., 2010; Witt et al., 2023).

Intrusive rocks dominate over volcanic successions between 1–2°S of the Ecuadorian arc. In contrast, in the southern-central segment both lithologies occur in nearly equal proportions, suggesting a higher degree of magmatic record preservation and exposure, and less erosion towards 2–4°S (Fig. 1.3). This implies that the central-southern arc segment more accurately documents the spatial and temporal evolution of arc migration. Based on the distribution of plutonic and volcanic ages along and across the arc distribution, Schütte et al. (2009) identified a relatively stable Paleocene–Eocene arc, followed by Late Oligocene broadening associated with a westward shift of the frontal arc by approximately 50 km in central-southern Ecuador. This feature is less evident farther north due to structural control and erosion of Oligocene–Miocene volcanic rocks. A subsequent Early–Mid Miocene eastward migration of the frontal arc was followed by a Late Miocene–Holocene phase of broad eastward expansion affecting both frontal and rear arc domains (Fig. 1.3). These patterns, reported by Schütte et al. (2009), reflect a relative Late Oligocene–Early Miocene flare-up phase, characterised by increased magmatic productivity rather than a large-scale flare-up in the strict sense.

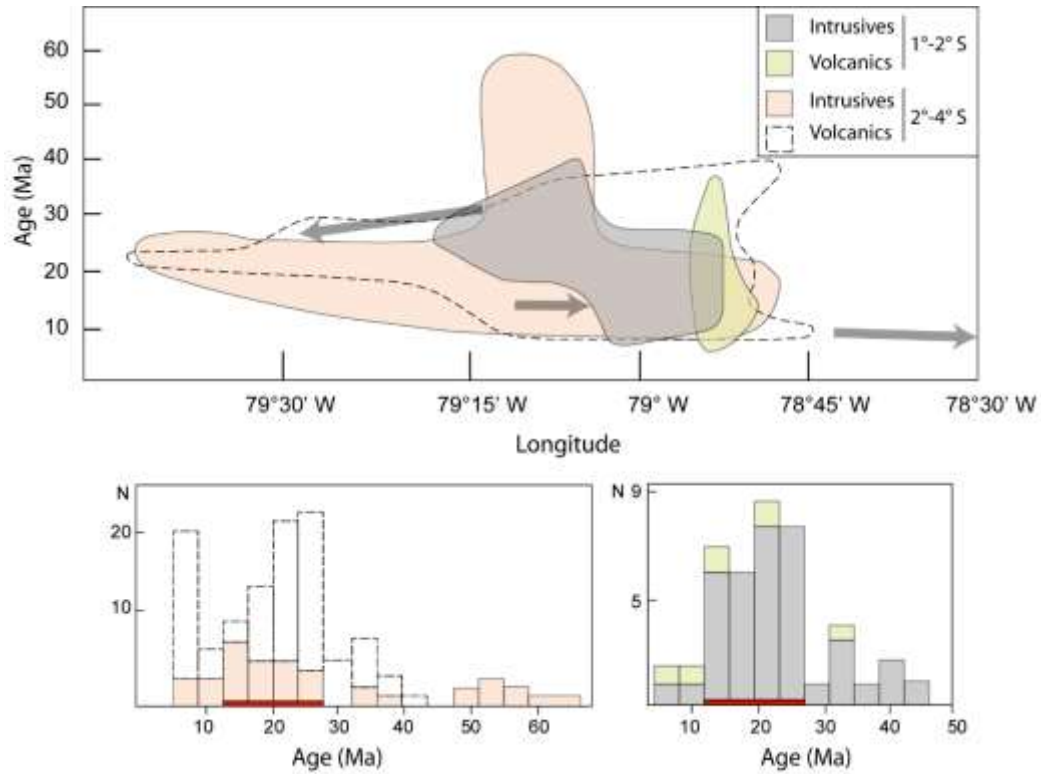


Figure 1.4 Radiometric ages of plutonic and volcanic rocks versus longitude, with age histograms showing sample distribution by arc segment. Red bars mark periods of peak magmatic activity (“flare-ups”) between 1° and 4°S. Modified from Schütte et al. (2010); age references therein.

The Cenozoic magmatic arc was subsequently emplaced across contrasting crustal domains: accreted oceanic terranes north of the CPP (north of 3°S) and autochthonous continental basement composed mainly of Paleozoic metamorphic rocks and Triassic intrusions south of the CPP (south of 3°S) (Jaillard, 2022; Sandoval-Espinel et al., 2026; Vallejo et al., 2009; Witt et al., 2017). Nevertheless, the tectono-magmatic architecture appears more heterogeneous than this binary model, with transitional zones and local occurrences of oceanic basement south of the CPP (this study).

1.3.1 Cenozoic magmatism on oceanic crustal domains

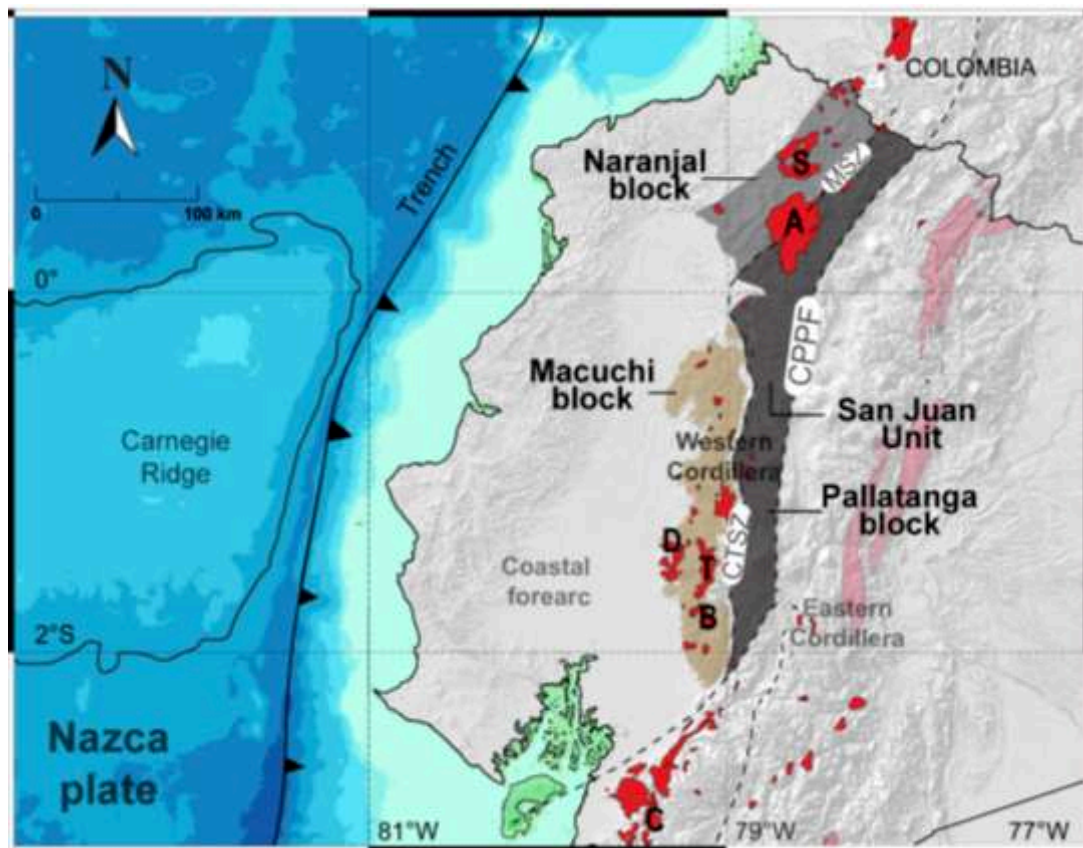


Figure 1.5 Simplified geological map showing the main crustal blocks interpreted along western Ecuador. Modified after Aizprua et al (2020) and references therein. Shown are the CPPF–Calacali Pallatanga Pujili fault, CTSZ–Chimbo Toachi Shear Zone, MSZ–Mulaute Shear Zone.

As mentioned above, Late Cretaceous plateau-type oceanic crust forms the basement of the Cenozoic forearc and Western Cordillera. The central segment of the Western Cordillera (0°–2°S) is primarily composed of three major crustal blocks define the forearc basement (Fig. 1.4): (1) The Pallatanga block comprises Early–Late Cretaceous mafic to ultramafic lithologies (basalts, gabbros, dolerites) overlain by volcanoclastic sediments, showing enriched MORB signatures indicative of a mantle plume origin (Kerr et al., 2002; Mamberti et al., 2003; McCourt et al., 1997; Vallejo et al., 2009). It represents an oceanic plateau sequence forming the basement of the Western Cordillera and includes Late Cretaceous volcanoclastic deposits and basaltic lavas of the Río Cala arc. Its easternmost sector, the San Juan unit, includes serpentinized peridotites, dolerites, and hornblende-bearing gabbros, and is interpreted as the intrusive equivalent of this plateau sequence, with U–Pb zircon ages of ~87 Ma constraining its crystallization (Jaillard, 2022; Kerr et al., 2002). (2) The Macuchi block, is in contact with Pallatanga along the Chimbo–Toachi fault, consists mainly of volcanoclastic material, basaltic

pillow lavas, andesitic to basaltic tuffs, breccias, and volcanic turbidites deposited in a submarine environment (Hughes and Pilatasig, 2002; Vallejo et al., 2009). Previously defined by geochemical data as an oceanic island arc active during the Late Eocene (Kerr et al., 2002; Hughes and Pilatasig, 2002), the Macuchi arc was later interpreted by Vallejo et al. (2009, 2016) as autochthonous, having developed on a thickened oceanic plateau crust during the Late Eocene (42–38 Ma); however, the timing of the onset and of the associated volcanoclastic deposits is still not well defined. (3) The Naranjal block, north of the Macuchi domain, bounded by the Mulaute shear zone (Fig. 1.4), comprises basaltic pillow lavas and andesites of volcanic arc affinity, probably correlating with the Ricaurte arc in southern Colombia (Boland et al., 2000; Kerr et al., 2002; Spadea and Espinosa, 1996; Vallejo, 2007). Collectively, these units form a fault-bounded mosaic of oceanic terranes representing accreted plateau fragments and associated arc systems later reworked during Cenozoic magmatism.

These blocks were intruded by type-I calc-alkaline granitoids, including Santiago, Apuela, El Corazón, Telimbela, Balzapamba, Echeandía, Undushig, among others (Fig. 1.2), many of which host porphyry-type and volcanogenic massive sulfide (VMS) deposits (McCourt et al., 1997; PRODEMİNCA, 2000; Vallejo et al., 2016). Some granitoids and high-level andesitic to dacitic intrusions of the Macuchi arc display adakite-like geochemical signatures, interpreted as resulting from interaction between mantle-derived magmas and intermediate to felsic melts within a thickened juvenile crust (Chiaradia, 2009; Vallejo et al., 2016). Alternatively, they may record a temporal shift from shallow, low-pressure fractionation of basaltic magmas to deeper-level differentiation during crustal thickening around 9 Ma, likely associated with the initial subduction of the aseismic Carnegie Ridge (Chiaradia, 2009; Chiaradia et al., 2004).

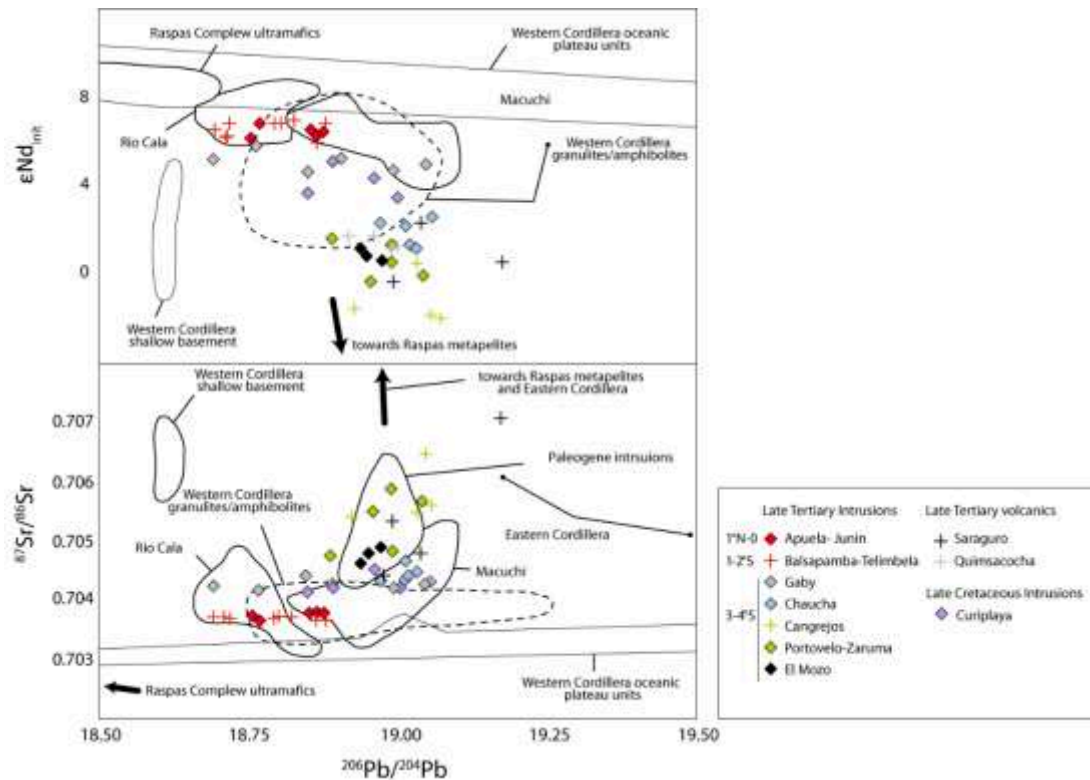


Figure 1.6 Sr, Nd, and Pb isotope compositions of Cretaceous to Late Tertiary intrusions, showing isotopic fields for potential crustal assimilants and magmas in the Ecuadorian Northern Andes. Modified from Schütte (2009a), references for isotopic fields therein.

Although the Western Cordillera hosts economically important mineral deposits, systematic geochronological and isotopic data remain limited. Previous isotopic studies have been largely restricted to Late Oligocene–Miocene magmatic units (Schütte, 2009a), leaving the Eocene record poorly constrained (Fig 1.5). Whole-rock Sr–Nd–Pb isotope variations reveal marked along-arc segmentation, interpreted as reflecting variable contributions from oceanic versus continental crustal sources at depth (Schütte, 2009a). A transition at around 9 Ma, although based on limited chronological evidence, has been inferred from whole-rock geochemistry, marking a shift from MORB-like mantle affinities to adakitic-like compositions (Chiaradia et al., 2004). This transition reflects progressive deepening of magma differentiation from shallow (<20 km) to deep (>40–50 km) crustal levels, a process thought to be related with crustal thickening (Fig. 1.6; Chiaradia et al., 2004). Earlier occurrences of adakitic-like signatures were also reported in the Eocene Macuchi arc (Chiaradia, 2009), representing mantle-derived melts evolving within the lower–mid crust of a thickened juvenile basement. These adakitic-like signatures, intercalated with calc-alkaline magmatism, persisted into the Neogene, and are interpreted as evidence of enhanced coupling between the subducting and

overriding plates, the establishment of deep crustal magma reservoirs, and progressive crustal thickening associated with the arrival of buoyant oceanic features such as the Carnegie Ridge.

Other models mainly based in zircon detrital record emphasize tectonic controls such as slab rollback and trenchward arc migration around ~40 Ma, which coincided with a transition from isotopically enriched to more juvenile magma sources as the arc shifted from continental crustal domains toward accreted oceanic terranes (Fig. 1.6; George et al., 2021). This model, mainly constrained by isotopic and U–Pb zircon data from the forearc and intramontane basins of southern Ecuador, provides a valuable regional framework for late Paleogene magmatism. However, other studies indicate that these areas primarily record the evolution of the arc developed over continental basement of southern Ecuador and northern Peru, rather than the segment emplaced on accreted oceanic crust to the north (Witt et al., 2017, 2023). Because the elevation of the Western Cordillera at the onset of forearc basin development was already sufficient to form a barrier throughout the Cenozoic, no direct connection likely existed between the forearc and the intramontane basins. These findings highlight that zircon provenance and isotopic variations along the margin reflect distinct crustal domains.

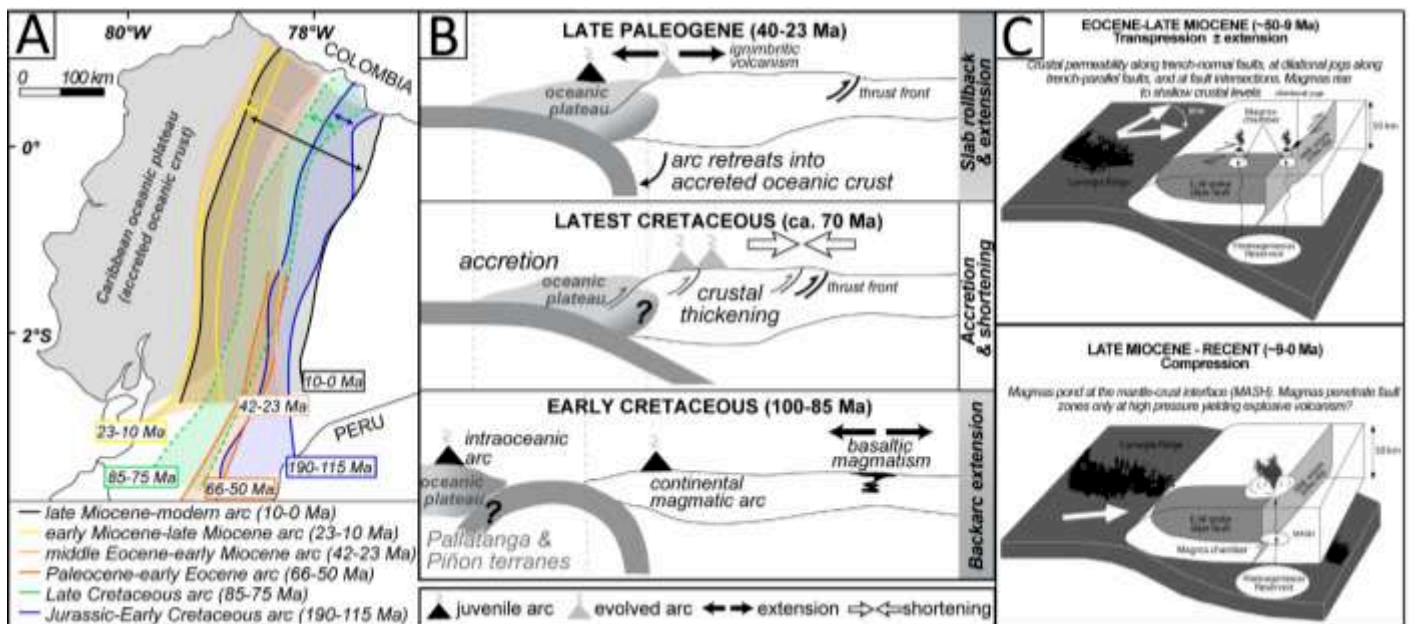


Figure 1.7 Model of George et al. (2021) showing A) the reconstructed locations of magmatic arcs in Ecuador since ca. 200 Ma, along with schematic B) cross sections illustrating the tectonomagmatic evolution of the Ecuadorian margin. C) Geodynamic model of Chiaradia et al. 2004. Modified from George et al. (2021) and Chiaradia et al. (2004).

1.3.2 Cenozoic magmatism on continental crustal domains

In central and southern Ecuador, intrusive magmatism spans from the Paleocene to the Late Miocene. The oldest recognized body is the San Lucas pluton, with ages between 68 and

51 Ma (Aspden et al., 1992). Within the central arc segment, the Chaucha batholith records emplacement ages between 13.3 and 9.8 Ma (Kennerley, 1980). To the southwest, along the margin of the Amotape terrane, the Cangrejos–Zaruma intrusive belt formed predominantly during the Miocene. The nearby Gaby–Papa Grande intrusive complex yielded a K–Ar age of 19.3 ± 1.0 Ma (PRODEMICA, 2000). Farther south, Portachuela batholith range from Early to Mid-Miocene (Chen et al., 2022a; Aspden et al., 1992; Jaillard et al., 1996).

For the magmatic arc emplaced onto autochthonous continental crust south of $\sim 3^\circ\text{S}$, only limited temporal and geochemical constraints have been established. Schütte et al. (2010) documented a major Late Oligocene–Early Miocene magmatic flare-up, coeval with reduced subduction obliquity and accelerated convergence rates, based on in situ geochemical and isotopic evidence (Fig. 1.3 and 1.4). This episode was thought to be followed by an along-arc broadening during the Mid- to Late Miocene, attributed to episodes of shallow slab subduction.

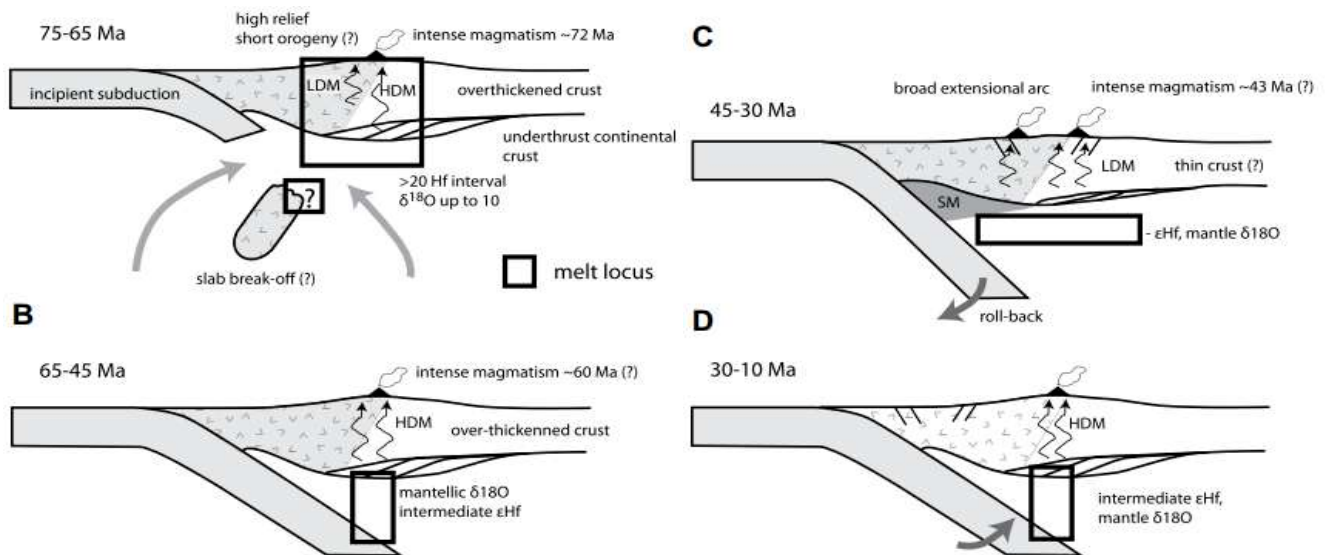


Figure 1.8 Model of Witt et al. (2023) illustrating the proposed tectonomagmatic configuration after the main accretion event, including zircon compositional signatures and inferred magmatic reservoirs (black rectangles). Abbreviations: HDM—high-differentiation magmatism; LDM—low-differentiation magmatism; SM—serpentinized mantle.

Complementary evidence from detrital zircon data sourced from southern Ecuador provides additional insights into the Late Cretaceous and Cenozoic evolution of the arc. The Late Cretaceous isotopic record (75–65 Ma), reflects strong crustal assimilation and the onset of continental arc stabilization following terrane accretion (George et al., 2021; Witt et al., 2023). During the Cenozoic, detrital zircon data reveal contrasting mantle- versus crustal-derived isotopic signatures and possible pulses of enhanced magmatic activity around ~ 60 and ~ 43 Ma, followed by a long-term trend toward less enriched magmas between 30 and 10 Ma

(Fig. 1.7; Witt et al., 2023). These variations reflect alternating mantle and crustal contributions to magma generation, possibly related to shifts between compressional and extensional regimes.

Together, these models depict a magmatic system strongly modulated by changing convergence parameters, crustal architecture, and the temporal superposition of compressional and (less constrained but likely) extensional tectonic regimes. Although the detrital zircon record retains robust U–Pb ages and geochemical–isotopic signatures that reveal the long-term evolution of crustal sources when a reliable source-to-sink model is proposed, it lacks the spatial and petrogenetic context of the magmatic systems from which the grains were derived; underscoring the need for more comprehensive isotopic and geochronological in-situ data to better constrain the spatio-temporal evolution of magmatism and to accurately link detrital records with their magmatic sources.

1.3.3 Regional Context of the Northern Andean Cenozoic Arc

To place the Ecuadorian Cenozoic arc within its broader Andean context, it is essential to consider the along-strike continuity of magmatic and tectonic processes across the northern Andes, particularly in southwestern Colombia and northern Peru. Regionally, Cenozoic magmatism in these areas defines a likely continuous magmatic belt linking southern Colombia with northern Ecuador, and southern Ecuador with northern Peru, reflecting the integrated geodynamic evolution of the Northern Andean margin.

In southwestern Colombia, magmatic rocks dated at ~65 Ma and ~39 Ma indicate evolution in a mature continental arc developed over previously accreted oceanic plateau crust, where thickened lithosphere and assimilation of sedimentary and mafic lower crustal components played a key role in magma genesis (Barbosa-Espitia et al., 2019; Kerr et al., 2002; McCourt et al., 1984). More recent magmatic activity in this region is recorded in the early Miocene. Botello et al. (2024) reported 23–21 Ma plutons displaying isotopic signatures indicative of mantle-derived magmas modified by interaction with non-radiogenic continental material. Similarly, Echeverri et al. (2015) documented in situ zircon U–Pb ages of ~23 Ma in the same region and, based on detrital zircon records, proposed continuous magmatic activity from the Late Oligocene to the Miocene. According to their interpretation, Middle to Late Miocene magmatism was influenced by a progressive shallowing of the subduction angle, triggered by the arrival of the Nazca Plate at the South American margin. These signatures parallel those observed in Ecuador (see chapter 3 of this study), suggesting a shared tectono-

magmatic evolution shaped by accretionary events, arc migration, and subduction reorganization across the northern Andes margin.

Further south, northern Peru, marked by the Huancabamba Deflection, the transitional zone between the NNE-oriented Northern Andes and the NNW-trending northern Peruvian Andes, records a similarly long-lived history of Cenozoic magmatism. Magmatic activity in northern Peru has been sustained since at least the Paleogene, as evidenced by Paleogene intrusive pulses within the Coastal Batholith (e.g., Martínez-Ardila et al., 2023) and by K–Ar and Ar–Ar ages obtained from sanidine, plagioclase, and hornblende that record magmatic activity from the Early to Late Eocene, reflecting the persistence of an active continental arc throughout much of the Cenozoic (Noble et al., 1990). Magmatic evolution in this region was strongly influenced by variations in subduction geometry, particularly episodes of flat-slab subduction associated with the Nazca Ridge and Inca Plateau (Margirier et al., 2015; Rosenbaum et al., 2005). Variations in convergence rates, inherited basement heterogeneities, and episodic ridge collisions collectively modulated forearc deformation and magmatic productivity through time (Espurt et al., 2018; Jaillard, 2022; Witt et al., 2023). In the Central Andes, Mamani et al. (2010) demonstrated that magmatic compositions record the tectonic history and progressive crustal growth, which is best explained by continuous crustal shortening and thickening rather than by abrupt processes such as lithospheric delamination or collapse.

1.4 Knowledge Gaps and Rationale for This Study

Only a limited number of studies (e.g., Aizprua et al., 2020; Chiaradia et al., 2004; George et al., 2021; Schütte, Chiaradia, et al., 2010; Schütte, Chiaradia, Massimo, et al., 2010; Vallejo et al., 2009, 2016; Witt et al., 2017, 2023) have advanced our understanding of Cenozoic arc tectonics and magmatism; therefore, significant knowledge gaps persist, preventing a comprehensive reconstruction of the spatiotemporal evolution of the Cenozoic arc in Ecuador and its broader regional context. As previously suggested, detrital studies provide indeed valuable indirect temporal information, but they lack the spatial control necessary to resolve the detailed evolution of the magmatic arc. Hence, they complement rather than replace magmatic geochronological frameworks. These knowledge gaps fall into three main categories: geochronological constraints, geochemical representativeness, and the petrogenetic characterization.

First, the absence of a regionally consistent and high-resolution geochronological framework for Ecuador significantly limits detailed interpretations of the tectono-magmatic

evolution of the Cenozoic arc. Existing chronological constraints rely predominantly on legacy K–Ar data, much of which is concentrated around areas of economic interest (e.g., the Santiago and Telimbela batholiths) rather than providing systematic regional coverage. Although K–Ar datasets are often carefully examined to exclude obviously disturbed ages, K–Ar ages remain susceptible to isotopic resetting through processes such as hydrothermal alteration and thus often yield only broad temporal constraints. As highlighted by Schütte (2009a), previous comparison with U–Pb dating suggest that K–Ar ages may serve as reasonable proxies for regional-scale magmatic activity, but their precision decreases when used to resolve local intrusive events. Consequently, legacy K–Ar ages require integration with modern high-precision methods such as U–Pb zircon dating to refine the timing of magmatic pulses at a local scale and better constrain the temporal relationships between intrusive activity and tectonic events.

Second, existing geochemical datasets are spatially and temporally biased. In one hand, many intrusive complexes, particularly those in remote or poorly exposed regions, remain unsampled or only partially characterized. On the other hand, whole-rock geochemistry can be variably disturbed by hydrothermal alteration, which obscures primary magmatic signatures and complicates petrogenetic interpretations. Integrating complementary parameters, such as single mineral geochemistry or isotope systematics, is therefore essential to improve the accuracy and reliability of geochemical reconstructions. While previous works have applied isotopic systematics (e.g., Chiaradia, 2009; Schütte, 2009a), these datasets remain geographically limited (mostly to regions of economic interest), heterogeneous, and limited to capture a complete spatial and temporal variability of magmatism across the arc.

Third, the petrogenetic characterisation of the Cenozoic arc remains partially constrained. While general patterns, such as the appearance of adakite-like signatures, contrasts in magma sources, and temporal changes in fractionation conditions, are documented, their driving mechanisms are poorly understood. It is unclear whether these patterns primarily reflect tectonic forcing (e.g., slab geometry, convergence parameters), crustal processes (e.g., thickening, assimilation), or magmatic differentiation. Therefore, understanding arcs evolution in complex subduction systems requires multi-parametric studies that integrate geochemistry and geochronology within a coherent tectono-magmatic framework across local and regional scales.

Given these limitations, the widespread availability and democratization of in-situ analytical techniques, such as U–Pb geochronology, ϵHf , and $\delta^{18}\text{O}$ isotopic analyses in zircon, offer an exceptional opportunity to generate more precise, spatially resolved, and directly

comparable datasets. Moreover, the growing interest in trace element systematics in zircon is providing meaningful insights into magmatic differentiation, crustal evolution, and magma source characteristics (e.g., Grimes et al., 2015; Kemp et al., 2007; Tang et al., 2014). Together, these advances enable the integration of temporal, chemical, and isotopic information across multiple scales, paving the way for a more comprehensive reconstruction of the tectono-magmatic evolution of the Ecuadorian Cenozoic arc.

1.5 Goals of the study

This PhD thesis aims to improve our understanding of the tectono-magmatic evolution and the nature of magmatic reservoirs in the Cenozoic arc of Ecuador. A primary objective is to establish a robust and spatially well-distributed geochronological framework through high-precision U–Pb zircon dating, in order to better constrain the timing, duration, and spatial distribution of magmatic pulses, as well as their temporal relationships with tectonic and crustal processes. This will represent a significant step forward for future cartographic and regional synthesis projects, enabling more accurate correlations between magmatic and structural events across the study area, and will also build upon previous comparisons with the extensive but older K–Ar age determinations.

A second objective focuses on establishing a comprehensive geochemical dataset for key intrusive complexes, particularly through high-resolution zircon petrochronology that combines trace-element and isotopic analyses (ϵHf – $\delta^{18}\text{O}$). The integration of these state-of-the-art zircon data with more classical whole-rock geochemistry, together with the increasingly refined use of trace elements in zircon, offers an unprecedented level of resolution in tracing magmatic sources and differentiation pathways. This combined approach significantly enhances the accuracy and interpretive power of geochemical reconstructions, enabling a more robust and temporally resolved characterization of magmatic evolution.

The third objective aims to integrate the geochronological and geochemical datasets, together with structural information where available, to evaluate the petrogenetic and geodynamic significance of magmatic trends. This multidisciplinary approach will link variations in magmatism to evolving subduction dynamics, crustal architecture, and tectonic regimes, thereby providing a comprehensive framework to reconstruct the spatio-temporal, chemical, and geodynamic evolution of the Cenozoic arc in Ecuador and to advance our understanding of convergent margin processes in the Northern Andes.

1.6 Thesis outline

The thesis is organized into six chapters. Chapter 1 introduces the research background, objectives, and the geological context of the Ecuadorian segment of the Andes. Chapter 2 details the analytical and methodological approaches employed in the study.

Chapter 3 focuses on the northernmost Ecuadorian arc, providing new geochronological and geochemical data that constrain its magmatic evolution; this chapter is published as an article in *Lithos*. Chapter 4 examines the Central Ecuadorian Andes, characterizing the temporal and compositional variability of magmatism in this region. Chapter 5 refines the spatial and temporal framework of magmatism in the southern Ecuadorian arc. Finally, Chapter 6 integrates these results, synthesizing the main conclusions and placing them within a broader regional perspective.

Additionally, part of the supplementary material includes also a published (*Lithos*) focused study on the Mesozoic magmatism in the Andes of southern Ecuador and northern Peru, which provides valuable context for understanding the pre-Cenozoic tectono-magmatic evolution of this region.

CHAPTER 2: Methodology

The study area encompasses the northern, central, and southern segments of the Ecuadorian Cenozoic arc within the Northern Andes. Several field campaigns were conducted to systematically sample intrusive rocks across the region. This collaborative effort produced a regional comprehensive dataset of more than 220 samples covering Ecuador and northern Peru, from which sixty-four samples, predominantly granitoids, were selected in this thesis. A multi-proxy analytical approach was applied, integrating zircon U–Pb geochronology, zircon Hf–O isotopic and trace-element analyses, whole-rock geochemistry, and detailed petrographic characterization. The following sections describe in detail the analytical techniques and data processing methods employed in this research.

2.1 Whole-Rock Geochemistry

Whole-rock geochemistry is a fundamental analytical approach in igneous petrology, tectonomagmatic reconstruction, and crustal evolution studies. It provides quantitative information of the chemical composition of rocks through the measurement of major, trace, and rare earth elements. This information is usually used to classify igneous rocks into established petrogenetic series, tectonic settings, characterization of magma affinity (e.g., tholeiitic vs. calc-alkaline, peraluminous vs. metaluminous), and the evaluation of magmatic processes including fractional crystallization, partial melting, magma mixing and crustal assimilation (Le Bas et al., 1986; Middlemost, 1994; Streckeisen & Le Maitre, 1979).

The principle of whole-rock geochemistry is to quantify the proportions of oxides and elements that define the bulk composition of igneous rocks. Major elements, generally those exceeding 0.1 wt%, are expressed as oxides (e.g., SiO₂, Al₂O₃, FeO_t, MgO, CaO, Na₂O, K₂O, TiO₂, P₂O₅, MnO), whereas trace elements are typically reported in parts per million (ppm). Rare earth elements (REEs) form a particularly useful subset because of their coherent geochemical behavior and sensitivity to residual mineral assemblages (McDonough and Sun, 1995).

Whole-rock analyses were performed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at MSA Laboratories (Langley, Canada) and at the Geo-Ocean laboratory (PSO – Pôle de Spectrométrie Océan, University of Brest, France). Geochemical data were processed using the

R programming language and the Geochemical Data Toolkit (GCDkit; Janoušek et al., 2016). The technical details of each analytical procedure are provided in the corresponding chapters.

ICP-MS and ICP-AES are two common techniques used to analyse the chemical composition of rocks. The main difference is that ICP-MS measures elements based on their mass, while ICP-AES measures the light emitted by excited atoms in the plasma (Montaser, 1998). ICP-MS is more sensitive and can detect very small amounts of elements, whereas ICP-AES is better suited for elements present in higher concentrations. Because of its high sensitivity, ICP-MS is often preferred for trace element studies, such as those focusing on rare earth elements or high field strength elements in magmatic systems (Jenner et al., 1990). In contrast, ICP-AES is less suitable when studying elements occurring at extremely low concentrations, for example rare earth elements in depleted mantle rocks or platinum-group elements in ultramafic systems. It may also be less effective for very small or strongly altered samples where element concentrations are low. Despite these limitations, ICP-AES remains a reliable and widely used method for major and minor elements in granitoid rocks. In the case of granitoids from subduction zones, which typically contain moderate element concentrations, ICP-AES provides consistent and accurate results. Therefore, while ICP-MS is essential for high-precision trace element work (Jenner et al., 1990; Linge, 2005), ICP-AES remains perfectly adequate for most petrological and geochemical studies.

The chemical data allow classification of the studied rocks within established magmatic series and tectonic environments. Several geochemical diagrams, including the Total Alkali–Silica (TAS), normative Q'-ANOR (where $Q' = \text{quartz} / (\text{quartz} + 20 \text{ feldspars})$ and $100 \text{ ANOR} = 100 \text{ anorthite} / (\text{orthoclase} + \text{anorthite})$), AFM, and K_2O vs. SiO_2 plots, were used to determine magma affinity (tholeiitic, calc-alkaline, or alkaline) as well as the peraluminous or metaluminous nature of the rocks (Irvine & Baragar, 1971; Le Bas et al., 1986; Pecerrillo & Taylor, 1976; Streckeisen & Le Maitre, 1979). In addition to classification, element ratios sensitive to fractionation and source processes are used to interpret magma evolution.

Whole-rock geochemical datasets were directly interpreted jointly with petrographic observations. Thin-section petrography identified mineral paragenesis, zoning patterns, and textural relationships that were cross-checked against whole-rock signatures.

Beyond classification, trace elements systematics provide first-order constraints on geodynamic parameters. Particularly the high-field strength elements (HFSE: Nb, Ta, Zr, Hf, Ti) and the large-ion lithophile elements (LILE: Rb, Ba, Sr, K), are essential in reconstructing tectonic settings because of their contrasting mobility and compatibility during melting and crystallization (Pearce, 2014). In convergent margin magmatism, subduction-related fluids

enrich the mantle wedge in LILE while HFSE remain immobile, producing characteristic Nb–Ta depletions. Consequently, diagrams such as Nb–Y, Th–Yb, and Ti–Zr (Pearce, 2008) effectively distinguish arc, within-plate, and mid-ocean ridge environments.

Whole-rock geochemical analyses provide valuable insights into the mineralogical controls on magma composition, particularly the influence of phases such as plagioclase, amphibole, and garnet, which strongly affect major and trace element distributions during magma differentiation and partial melting. The stability of these minerals is strongly pressure-dependent: plagioclase is typically stable at low pressures, amphibole at intermediate pressures, and garnet at higher pressures within the crust and upper mantle. Consequently, ratios such as La/Yb, Dy/Yb, and Sr/Y are widely used as proxies for crustal thickness and for evaluating the role of garnet, amphibole, or plagioclase as residual or fractionating phases during partial melting (Chapman et al., 2015; Chiaradia, 2015; Defant & Drummond, 1990; Profeta et al., 2015); high Sr/Y (>50) often signifies amphibole stability and garnet in the residue, characteristic of adakitic or high-pressure melts (Defant & Drummond, 1990). Conversely, low Sr/Y (<20) is typical of low-pressure crystallization under thin crustal conditions. Also the slope of the REE pattern, commonly expressed as $(La/Yb)_n$, reflects the presence of garnet or amphibole in the source, given their differential partition coefficients (Defant and Drummond, 1990; Rollinson, 2014). A steeply fractionated pattern ($La/Yb_n > 10$) suggests melting in a thickened crust (>40 km) where garnet remains stable, whereas flatter patterns indicate shallower melting or more mafic sources (Chapman et al., 2015; Profeta et al., 2015).

Similarly, the role of source composition and melting depth can also be evaluated using HFSE ratios such as Nb/Ta and Zr/Hf, as both pairs behave coherently but fractionate slightly under different mineral equilibria (Rudnick and Gao, 2003; Tang et al., 2019). In this sense, whole-rock geochemistry contributes to linking magma compositions with crustal architecture and tectonic processes, particularly when combined with isotopic and mineral-scale data.

Nevertheless, whole-rock geochemical datasets may be affected by post-magmatic alteration. Hydrothermal processes, metamorphism, or surface weathering can modify major element concentrations and mobilize certain trace elements, potentially obscuring the original magmatic signal (Rollinson, 2014; Winchester and Floyd, 1977). Given these limitations, whole-rock geochemistry is most effective when integrated with additional analytical approaches. Coupling it with in situ mineral chemistry, such as zircon geochemistry (U–Pb geochronology, Hf and O isotopes, and trace element analyses), provides significantly enhanced petrogenetic interpretations.

2.2 Zircon petrochronology

Over the last few decades, the development of high-spatial-resolution in-situ analytical techniques such as LA–ICP–MS and SIMS has revolutionized the isotopic and trace-element analysis of small magmatic minerals like zircon (Chew et al., 2021; Hawkesworth and Kemp, 2006). This technological progress has developed the growth of petrochronology, a discipline that integrates geochronology (i.e., the age and duration of magmatic events) with petrology and geochemistry to provide a petrogenetic context, that is, to link the timing of events to the specific processes and physical conditions under which rocks form (Engi et al., 2017).

Zircon (ZrSiO_4) is a common accessory mineral in intermediate to felsic igneous and metamorphic rocks due to its unique physicochemical resilience and its ability to retain primary isotopic and geochemical information through complex geological processes (e.g., Watson and Harrison, 1983), including weathering, transport, diagenesis, hydrothermal alteration, and even partial melting of the crust. Its robustness against chemical alteration, high closure temperature ($>900^\circ\text{C}$), and low diffusion rates for most trace elements make zircon an ideal recorder of magmatic histories (Cherniak et al., 1997; Corfu, 2013; Watson and Harrison, 2005).

In granitoid systems, zircon crystallizes primarily from late magmatic stages, incorporating trace elements such as Hf, Th, U, Y, and REEs, which substitute for Zr^{4+} in its crystal lattice according to charge and radius constraints (Belousova et al., 2002). These geochemical features enable the use of zircon as a natural archive, preserving temporal, compositional, and isotopic information that reflects the processes of magma generation, differentiation, and crust–mantle interaction (Belousova et al., 2002; Schaltegger & Davies, 2017).

Among the records hosted by zircon are both radiogenic and non-radiogenic isotopic systems of major geochronological and petrogenetic significance. The U–Pb and Th–Pb systems provide robust constraints on crystallization ages. In addition, the Lu–Hf system serves as a powerful tracer of crustal growth and mantle–crust interaction, as zircon typically preserves its Hf isotopic composition even through recycling processes involving lower crustal delamination or sediment subduction into the mantle (Hawkesworth and Kemp, 2006; Matteini et al., 2010; J. D. Vervoort and Kemp, 2016). Among the non-radiogenic systems, oxygen isotopes ($\delta^{18}\text{O}$) provide valuable insights into magma sources and crustal assimilation processes, as zircon effectively records the isotopic signature of its parental melt with minimal post-crystallization modification (Bindeman, 2008; Valley et al., 2005). In addition, trace-element concentrations in zircon provide valuable constraints on crystallization temperatures

and help characterize the sources of parental magmas (Belousova et al., 2002; Claiborne et al., 2010; Grimes et al., 2015; Valley et al., 2005; Watson and Harrison, 2005). As a result, zircon offers a unique window into the origin and evolution of magmas from which it crystallized.

2.2.1 Sample Preparation and Analytical Workflow

In this study, zircon grains were extracted from sixty-four granitoid samples collected throughout the Ecuadorian Cenozoic arc. Zircons were processed and separated using standard gravimetric and magnetic techniques as described by Malusà & Fitzgerald (2019). Rock samples were first crushed in a steel jaw crusher and milled to liberate accessory minerals. Heavy liquid separation (e.g., sodium polytungstate; $\rho = 2.85 \text{ g/cm}^3$) and magnetic separation with a Frantz® isodynamic separator concentrated the zircon fraction. Individual grains were then hand-picked under a binocular microscope to select transparent, inclusion-free crystals, avoiding metamict or altered domains that might compromise age interpretations. Selected zircons were mounted in epoxy mounts, polished to expose interiors. Cathodoluminescence imaging was used to reveal internal zoning, inherited cores, and magmatic or overgrowths and led laser-ablation spot placement to ensure pure magmatic domains analyses. In certain cases, high-resolution cathodoluminescence imaging was conducted after the analyses to further examine internal structures. Analytical protocols, data reduction methods, and filtering criteria are presented in detail in the respective results chapters of this thesis.

U–Pb dating, Lu–Hf isotopic, and trace-element analyses were conducted in the same mounts using a combination of analytical setups. A split-stream LA-ICP-MS configuration (Kylander-Clark et al., 2013) was employed to simultaneously acquire Hf isotopic and trace-element data, or Hf isotopic and U–Pb age information, from the same analytical spot. In addition, U–Pb dating alone or combined U–Pb and trace-element analyses were performed using a classical single stream LA-ICP-MS system. Finally, oxygen isotopes were measured by Secondary Ion Mass Spectrometry (SIMS).

2.2.2 U–Pb Geochronology

The U–Th–Pb system in zircon constitutes a robust geochronometer because it includes three independent radioactive decay chains with distinct half-lives. Specifically, the decay of uranium ^{238}U and ^{235}U and ^{232}Th isotopes to stable lead isotopes ^{206}Pb , ^{207}Pb and ^{208}Pb , respectively, follows the general decay equation:

$$P = P_0 e^{-\lambda t}$$

where N_p is the number of parent isotopes remaining, N_0 is the initial amount of parent isotope, λ is the decay constant, and t is the time elapsed. The initial number of parent isotopes $P_0 = P + D^*$, where D^* is the number of radiogenic daughter isotopes, thus the last equation can therefore be expressed as:

$$D^* = P (e^{\lambda t} - 1)$$

in the case of initial daughter isotope existence (D_0), total $D = D_0 + D^*$. Thereby,

$$D = D_0 + P (e^{\lambda t} - 1)$$

During crystallization, zircon incorporates U and Th into its crystal lattice but excludes Pb; thus, any Pb present is radiogenic and time-dependent, directly recording the timing of zircon growth (Chelle-Michou and Schaltegger, 2023). Dividing both sides by P gives the fundamental relationship between parent and daughter isotopes:

$$\frac{D}{P} = e^{\lambda t} - 1$$

This equation forms the basis for radiometric age determination in all isotopic systems. For the U–Th–Pb system, the accumulation of radiogenic daughter isotopes over time is described by:

$$\begin{aligned} \frac{Pb^{206}}{U^{238}} &= e^{\lambda_{238}t} - 1 \\ \frac{Pb^{207}}{U^{235}} &= e^{\lambda_{235}t} - 1 \\ \frac{Pb^{208}}{Th^{232}} &= e^{\lambda_{232}t} - 1 \end{aligned}$$

Where $\lambda_{238} = 1.55125 \times 10^{-10} \text{ yr}^{-1}$ ($t_{1/2} = 4.468 \text{ Ga}$), $\lambda_{235} = 9.8485 \times 10^{-10} \text{ yr}^{-1}$ ($t_{1/2} = 703.8 \text{ Ma}$), and $\lambda_{232} = 0.495 \times 10^{-10} \text{ yr}^{-1}$ ($t_{1/2} = 14.05 \text{ Ga}$) (Schoene, 2014).

Additionally, another isochron equation can be calculated:

$\left(\frac{Pb^{207}}{Pb^{206}}\right)^* = \left(\frac{U^{235}}{U^{238}}\right) \frac{(e^{\lambda_{235}t} - 1)}{(e^{\lambda_{238}t} - 1)}$, where $*$ represents the ratio of radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$. An important advantage of this equation is that age calculation does not necessitate direct measurement of the uranium isotopic ratio, as the present-day $^{235}\text{U}/^{238}\text{U}$ value is effectively invariant and equal to 137.818 ± 0.045 (2σ ; Hiess et al., 2012). However, for samples younger than approximately 1 Ga, $^{207}\text{Pb}/^{206}\text{Pb}$ ages presents uncertainties due to the extremely low amount of radiogenic ^{207}Pb produced by the decay of ^{235}U . This results in poor counting

statistics, large analytical uncertainties, and high sensitivity to common-Pb corrections, which together yield imprecise or geologically meaningless ages (Schoene, 2014; Spencer et al., 2016). Consequently, for young zircons, $^{206}\text{Pb}/^{238}\text{U}$ ages are preferred, as they provide significantly higher precision and robustness in the interpretation of magmatic crystallization ages (e.g., Vermeesch, 2021).

The intersection of the $^{206}\text{Pb}/^{238}\text{U} - ^{207}\text{Pb}/^{235}\text{U}$ decay systems defines the “concordia curve”, first introduced by Wetherill (1956) as a graphical approach to represent the simultaneous decay of uranium isotopes to lead. Points lying along the concordia correspond to analyses where both decay systems yield identical ages, indicating a closed isotopic system since crystallization. In contrast, analyses that fall below the curve, termed discordant, reflect open-system behaviour caused by processes such as Pb loss, inheritance, mixing between domains of different ages, the presence of non-radiogenic “common” lead (e.g., Corfu, 2013; Schoene, 2014; Vermeesch, 2021). Discordant data can nevertheless retain valuable chronological information: their regression lines typically intersect concordia at two points, where the upper intercept represents the time of zircon crystallization, and the lower intercept records the timing of Pb loss or subsequent disturbance (Schoene, 2014).

In practice, the selection of which age to report, depends on the isotopic coherence of the dataset and its geological context. When analyses are concordant or nearly concordant, and scatter is within analytical uncertainty, a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age is generally adopted to represent the timing of crystallization. If analyses define a linear discordia array, a regression approach is applied, with the upper intercept marking the crystallization age and the lower intercept corresponding to the timing of Pb loss or subsequent disturbance (Corfu, 2013; Condo et al., 2024; Schoene, 2014; Vermeesch, 2021). For heterogeneous zircon populations, additional petrographic or isotopic evidence (e.g., trace elements or Hf–O systematics) helps discriminate between inherited, magmatic, and altered domains, ensuring that the chosen age best reflects the geologic process of interest (e.g., Schoene et al., 2010).

Initial lead, commonly referred to as common Pb, includes both natural non-radiogenic Pb incorporated before zircon crystallization and any Pb contamination or laboratory blank introduced during analysis. The presence of common Pb, whether acquired during zircon growth or subsequent alteration, can bias U–Pb isotopic ratios, particularly in young samples where radiogenic ^{207}Pb is scarce (Vermeesch, 2021). On Wetherill concordia diagrams, uncorrected common Pb typically produces discordant trends reflecting the isotopic composition of uranium, whereas on Tera–Wasserburg plots, which display $^{238}\text{U}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$, the regression line intersects concordia at the true crystallization age and the y-axis

at the initial Pb composition. This representation thus combines the ability to visualize initial Pb components, as in isochron plots, with the diagnostic power of concordia diagrams to test for closed-system behaviour (Schoene, 2014).

Linear arrays on either concordia diagram as those observed by the presence of common Pb may also result from mixing or Pb loss. In young samples, arrays generated by common Pb typically plot at steep angles to concordia and yield upper intercepts older than 4.5 Ga, making them readily distinguishable from Pb-loss trends. In contrast, for Paleoproterozoic and Archean samples, Pbc-related arrays may become nearly parallel to discordias produced by Pb loss or age-domain mixing, making the distinction between these processes far less clear (Schoene, 2014).

U–Pb dating in zircon is commonly performed using microbeam and isotope dilution techniques that provide high spatial resolution and have revolutionized geochronology over the past decades. Among these, the most widely used methods are laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS), thermal ionization mass spectrometry (TIMS), and secondary ion mass spectrometry (SIMS), including the Sensitive High-Resolution Ion Microprobe (SHRIMP) (e.g., Schaltegger et al., 2015), each with distinct analytical strengths and limitations (e.g., Bowring et al., 2006; Schoene, 2014).

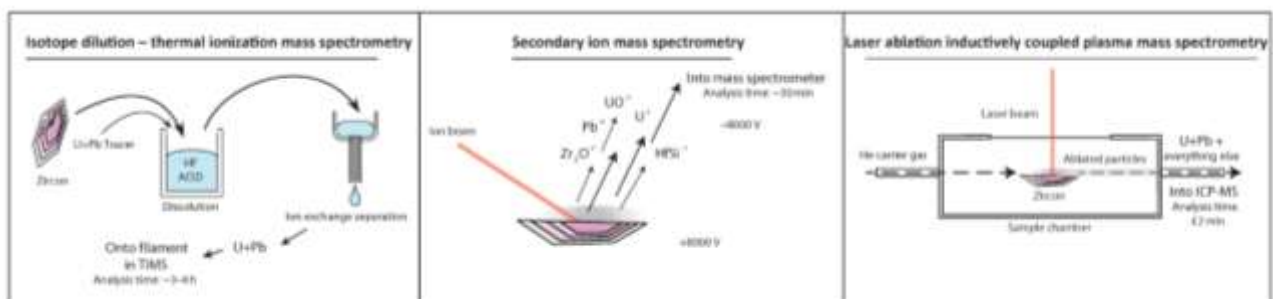


Figure 2.1 The three primary methods for U–Pb geochronology, as conceptualized by Schoene, (2014).

TIMS by isotope dissolution remains the benchmark for U–Pb geochronology in terms of precision and accuracy. This method involves dissolving zircon grains, spiking them with a mixed U–Pb tracer, chemically separating the isotopes, and measuring them by thermal ionization. Modern implementations, particularly chemical abrasion–TIMS (CA–TIMS), remove radiation-damaged zircon domains prone to Pb loss, significantly improving data reliability (Mattinson, 2005). Thanks to its stable ion beams and isotope dilution calibration, ID–TIMS routinely achieves precisions better than $\pm 0.1\%$ on $^{206}\text{Pb}/^{238}\text{U}$ ages, making it the method of choice for standard calibration and reference materials (Schmitz and Schoene, 2007).

By contrast, SIMS and LA–ICP–MS enable in situ analyses that preserve textural context and reveal age zoning within single crystals. SIMS, measures isotopic compositions by sputtering the sample surface with an ion beam, achieving high spatial resolution (10–40 µm) and shallow pit depths (<4 µm) (Li and Li, 2016). It is particularly suited for complex zircon populations and fine-scale temporal resolution within individual grains. Although its typical analytical precision (~2–3%) is lower than that of ID–TIMS, SIMS remains a powerful tool for petrochronology (Schoene, 2014).

LA–ICP–MS has become the most widely used method due to its speed, flexibility, and moderate cost (Pullen et al., 2014).. The technique uses a focused laser beam to ablate microscopic portions of zircon, with the resulting aerosols transported to an inductively coupled plasma for ionization and isotopic measurement (Schoene, 2014). Although precision is generally around 1–2%, lower than ID–TIMS but comparable to SIMS, LA–ICP–MS allows the rapid generation of large datasets and is ideal for regional-scale studies. This technique provides precise and accurate zircon ages across a wide geological spectrum (Chang et al., 2006), enabling quantification of magma recharge rates, crystallization durations, and pluton assembly timescales in long-lived magmatic systems. In felsic settings, the youngest zircon populations typically constrain the timing of final magma emplacement, while older grains often represent antecrysts or xenocrysts inherited from earlier magmatic or crustal sources (Miller et al., 2007).

2.2.3 Hafnium and Oxygen Isotopes in Zircon (ϵHf_t - $\delta^{18}\text{O}$)

The lutetium–hafnium (Lu–Hf) isotopic system in zircon is an essential tool in geochronology and crustal evolution studies because it enables the reconstruction of mantle–crust differentiation processes and the characterization of magma sources throughout Earth’s history (e.g., Hawkesworth et al., 2010; Hawkesworth & Kemp, 2006; Vervoort & Kemp, 2016). This method relies on the radioactive decay of ^{176}Lu to ^{176}Hf , which has a half-life of approximately 37 Ga, allowing the investigation of long-term geological events (Hawkesworth and Kemp, 2006; Söderlund et al., 2004). Lu, one of the rare-earth elements, occurs in nature as two isotopes: the stable ^{175}Lu and the radioactive ^{176}Lu . Hf, a high-field-strength element (HFSE), has six stable isotopes, with ^{176}Hf being radiogenic, produced by the decay of ^{176}Lu , and five stable isotopes (J. Vervoort, 2014).

$$^{176}\text{Hf} = ^{176}\text{Hf}_0 + ^{176}\text{Lu} (e^{\lambda t} - 1)$$

Among these, the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio is widely used because ^{177}Hf is stable and non-radiogenic, providing a reference for normalization and comparison with the chondritic uniform reservoir (CHUR) model, which represents the primitive, undifferentiated composition of the Earth (Blichert-Toft and Albarède, 1997; Bouvier et al., 2008).

During partial melting, hafnium behaves as a more incompatible element than lutetium, leading to fractionation between crust and mantle reservoirs. As a result, the continental crust becomes enriched in Hf and exhibits low Lu/Hf ratios, while the depleted mantle retains higher Lu/Hf ratios (Vervoort, 2014). These differences are expressed using the epsilon notation (ϵHf), which quantifies deviations of the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio from CHUR and provides insights into whether magmas are derived from juvenile mantle sources (positive values) or reworked crustal material (negative values).

$$\epsilon\text{Hf}_{(t)} = \left[\frac{(^{176}\text{Hf}/^{177}\text{Hf})_{\text{sample},t}}{(^{176}\text{Hf}/^{177}\text{Hf})_{\text{CHUR},t}} - 1 \right] \times 10^4$$

Moreover, depleted mantle model ages (T_{DM}) can be calculated to estimate the time when a magma source separated from the mantle, thus helping to trace the long-term growth and recycling of continental crust (Nebel et al., 2007). These ages are computed by back-projecting the measured isotopic composition to the depleted mantle evolution curve (Matteini et al., 2010):

$$T_{\text{DM}} = t - \frac{1}{\lambda} \ln \left[\frac{(^{176}\text{Hf}/^{177}\text{Hf})_{\text{sample}} - (^{176}\text{Hf}/^{177}\text{Hf})_{\text{DM}}}{(^{176}\text{Lu}/^{177}\text{Hf})_{\text{sample}} - (^{176}\text{Lu}/^{177}\text{Hf})_{\text{DM}}} \right]$$

Zircon incorporates significant amounts of Hf while containing very low concentrations of Lu, leading to minimal internal radiogenic growth, and enabling precise determination of initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios in magmas (Hawkesworth and Kemp, 2006; Matteini et al., 2010). Furthermore, Hf diffusion in zircon crystal lattice is extremely slow, preserving isotopic signatures even under metamorphic conditions (Cherniak et al., 1997). Advances, particularly the development of laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS), now allow simultaneous U–Pb geochronology and Lu–Hf isotope analysis in single zircon domains (Harrison et al., 2005; Kemp et al., 2009).

In addition to the considerable value of the Lu–Hf isotopic system in deciphering juvenile versus recycled crustal sources, oxygen isotope systematics provide complementary constraints that help characterize the crustal component more precisely. Oxygen isotopes are expressed as $\delta^{18}\text{O}$ and offer invaluable insights into crustal processes (e.g., Hawkesworth &

Kemp, 2006; Jones et al., 2015). Theoretically, $\delta^{18}\text{O}$ represents the ratio of the stable isotopes ^{18}O to ^{16}O in a sample compared to standard mean ocean water (SMOW), expressed in per mil (‰) (Bindeman, 2008).

$$\delta^{18}\text{O} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}} - 1 \right] \times 10^3$$

Zircons in equilibrium or crystallizing directly from mantle-derived magmas typically inherit the mantle's remarkably homogeneous $\delta^{18}\text{O}$ range, approximately $5.3\text{‰} \pm 0.6\text{‰}$, thereby preserving this primary isotopic signature, despite processes of metamorphism, hydrothermal alteration, and magmatic assimilation, anatexis, or even differentiation (Mattey et al., 1994; Valley, 2003; Valley et al., 1998). This ratio is sensitive to low-temperature processes such as weathering and sedimentary recycling but remains unaltered by high-temperature events (Bindeman, 2008; Monani and Valley, 2001; Valley, 2003). Deviations from the $\delta^{18}\text{O}$ mantle range are linked to the sensitivity of this isotopic system to define different sources. High $\delta^{18}\text{O}$ zircon values, reflects a source influenced by partial melting, or assimilation of metasedimentary rocks with $\delta^{18}\text{O}$ signatures around $\sim 7\text{--}9\text{‰}$ (Valley, 2003), or a low temperature seawater interaction source (Cavosie et al., 2011). In contrast, sub-mantellic $\delta^{18}\text{O}$ values reflect a source derivate from hydrothermally altered rocks by high temperature meteoric or seawater (Bindeman, 2008; Valley et al., 2005).

The integration of zircon U–Pb ages, $\varepsilon\text{Hf}(t)$ values, and $\delta^{18}\text{O}$ compositions has become one of the most powerful approaches to studying capable of resolving the timing, source, and evolution of magmatic processes. This methodology allows distinction between magmas derived from depleted/enriched mantle sources during arc growth and those influenced by crustal recycling or subduction-modified lithosphere, providing essential information for understanding continental growth and geodynamic evolution (Hawkesworth and Kemp, 2006; Kemp et al., 2007).

The isotopic composition of Hf, together with U–Pb ages and trace-element concentrations, was determined in situ by high-spatial-resolution LA-ICP-MS operated in a split-stream configuration, allowing simultaneous acquisition of isotopic and elemental data (Kylander-Clark et al., 2013). Additionally, U–Pb dating alone or combined U–Pb and trace-element analyses were performed using a conventional LA-ICP-MS system. In parallel, oxygen isotope ratios ($\delta^{18}\text{O}$) were analyzed using Secondary Ion Mass Spectrometry (SIMS), which provides the precision required for accurate $\delta^{18}\text{O}$ determinations at the micrometer scale (Valley, 2003). All analyses were carried out on the same polished zircon mounts described in the U–Pb methods section, with analytical spots positioned on well-preserved magmatic

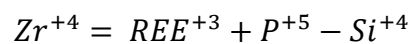
domains as identified by CL imaging, following the same targeting criteria used for geochronology. This integrated approach ensures that U–Pb ages, Hf isotopic compositions, and $\delta^{18}\text{O}$ values correspond to the same magmatic event, thereby enhancing the robustness of petrogenetic interpretations.

2.2.4 Trace Elements concentrations

Along with the improvement of in situ analytical techniques (Schoene, 2014), the amount of geochemical information that can be obtained from a single zircon grain has expanded dramatically. This analytical capability has generated considerable enthusiasm to integrate trace-element data with U–Pb chronology, as both can be acquired simultaneously and provide complementary insights into magmatic processes (Schoene et al., 2010).

Trace element concentrations in zircon provide a crucial complement to U–Pb and Hf–O isotope data, as they record the chemical and thermal conditions of zircon crystallization and thus help to link isotopic signatures with petrogenetic processes. Because zircon incorporates a wide range of incompatible and HFSEs, such as Hf, U, Th, Y, Nb, Ta, and the REEs, into its crystal lattice, its trace-element composition reflects both the composition of the parental melt and the physicochemical parameters prevailing during crystallization (Belousova et al., 2002; Claiborne et al., 2010; Grimes et al., 2015). These geochemical fingerprints help to constrain the tectonic setting, crystallization temperature and pressure, coexisting mineral assemblages, and ultimately, the characteristics of the magma source (Bell and Kirkpatrick, 2021; Harrison et al., 2007; Kirkland et al., 2015; Watson and Harrison, 2005).

The crystal chemistry of zircon strongly governs its trace-element incorporation. Cations of similar charge and ionic radius can substitute for Zr^{4+} in the zircon lattice following the coupled substitution scheme:



and similarly for Y^{3+} and U^{4+} (Hoskin and Schaltegger, 2003). The REEs, particularly heavy REEs (HREEs), fit well into the zircon structure, whereas light REEs (LREEs) are typically depleted due to size mismatch. Consequently, most igneous zircons exhibit steeply fractionated REE patterns, characterized by strong HREE enrichment and typically negative Eu anomalies, and positive Ce anomalies related to magma oxidation state. These features reflect the exclusion of Eu^{2+} during plagioclase fractionation and the compatibility of HREEs in zircon in the absence of co-crystallizing garnet (Belousova et al., 2002; Hoskin and Schaltegger, 2003).

Trace element systematics have been applied to discriminate tectono-magmatic environments. Multi-element discrimination diagrams using combinations of U, Th, Yb, Nb, Sc, Ce, and Gd can distinguish zircons formed in subduction-related arcs from those crystallized in within-plate or mid-ocean ridge settings (Grimes et al., 2007, 2015). Ratios such as Th/U also serve as robust indicators of zircon growth processes: values <0.1 are typically associated with metamorphic sources, whereas values >0.1 generally suggest igneous origins, with more specific ranges pointing to felsic (0.1–0.7) or mafic (>1.5) systems (Kirkland et al., 2015; Rubatto, 2002).

Additionally, zircon trace element ratios provide constraints on pressure-sensitive mineral fractionation and magma evolution. Yb/Gd ratios are sensitive to amphibole or garnet fractionation, and Nb/Ta ratios indicate the presence of rutile in the residue (Drabon et al., 2024; Grimes et al., 2015; Tang et al., 2019, 2024). These proxies are not only useful for identifying co-crystallizing phases but also for estimating crustal thickness and melt conditions (Balica et al., 2020; Bell and Kirkpatrick, 2021; Sundell et al., 2022; Tang et al., 2021), and are particularly informative when combined with whole-rock Sr/Y and La/Yb systematics, enabling independent verification of crustal thickness and arc maturity (Chiaradia, 2015; Chapman et al., 2015).

For instance, $Eu/Eu^* = Eu_N / (Sm_N \times Gd_N)^{0.5}$ anomalies have been proposed to reflect the role of plagioclase fractionation and thus crustal depth (Tang et al., 2021). However, several studies highlighted that Eu/Eu^* is influenced not only by plagioclase stability but also by temperature, redox conditions, melt composition, and source contamination (Roberts et al., 2024; Tang et al., 2024; Yakymchuk et al., 2023; Yakymchuk and Kirkland, 2025). Meanwhile, the correlation between Eu anomalies and crustal thickness should be applied with caution.

In addition, Ti concentrations in zircon serve as the basis of the Ti-in-zircon thermometer (Harrison et al., 2007; Watson and Harrison, 2005), providing quantitative crystallization temperature estimates that complement pressure and redox indicators derived from other elemental proxies. The Ti-in-zircon thermometer is expressed as:

$$T(^{\circ}C) = \frac{5080}{\log_{10}(a_{TiO_2}) + \log_{10}(a_{SiO_2}) + 5.711}$$

where a_{TiO_2} and a_{SiO_2} represent the activities of TiO_2 and SiO_2 in the melt, respectively. Under typical granitic conditions (assuming quartz and rutile saturation, $a_{SiO_2} \approx 1$, $a_{TiO_2} \approx 0.6–1$), zircon crystallization temperatures range from 650 to 800 °C. These values provide constraints

on magma cooling histories and emplacement depths (Ferry and Watson, 2007; Hayden and Watson, 2007).

Detailed analytical conditions, data reduction routines, and quality-control strategies are described in the corresponding results chapters. As shown here, when integrated with isotopic and petrographic information, zircon trace-element geochemistry constitutes a powerful approach for unravelling the petrogenetic evolution of continental magmatic arcs. In the following chapters, these analytical and interpretative tools are applied to the Ecuadorian Cenozoic arc, offering new insights into the temporal evolution, compositional diversity, and tectono-magmatic processes that have shaped the crustal architecture of the Northern Andes through time.

CHAPTER 3: Geochronology and geochemistry of Cenozoic magmatism in the north-western Ecuadorian Andes: the role of crustal thickness

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Declaration

This chapter aims to reconstruct the tectono-magmatic evolution of the northern Ecuadorian Cenozoic arc by integrating whole-rock geochemistry with zircon U-Pb geochronology, trace element analysis, and Hf-O isotope geochemistry to identify distinct magmatic periods and link changes in magma composition to evolving tectonic processes. Its content was published as Iglesias, J., Witt, C., Poma, O., Bruguier, O., Bosch, D., Bosch, V., Zattin, M., Seyler, M., Chanier, F., Averbuch, O., 2025 in *Lithos*, 514–515, 108159 (doi: 10.1016/j.lithos.2025.108159). The author contributions for this work were as follows: **Iglesias, J.:** Conceptualization, Investigation, Data curation, Methodology, Writing – original draft; **Witt, C.:** Conceptualization, Supervision, Writing – review & editing; **Poma, O.:** Conceptualization, Writing – review & editing; **Bruguier, O.:** Methodology, Data curation, Writing – review & editing; **Bosch, D.:** Methodology, Data curation, Writing – review &

editing; Bosch, V.: Methodology, Data curation, Writing – review & editing; Zattin, M.: Writing – review & editing; Seyler, M.: Methodology, Data curation, Writing – review & editing; Chanier, F.: Writing – review & editing; Averbuch, O.: Writing – review & editing.

Abstract

The Ecuadorian Cenozoic arc developed over autochthonous continental and accreted oceanic terrains. We reconstruct the tectono-magmatic evolution of the northernmost part of this arc using a comprehensive, multi-proxy approach that incorporates whole-rock chemistry and zircon petrochronology, including U-Pb geochronology, trace element geochemistry, and Hf-O isotopic analysis. Our results reveal two distinct magmatic periods at 41–16 Ma and 14–7 Ma. The older period is characterized by tonalitic rocks that exhibit trace element ratios, $\delta^{18}\text{O}$ values (6.4–3‰), and $\epsilon\text{Hf}_{(t)}$ values (+17–+12) in zircons that are indicative of highly juvenile sources, while the younger period comprises granodioritic rocks derived from a more enriched reservoir ($\delta^{18}\text{O}$: 8.2 – 5.8‰ and $\epsilon\text{Hf}_{(t)}$: +13 – +7). The older magmas formed within the amphibole stability field in a moderately thick crust (~ 35 km), while the younger magmas were generated within the garnet stability field in thickened crust (~60 km). The transition from intermediate crustal thickness and juvenile settings to a thicker crust and more enriched settings occurred at around 14 Ma. This shift was most likely related to the arrival of the young (and buoyant) Nazca plate at the South American margin, which would have resulted in the shallowing of the subduction angle, increased compressional stresses, and facilitated melting of an evolved oceanic crust. This study highlights the utility of zircon petrochronology in unraveling the crustal-scale evolution of Cordilleran arcs, providing valuable insights into the dynamic processes that control continental growth and orogeny.

3.1 Introduction

Continental arcs form through subduction-related magmatism interacting with continental lithosphere, as well as accreted oceanic or transitional crustal domains (e.g., Ducea et al., 2015). The chemical composition, spatial extent, and location of these continental arcs are controlled by the relationship between slab-related processes (external) and processes occurring within the arc system (internal), such as crustal tectonic thickening, thrust belt shortening, and subduction-related accretion and erosion processes (DeCelles et al., 2009; Ducea et al., 2015a; Chapman and Ducea, 2019). Continental arcs are primary sites of intermediate magmatism; the composition of these magmas results from the interaction of multiple reservoirs, including the mantle wedge, the continental crust, and slab fluids

associated with magma formation, ascent, and differentiation (Jones et al., 2015; Turner and Langmuir, 2015a; Farner and Lee, 2017).

There is a strong, global correlation between elevation and crustal thickness in non-cratonic regions: over long wavelengths (>10 km) and timescales (>10 ky), higher elevations are primarily controlled by isostasy (Lee et al., 2015). At subduction zones, plate convergence leads to the shortening of the upper crust via thrusting both behind and in front of the arc, and, in some cases, by the underthrusting of the lower continental lithosphere beneath the arc. Both processes result in increased crustal thickness and are typically associated with shallow angle subduction (DeCelles et al., 2009; Ducea et al., 2015a; Horton, 2018). Magmatic underplating is also considered a significant contributor to crustal thickening (Garzione et al., 2008; Chiaradia, 2009; Stirling et al., 2023). Conversely, retreating slab dynamics (i.e., roll-back) induce extensional strain, leading to crustal thinning (e.g., Horton, 2018; Lallemand et al., 2005).

Despite its oceanic nature, the crustal root in Ecuador is notably thick (Jaillard, 2022; Koch et al., 2021), while the average elevation of the Ecuadorian Andes is relatively low compared to southern Peru and Bolivia. Several studies suggest that lithospheric thickness plays a significant role in arc magma composition by controlling the extent of mantle melting (e.g., Chiaradia, 2015; Farner & Lee, 2017; Turner & Langmuir, 2015b). It is now widely accepted that the majority of geochemical diversity in arcs is generated at greater depths, especially near the base of the crust, through melting, assimilation, storage, and homogenization (MASH) processes (Hildreth and Moor bath, 1988). In addition, the extension of magmatic pathways during ascent through the crust (from its segregation and extraction in deep zones), also has a strong effect on differentiation processes, ultimately leading to the formation of more evolved magmas (e.g., Farner & Lee, 2017; Chiaradia, 2021).

Changes in crustal thickness have been studied using several approaches in subduction settings, including 1) whole rock (WR) geochemistry (e.g., Sr/Y; La/Yb; Chiaradia, 2015; Profeta et al., 2015; Sundell et al., 2021), and 2) zircon geochemistry (e.g., Eu/Eu*; Sm/Yb; Ce/Y; Tang et al., 2024; Sundell et al., 2022). The latter has received increasing attention in recent years, due to the ubiquity, refractory nature, and chemical resistance of zircons. In particular, zircon analysis provides deeper insights than WR into the mechanisms and interaction between the deep crust and the mantle and, potentially, the subsequent ascent of magma through the crust. Both approaches rely on the presence or absence of pressure-sensitive mineral phases (mostly garnet, plagioclase, and amphibole) to infer the magma

fractionation depth, which, assuming that fractionation occurs within the crust, provides a minimum crustal thickness.

Zircons preserve the initial $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic composition of the magmatic reservoir at the time of crystallization (Roberts and Spencer, 2015; Reiners et al., 2017). Furthermore, the isotopic composition of oxygen in zircons can help identify the reservoirs (i.e., crust, mantle, and slab fluids) involved in magma genesis (Bindeman, 2008). Zircons in equilibrium with mantle-derived melts span a narrow range of $\delta^{18}\text{O}$ values ($5.3 \pm 0.6\text{‰}$) (Valley, 2003). Higher $\delta^{18}\text{O}$ values ($> 5.3 \pm 0.6\text{‰}$) are indicative of intracrustal melting (Valley et al., 2005; Bindeman, 2008), while lower $\delta^{18}\text{O}$ values ($< 5.3 \pm 0.6\text{‰}$) are indicative of sources of low $\delta^{18}\text{O}$ in the mantle or interactions with hydrothermally altered crust (Monani and Valley, 2001; Valley et al., 2005; Bindeman, 2008). Coupling the analysis of radiogenic isotopes (e.g., Hf) with stable isotopes (e.g., O) allows researchers to differentiate between evolved (crustal) and juvenile (mantle-derived) isotopic signatures (e.g., Hawkesworth & Kemp, 2006b; Kemp et al., 2007).

Zircon trace element (TE) concentrations, such as U, Th, Hf, Y, Yb, Ce, Eu, Nb, and Ti, as well as their ratios (e.g., U/Yb, Th/Yb, Th/U, Eu/Eu*, LREE/HREE, Yb/Gd), can provide valuable insights into the characteristics of the parent melt, magmatic differentiation processes, mineral fractionation (e.g., plagioclase, amphibole, titanite), crustal thickness, and crystallization temperature (e.g., Belousova et al., 2002; Grimes et al., 2007, 2015; Claiborne et al., 2010; Kydonakis et al., 2014; Bell & Kirkpatrick, 2021; Sundell et al., 2022; Watson & Harrison, 2005). When coupled with U-Pb ages and isotopic signatures (e.g., ϵHf and $\delta^{18}\text{O}$), the zircon TE record provides a remarkable window into the spatial and temporal variability of magmatic processes and their associated reservoirs. It also serves as an excellent tracer of the tectonic environment in which the arc was emplaced (Attia et al., 2020; Jara et al., 2021; Jones et al., 2015).

The Andes are the largest active subduction system and host one of the most geologically diverse Cenozoic continental arcs in the world. In central and northern Ecuador (southern Northern Andes), Cenozoic magmatism was emplaced in oceanic (transitional) crust associated with an oceanic plateau and island arc system that accreted against the continental margin about 75–70 Ma ago (George et al., 2021; Jaillard, 2022; Vallejo et al., 2009; Witt et al., 2023). Throughout the Cenozoic, significant intermediate to acidic magmatism developed in these accretionary terrains, establishing geochemical trends indicative of progressive crustal thickening (Chiaradia, 2009; Schütte et al., 2010). This trend was interrupted by episodic periods of extension and crustal thinning (George et al., 2021; Witt et al., 2023), highlighting

the complexity of this arc system. Consequently, the Ecuadorian Andes provide an excellent natural laboratory to test innovative zircon-based geochemical constraints and their links to crustal thickness and, more broadly, compare the characteristics of settings associated with shallow and deep fractionation.

This study focuses on the northernmost section of the Ecuadorian arc, which has the greatest crustal thicknesses (60–65 km; Koch et al., 2021). This study aims to contribute to our understanding of the spatial distribution, petrography, geochronology, chemical evolution, and reservoir characterization of the Santiago (41–31 Ma) and Apuela (23–7 Ma) batholiths (henceforth referred to as SB and AB, respectively), alongside other minor igneous occurrences. Additionally, we evaluate widely used whole-rock crustal thickness markers and test several zircon-based crustal thickness proxies. These data allow us to propose a geodynamic model that explores the mechanisms and rates of orogenic exhumation.

3.2 Geodynamic and geological framework

The Northern Andes (encompassing the Andes of Ecuador, Colombia and Venezuela) are characterized by the accretion of oceanic lithosphere either during a single Late Cretaceous event (Luzieux et al., 2006; Vallejo et al., 2009) or multiple Late Cretaceous – Eocene accretion events. In addition to differences in timing, these models imply distinct tectonic processes: the single-event model involves westward subduction followed by collision, leading to ophiolitic obduction (i.e., oceanic crust over continental crust). In contrast, the multiple-event model involves successive collisions and subduction jams caused by the arrival of buoyant oceanic plateaus, resulting in the stacking of oceanic crust beneath oceanic crust (see Jaillard, 2022 for details). In Ecuador, the main relicts of the accreted crust can be observed along the Western Cordillera (WC), which consists mainly of poorly dated Late Cretaceous oceanic plateau basalts, ultramafic rocks, and other submarine arc sequences (e.g., Hughes & Pilatasig, 2002; Jaillard, 2022; Kerr et al., 2002; Vallejo et al., 2009).

The Ecuadorian Cenozoic arc resulted from the eastward subduction of the Farallon and Nazca plates beneath the South American Plate (Fig. 3.1). The Nazca plate separated from the Farallon plate around 25 Ma and arrived at the Ecuadorian margin around 15 Ma (Meschede and Barckhausen, 2001). The Cenozoic arc is highly segmented and is emplaced within accreted oceanic crust to the north and continental crust to the south of a suture zone defined by the Calacali-Pujili Pallatanga Fault Zone (CPPF; Fig. 3.1). The magmatic arc was emplaced following these accretion event(s) by at least ~60 Ma, as evidenced by the ubiquitous presence

of magmatic zircons in the detrital record (George et al., 2021; Witt et al., 2023) and Paleocene intrusions in southern Ecuador (e.g., the San Lucas pluton). However, direct evidence for in situ ~55–45 Ma magmatic activity remains sparse.

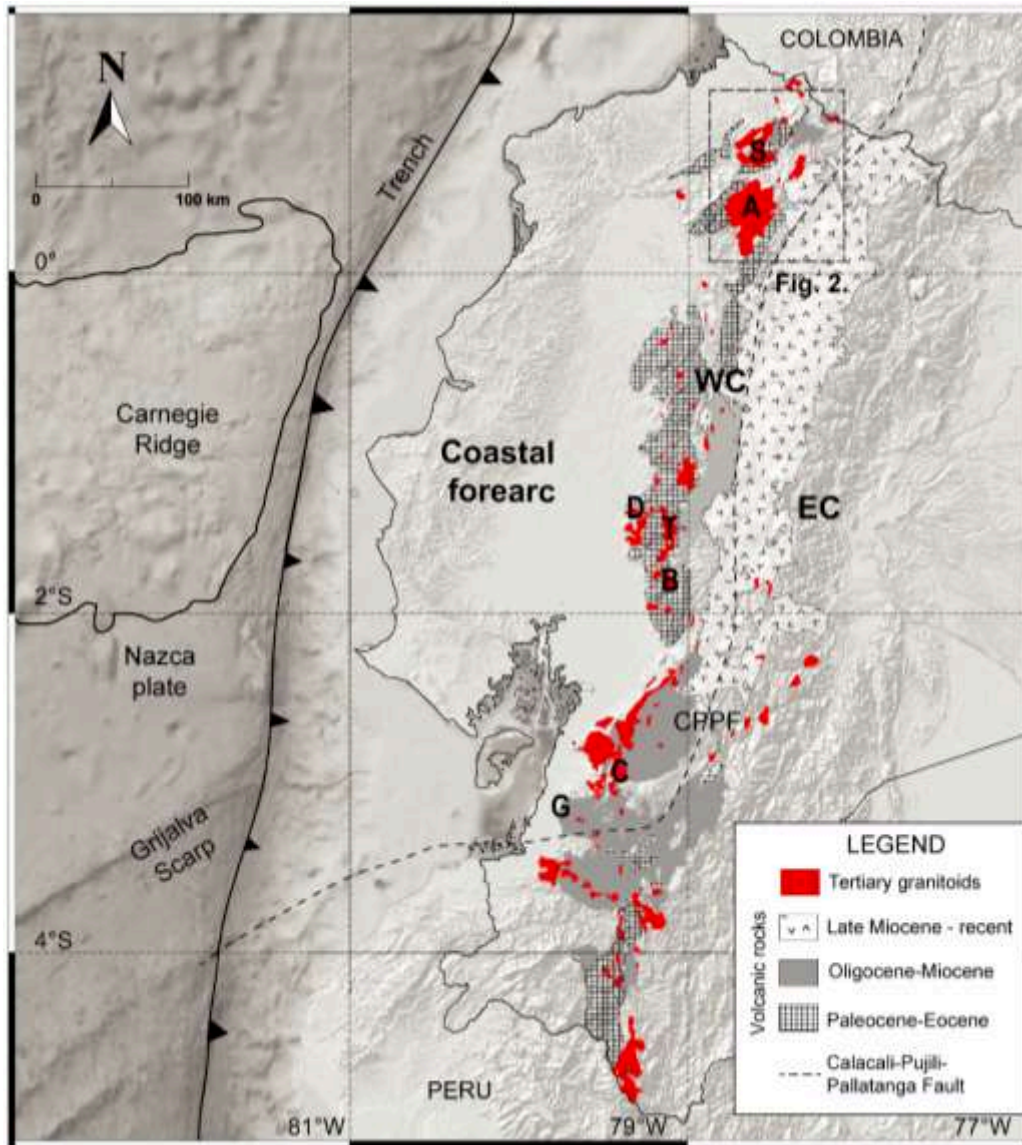


Figure 3.1 Geodynamic sketch of Ecuador, highlighting the location of the study area (indicated by the square) detailed in Fig. 2. Major intrusive bodies are labeled as follows: S-Santiago, A-Apuela, D-Domo, T-Telimbela, B-Balzapamba, C-Chaucha, G-Gaby. WC-Western Cordillera, EC-Eastern Cordillera.

Several models for arc evolution have been proposed, including: 1) different isotopic signatures correlated with different oceanic/continental assimilants at depth (Schütte, 2009b); 2) a ~ 9 Ma change in reservoir signatures from a MORB-type mantle to adakitic-like signatures as a result of crustal thickening driven by a change in the tectonic setting due to the onset of the subduction of the Carnegie ridge (Chiaradia et al., 2004); 3) a Late Oligocene-Early Miocene arc magmatic flare-up associated with accelerating and less oblique subduction

(Schütte, Chiaradia, et al., 2010); 4) the development of adakitic-like signatures younger than ~40 Ma in the Macuchi Arc formed by mantle-derived melts that evolved in the lower mid-crustal sections of a thickened, juvenile (accreted) crust (Chiaradia, 2009); 5) slab roll-back and trenchward migration of the arc from the continental to accreted crust at ~40 Ma (George et al., 2021), and 6) possible periods of intense magmatism at ~60 and ~43 Ma with various reservoir signatures related to the melting of both crustal materials and enriched mantle sources as well as a trend towards less enriched magmas between 30 and 10 Ma, most likely related to the emplacement of the arc in the continental crust in southern Ecuador (Witt et al., 2023).

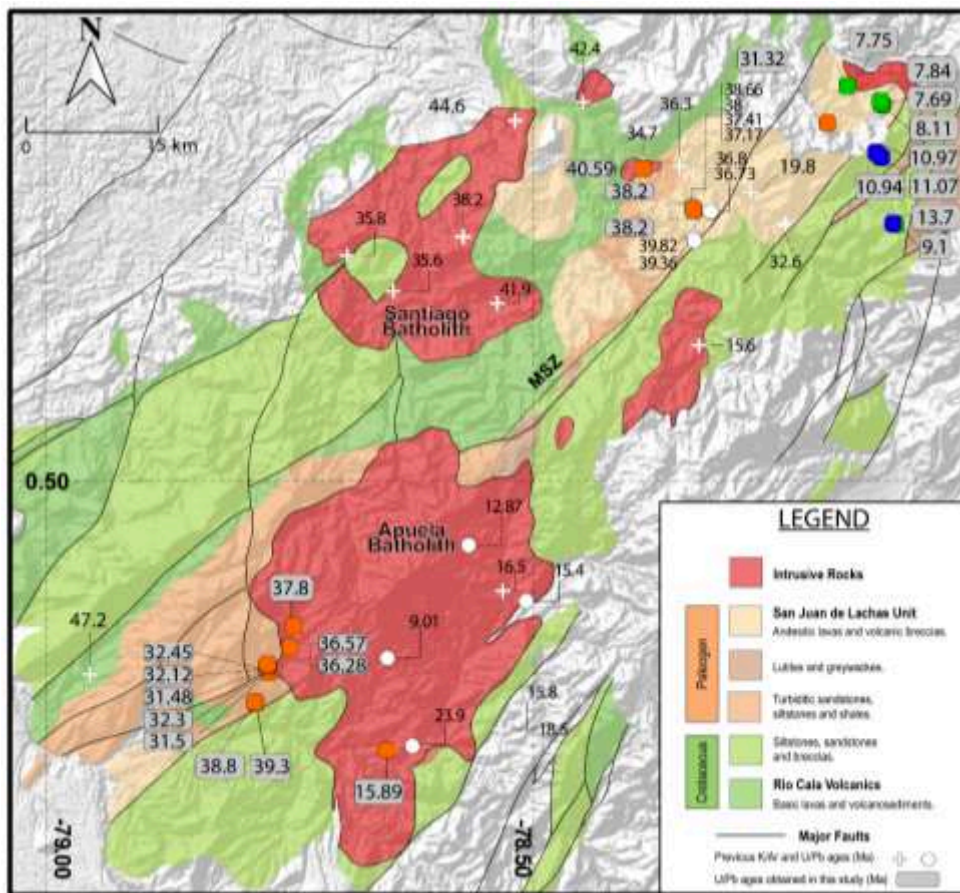


Figure 3.2 Geological map of northwestern Ecuador (refer to Fig. 1 for location), showing sample locations and ages (in Ma) determined in this study. Previously reported ages from Boland et al. (2000), Schütte et al. (2010) and Margirier et al. (2023) are color-coded as follows: orange (41–16 Ma), blue (14–9 Ma), and green (7–9 Ma).

The studied area lies within the Naranjal Block (NB; Boland et al., 2000), located near the junction of the forearc and the WC in northern Ecuador (Fig. 1). The coastal forearc is primarily composed of mostly siliciclastic Cenozoic sedimentary deposits that overlie the accreted plateau oceanic crust (Luzieux et al., 2006; Aizprua et al., 2020; Hernández et al., 2024). The NB is in faulted contact with the Pallatanga block and is crossed by the Mulaute

shear zone (Fig. 3.2; Boland et al., 2000). There are two major intrusive batholiths in the study area (Fig. 3.2). The SB is primarily consists of tonalites that have been dated between 44 and 35 Ma using K-Ar dating on hornblendes and biotites (Boland et al., 2000). In contrast, the AB consists of quartz-diorites and has been dated between 23 and 7 Ma using K-Ar dating on hornblende and biotite as well as U/Pb dating on zircon (Fig. 3.2; Boland et al., 2000; Schütte et al., 2010; Castro, 2020; Margirier et al., 2023; this work). Both batholiths are hosted within the poorly dated volcanoclastic units of the Rio Cala and sequences of the Macuchi Island arc (Boland et al., 2000). Geochemically, the SB is calc-alkaline metaluminous while the AB is calcic-metaluminous (Boland et al., 2000). The NB hosts two of the most significant mineral deposit discoveries in Ecuador over the last 20 years: the Eocene Cascabel porphyry Cu-Au and the late Miocene Llurimagua (Junín) porphyry Cu-Mo deposits (Chiaradia et al., 2004; Schütte et al., 2012) are hosted by the SB and the AB, respectively.

3.3 Analytical basis and description of methods

A total of 24 samples were collected from the western part of the AB as well as from intrusive bodies to the east of the SB. Sampling locations are indicated in Fig. 3.2 and Table 1. These locations were selected for their accessibility and suitability for sampling, and in most cases represent areas of mining interest.

3.3.1 Whole-rock major and trace elements

Whole-rock geochemical analyses were conducted on 23 samples using the lithium metaborate/tetraborate fusion technique. Major element oxides in the resulting diluted solutions were measured using inductively coupled plasma atomic emission spectrometry (ICP-AES), while trace and rare-earth elements were measured using inductively coupled plasma mass spectrometry (ICP-MS) at the MSALABS laboratory (Langley, Canada). Additional details, including fusion parameters and detection limits are provided in the Supplementary Information. Geochemical data were processed using the R programming language and the Geochemical Data Toolkit (GCDkit) software (Janoušek et al., 2016).

Table 3.1 Sample Location and description

Sample	Latitude	Longitude	Lithology	Age	
NB-03	0.350	-78.746	Granodiorite	37.8 ± 0.51 Ma (n=13)	206Pb/238U Mean
NB-04	0.834	-78.143	Quartzodiorite	11.07 ± 0.4 Ma (n=10)	Lower Intercepts
NB-05	0.839	-78.149	Dacitic Porphyry	10.94 ± 0.12 Ma (n=9)	206Pb/238U Mean
NB-11	0.764	-78.129	Dacitic Porphyry	9.1 ± 0.24 Ma (n=11)	Lower Intercepts
NB-13	0.766	-78.131	Diorite	13.7 ± 0.3 Ma (n=8)	Lower Intercepts
NB-16	0.837	-78.147	Dacitic Porphyry	10.97 ± 0.19 Ma (n=10)	Concordia
NB-18	0.302	-78.772	Diorite	31.5 ± 0.88 Ma (n=8)	206Pb/238U Mean
NB-19	0.306	-78.773	Dioritic Porphyry	32.27 ± 0.97 Ma (n=7)	Concordia
NB-20	0.888	-78.141	Andesitic Porphyry	8.11 ± 0.28 Ma (n=12)	Lower Intercepts
NB-21	0.889	-78.143	Dacitic Porphyry	7.69 ± 0.29 Ma (n=10)	Lower Intercepts
NB-22	0.892	-78.144	Quartzodiorite	7.84 ± 0.18 Ma (n=12)	Concordia
NB-24	0.907	-78.178	Andesitic Porphyry	7.75 ± 0.18 Ma (n=12)	Lower Intercepts
NB-27	0.309	-78.772	Diorite	31.48 ± 0.56 Ma (n=9)	Concordia
NB-28	0.310	-78.773	Dioritic Porphyry	32.12 ± 0.75 Ma (n=8)	Lower Intercepts
NB-29	0.310	-78.773	Granodiorite	32.45 ± 0.69 Ma (n=10)	Concordia
NB-30	0.328	-78.750	Granodiorite	36.57 ± 0.39 Ma (n=12)	Concordia
NB-37	0.869	-78.198	Dioritic Porphyry	31.32 ± 0.81 Ma (n=6)	Lower Intercepts
NB-41	0.823	-78.387	Granodiorite	40.59 ± 0.52 Ma (n=13)	Lower Intercepts
NB-57	0.7791	-78.3357	Hb-Quartzodiorite	38.2 ± 2.1 Ma (n=9)	Concordia
NB-60	0.7804	-78.3355	Hb-Quartzodiorite	38.2 ± 2 Ma (n=10)	Concordia
NB-63	0.3280	-78.7502	Quartzodiorite	36.2 ± 1.6 Ma (n=10)	Concordia
NB-64	0.2219	-78.6510	Granodiorite	15.89 ± 0.86 Ma (n=10)	Concordia
NB-65	0.2700	-78.7857	Quartzdiorite	39.3 ± 0.49 Ma (n=3)	206Pb/238U Mean
NB-66	0.2715	-78.7858	Quartzodiorite	38.8 ± 0.7 Ma (n=10)	206Pb/238U Mean

3.3.2 U-Pb dating

Zircon separation was performed at the University of Lille, France following a standard density and magnetic separation procedure (Malusà & Fitzgerald, 2019; and references therein). Zircon grains were handpicked under binocular microscopes, mounted on epoxy resin, and polished to reveal the center of each crystal. The internal structures of each zircon crystal were examined, and appropriate dating zones were selected using cathodoluminescence imaging (see Supplementary Fig. 1 for representative images). In situ laser ablation multi-collector-inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) was carried out on 20 samples at the Geosciences Laboratory in Montpellier, France (e.g., Bruguier et al., 2017; Genge et al., 2025). Four other samples were analyzed using LA-ICP-MS at the Magmas and Volcans Laboratory in Clermont Ferrand, France. All data acquisition parameters are provided in the Supplementary information. Concordia diagrams were generated using Isoplot R (Vermeesch, 2018). All diagrams are presented in Supplementary Fig. 2.

3.3.3 ϵHf and $\delta^{18}\text{O}$ systematics

In situ Lu-Hf isotope analyses were performed at the Geosciences Montpellier Laboratory, University of Montpellier-France (AETE–ISO regional facility of the OSU OREME) using a Thermo Finnigan Neptune+ multi-collector-inductively coupled mass spectrometer (MC-ICP-MS) coupled with a Photon-Machine Analyte G2 excimer laser. To ensure data quality and reproducibility, the following reference materials were analyzed at the start of the session and after approximately every 15 samples: 91500 ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282315$; Blichert-Toft, 2008); Plešovice ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282482$; Sláma et al., 2008); GJ-1 ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282000$; Morel et al., 2008). Zircon initial ϵHf values and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios were calculated using the ^{176}Lu decay constant of $1.87 \times 10^{-11} \text{ yr}^{-1}$ (Söderlund et al., 2004), $^{176}\text{Hf}/^{177}\text{Hf}_{\text{CHUR}} = 0.282785$, and $^{176}\text{Lu}/^{177}\text{Hf}_{\text{CHUR}} = 0.0336$ parameters from Bouvier et al. (2008). Additional technical information can be found in the Supplementary Information.

Oxygen isotope analyses were performed at the Centre de Recherches Pétrographiques et Géochimiques (CRPG), Université de Lorraine, Nancy, France. Analyses were conducted with a Cameca IMS1270 in FC/FC detection mode using a Cs^+ primary ion beam with a 2.5nA intensity and 10kV acceleration. The instrument was calibrated for instrumental mass fractionation using the 91500-zircon reference material, which exhibits raw $\delta^{18}\text{O}$ values ranging from 7.08‰ to 7.34‰ (SMOW).

3.3.4 Trace-elements in Zircon

Zircon trace element concentrations were determined by LA-ICP-MS at Geosciences Montpellier Laboratory, University of Montpellier, France. The measurement parameters were a laser spot diameter of 30 μm , a repetition rate of 4 Hz, and a fluence of 6.8 J/cm². The spots were placed as close as possible to the sites where U-Pb dating had already been conducted to obtain readings that were in good agreement with the obtained U-Pb ages and trace element measurements. NIST 612 synthetic glass and the G91500 zircon standard were used as reference materials, while element concentrations were normalized to SiO₂ and calculated using Glitter 4.0 software.

3.4 Results

3.4.1 Zircon U-Pb dating

Zircon U-Pb dating was performed on 24 samples, identifying four distinct periods: Eocene (40.6 $\pm$ 0.52 to 36.2 $\pm$ 1.6 Ma; 8 samples), Oligocene (32.5 $\pm$ 0.69 to 31.3 $\pm$ 0.81 Ma; 6 samples), early Miocene (15.9 $\pm$ 0.86 to 13.6 $\pm$ 0.12 Ma; 2 samples), and late Miocene (11.07 $\pm$ 0.4 to 7.7 $\pm$ 0.29 Ma; 8 samples). No filtering of the highest and lowest concordant dates was applied when calculating the concordia or weighted mean ages. Errors in age calculations, both quantitative and graphical (e.g., error bars, ellipses), are reported at 95 % confidence intervals (2 σ).

Concordia ages were determined for samples NB-63, NB-60, NB-57, NB-30, NB-16, and NB-22 and presented on Wetherill diagrams. The weighted mean ages were computed based on ²⁰⁶Pb/²³⁸U dates for samples with discordant analyses, which included NB-66, NB-65, NB-64, NB-29, NB-27, NB-5, and NB-3, as well as those with lower intercept ages, which included NB-41, NB-37, NB-28, NB-24, NB-21, NB-20, NB-13, NB-11, and NB-4. These results are presented on both concordia and inverse concordia diagrams, allowing for the interpretation of discordance and age distribution across the sample set. Complete zircon U-Pb data are presented in Table 2 and Table 2.1 in the Supplementary Data. Representative analyses for each period are shown in Fig. 3.3. Remarkably, only one sub-concordant inherited zircon at 604 Ma was observed during U-Pb dating in a total of 253 analyzed grains (Table 2; Supplementary Data).

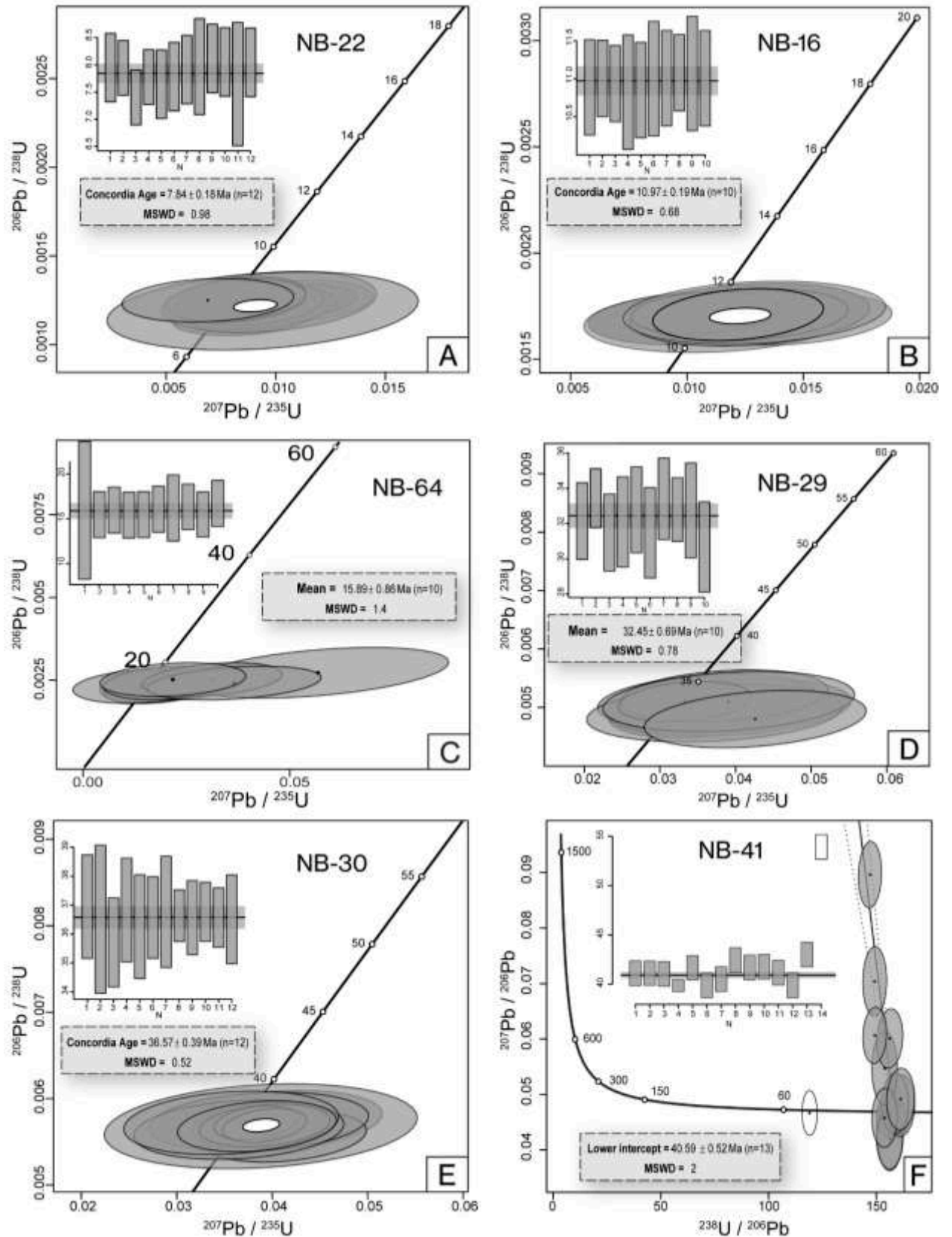


Figure 3.3 Representative zircon concordia and inverse concordia diagrams showing the $^{206}\text{Pb}/^{238}\text{U}$ dates of the analyzed zircons, with 2σ (two-sigma) error margins. Weighted mean age plots for the $^{206}\text{Pb}/^{238}\text{U}$ dates are also included.

3.4.2 Petrographic characteristics and whole-rock major and trace element Concentrations

A total of 21 samples were analyzed for major and trace elements, while an additional 2 samples were analyzed exclusively for trace elements. The full results are presented in Table 3 in the Supplementary Data. The sample set is primarily composed of tonalitic and granodioritic rocks (Fig. 3.4A). Tonalites dominate the 41–16 Ma and 14–9 Ma intervals, while the younger samples were mostly comprised of granodiorites (Fig. 3.4A). The tonalites and granodiorites exhibited relatively homogeneous, medium-grained, hypidiomorphic textures (Supplementary Fig. 3A). A few samples display porphyritic textures, characterized by phenocrysts embedded in a fine-grained matrix. The major mineral phases in all rock types were quartz (20–40 %), plagioclase (oligoclase–andesine; 60–40 %) and magnesio-hornblende; biotite (up to 10 %) and K-feldspar (up to 5 %) occur sporadically. Magnetite, titanite, epidote, fluorapatite, and zircon are the main accessory minerals. Amphibole occurs as euhedral, occasionally poikilitic crystals that enclose plagioclase and quartz; in general, the abundance of this mineral decreases as the magmas transitioned from tonalites to granodiorites, forming about 7–10 % in the 41–16 Ma group, 5–8 % in the 14–9 Ma group, (with a few values up to 18 %, usually in association with the biotite; Supplementary Fig. 3), and 9–10 % in the 9–7 Ma group. When present, biotite forms euhedral crystals or is co-crystallized with amphibole (Supplementary Fig. 3). Magnetite, apatite, and zircon are each present in abundances of less than 2 %, either interstitial to other minerals or enclosed in quartz, plagioclase, and amphibole. A few hornblende-rich samples contain up to 2.5 % coarse magnetite crystals that commonly enclose fluorapatite. Titanite ($\pm$ epidote) occurs along amphibole rims or in association with biotite (Supplementary Fig. 3).

In terms of the major oxides (Supplementary Fig. 4), the chemical compositions of the samples are indicative of calc-alkaline, medium-K rocks. The older rocks are andesitic to dacitic (recalculated volatile-free 60.4–73.3 wt% SiO₂) while the two younger groups display more restricted compositions within the dacitic–rhyodacitic fields (65.9–74.4 wt% SiO₂); in addition, the younger samples exhibit higher Na₂O enrichment at similar SiO₂ levels. Plots of major oxides vs. SiO₂ content show that, despite some variations, especially in the Fe₂O₃ and P₂O₅ contents, all samples follow calc-alkaline trends (Supplementary Fig. 4). The variations in the AFM diagram are also typical of a calc-alkaline trend (Fig. 4B).

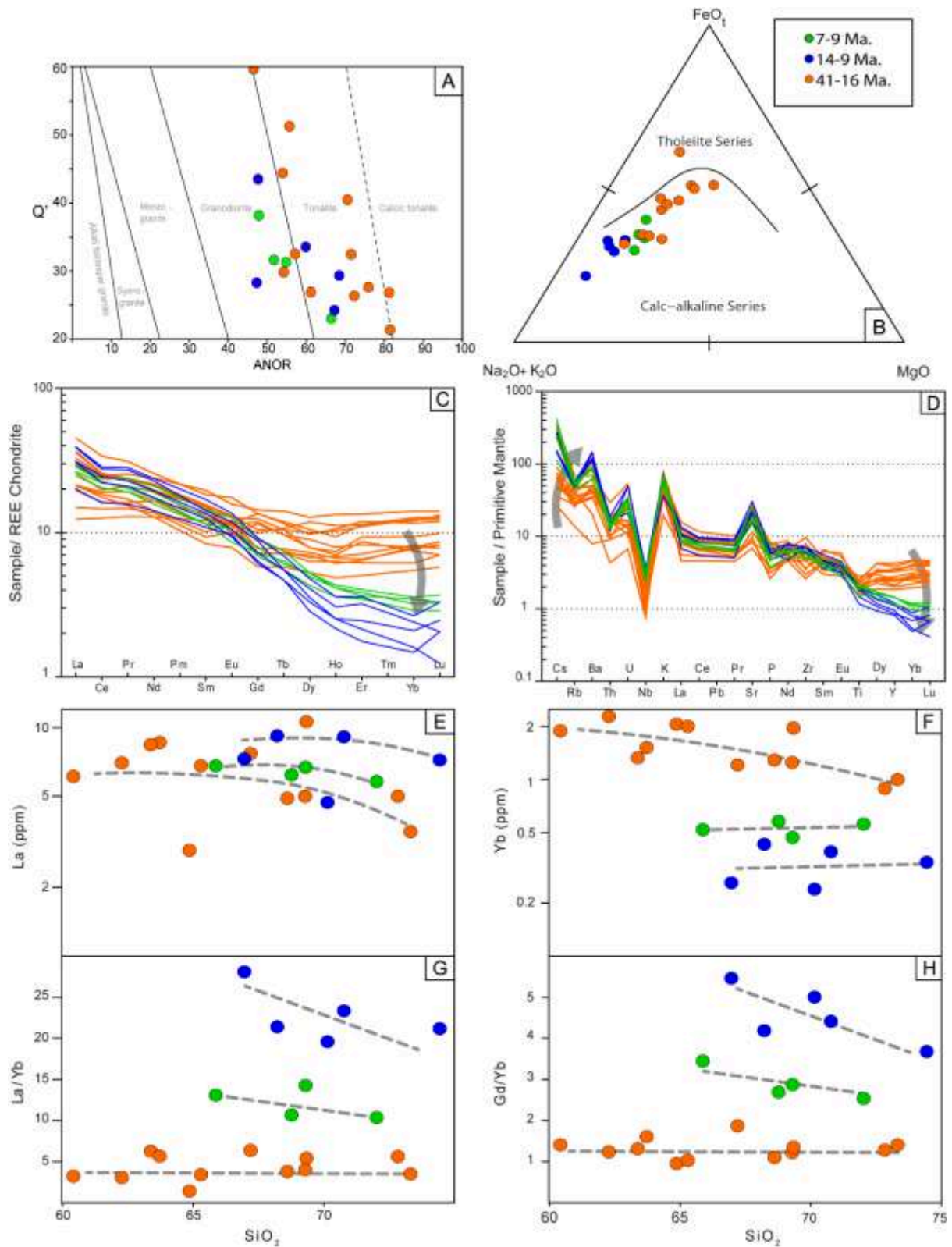


Figure 3.4 Classification and selected geochemical characteristics for representative granitoids of this study. A) Normative Q'-ANOR diagram of Streckeisen & Le Maitre (1979). $Q' = \text{quartz} / (\text{quartz} + 20 \text{ feldspars})$. $100 \text{ ANOR} = 100 \cdot \text{anorthite} / (\text{orthoclase} + \text{anorthite})$. B) A-F-M plot of Irvine and Baragar (1971) showing the calc-alkaline nature of the studied samples. C) Primitive mantle normalized multi-element patterns. D) Chondrite normalized rare earth element diagram. Normalizing values of the primitive mantle and chondrite are from Sun and

McDonough (1989). E) Variations of La vs. SiO₂ (wt%). F) Variations of Yb vs. SiO₂. G) Variations of La/Yb ratios vs. SiO₂ (wt%). H) Variations of Gd/Yb ratios vs. SiO₂ (wt%).

Chondrite normalized REE values are relatively distinct between the older and younger samples (Fig. 4C). The Eocene-Oligocene rocks are characterized by variable, null to moderate enrichments in LREE relative to HREE ($\text{La}_N/\text{Yb}_N = 0.96\text{--}4.32$) as well as flat MREE–HREE sections ($\text{Sm}_N/\text{Yb}_N = 0.99\text{--}1.98$). In contrast, the Miocene rocks are more strongly depleted in HREE, with $\text{La}_N/\text{Yb}_N = 13.30\text{--}19.07$ for the 14–9 Ma group and $\text{La}_N/\text{Yb}_N = 7.04\text{--}9.68$ for the 9–7 Ma group. The MREE–HREE slopes are also more pronounced in the 14–9 Ma rocks ($\text{Sm}_N/\text{Yb}_N = 5.80\text{--}8.37$) than in the youngest rocks ($\text{Sm}_N/\text{Yb}_N = 3.26\text{--}3.44$). However, the LREE enrichments relative to the MREEs are rather low and relatively similar in all samples ($\text{La}_N/\text{Sm}_N = 1.01\text{--}2.79$). A primitive mantle-normalized multi-element diagram (Fig. 4D) shows that, relative to the adjacent REEs, the samples from all three periods are strongly enriched in K and Sr as well as the most incompatible large ion lithophile elements (LILEs), such as Cs, Rb, and Ba. The samples are also depleted in high field strength elements (HFSEs) such as Nb, Ti, and P. These characteristics are typical of arc magmatism. The older and younger rocks can also be distinguished by variations in their La, Yb, and La/Yb and Gd/Yb ratios relative to their SiO₂ contents (Fig. 3.4E, F, G, H). Although these ratios remain relatively constant during differentiation for the 41–16 Ma rocks, they progressively decrease by a factor of ~4 with decreasing SiO₂ for the younger rocks. Sr/Y ratios for the older rocks vary between 8 and 44, with no correlation with the ages or the SiO₂ content (Fig. 3.5). In contrast, Sr/Y ratios range between ~80 and 135 for the 14–9 Ma interval, and between 49 and 78 for the youngest rocks. Similar patterns are observed in the $(\text{La}/\text{Yb})_N$ ratios, with values between 13 and 20 for the 14–9 Ma interval and between ~7–10 for the youngest rocks (Fig. 3.5).

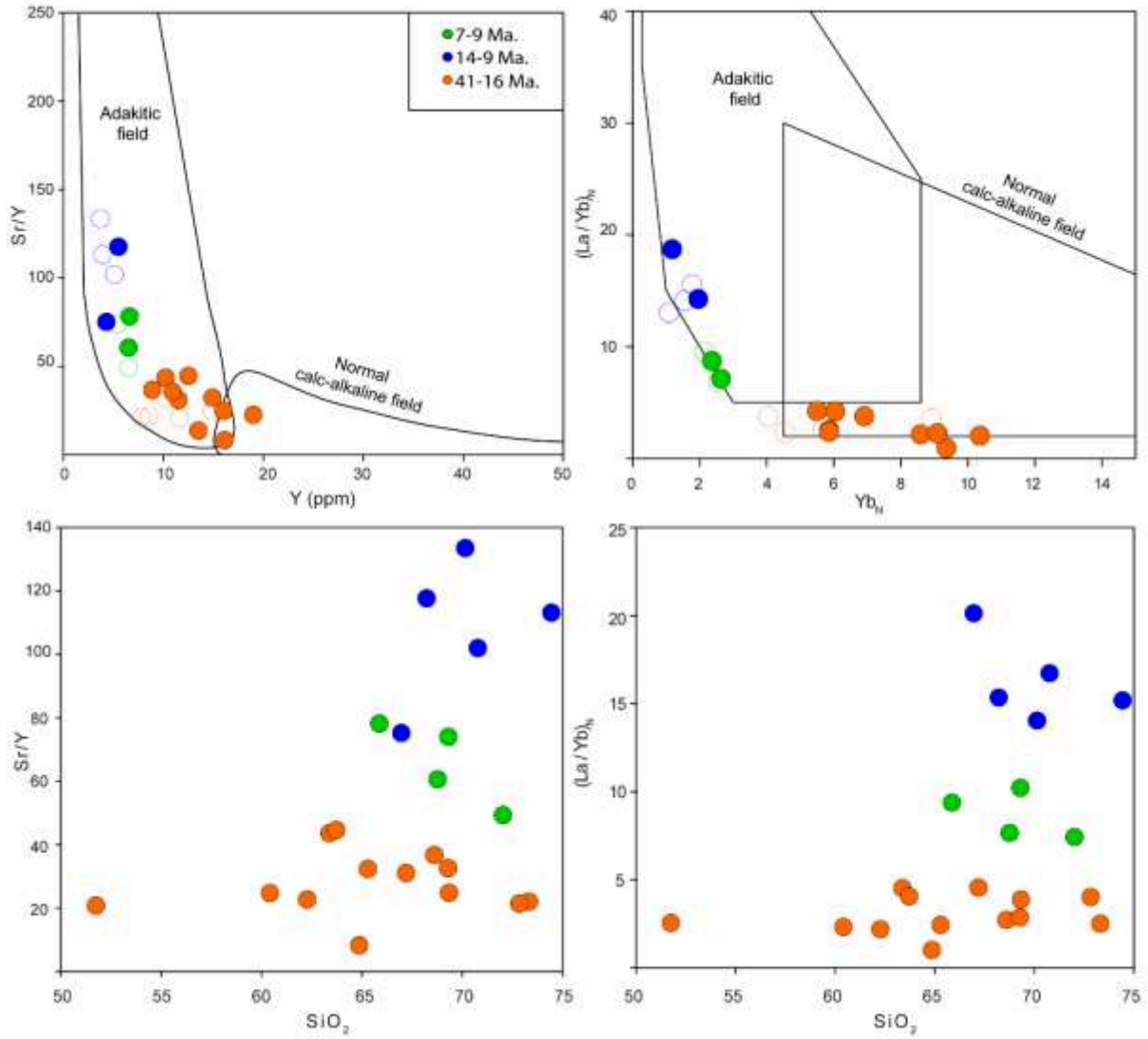


Figure 3.5 Adakite discrimination diagrams. A) Sr/Y vs. Y, and B) (La/Yb) N vs. Yb N. Rejected data points, represented by empty circles, do not meet the filtering criteria (55%–68% SiO₂, 0%–4% MgO, and 0.05–0.2% Rb/Sr) established in Profeta et al. (2015) for crustal thickness calculations.

3.4.3 ϵHf and $\delta^{18}\text{O}$ in zircon

The $\epsilon\text{Hf}_{(t)}$ values (Fig. 6 and Table 4; Supplementary Data) are indicative of a consistent trend of enrichment across all analyzed periods. In the 41–31 Ma interval, $\epsilon\text{Hf}_{(t)}$ values range from +16.9 to +13.2. In contrast, $\epsilon\text{Hf}_{(t)}$ values show a general decreasing trend in the Miocene, ranging from +13 to +7.4, interrupted by higher values around 12 Ma. The $\epsilon\text{Hf}_{(t)}$ values (Fig. 3.6 and Table 4; Supplementary Data) are indicative of a consistent trend of enrichment across all analyzed periods. In the 41–31 Ma interval, $\epsilon\text{Hf}_{(t)}$ values range from +16.9 to +13.2. In

contrast, $\epsilon_{\text{Hf}(t)}$ values show a general decreasing trend in the Miocene, ranging from +13 to +7.4, interrupted by higher values around 12 Ma.

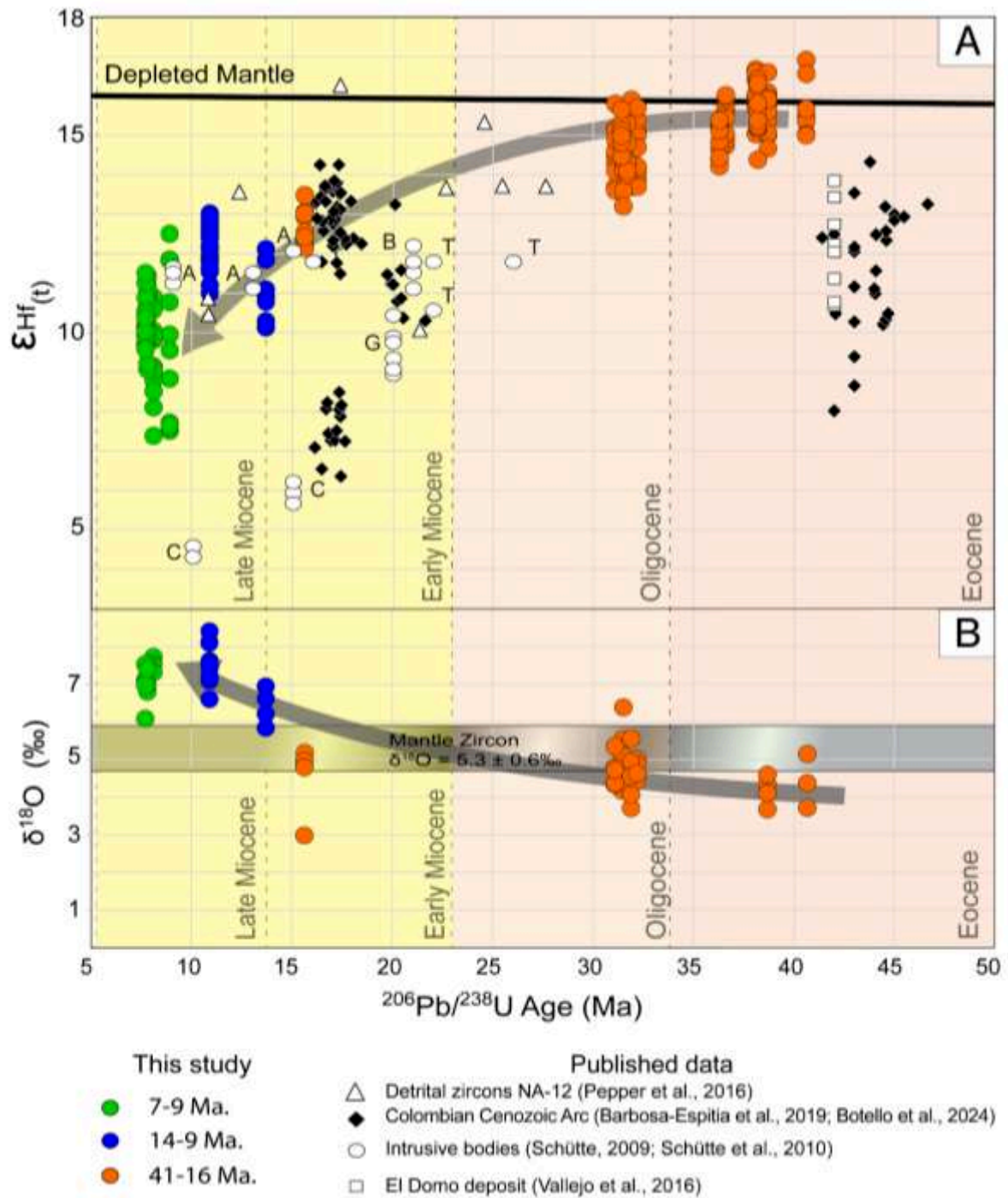


Figure 3.6 Plots showing: A) $\epsilon_{\text{Hf}(t)}$ vs. crystallization age, and B) $\delta^{18}\text{O}$ vs. crystallization age for the studied zircons. Intrusive bodies are labeled as follows: A, Apuela; T, Telimbela; B, Balsapamba; C, Chaucha; G, Gaby.

3.4.4 Trace elements in zircon

All the analyzed zircons fall within the continental domain proposed by Grimes et al. (2007), with a marked increase in U/Yb ratios with increasing melt fractionation (Fig. 3.7A). The Th/U ratio serves as an indicator of zircon origin, with values <0.1 suggesting a metamorphic source and values >0.1 pointing to an igneous origin—either felsic (0.1–0.7) or mafic (>1.5) (Kirkland et al., 2015; and references therein). Th/U ratios ranging between 0.1 and 0.7, confirm an igneous origin with a felsic composition. The Th/U values cluster around ~ 0.5 in the Eocene-Oligocene and decrease to ~ 0.2 during the Miocene (Fig. 3.7B). REE patterns show the enrichment of HREE and the depletion of LREE, as well as negative Eu and positive Ce anomalies; these are all characteristic of igneous zircons (Supplementary Fig. 5). A slightly greater HREE depletion is observed in the Late Miocene compared to older samples.

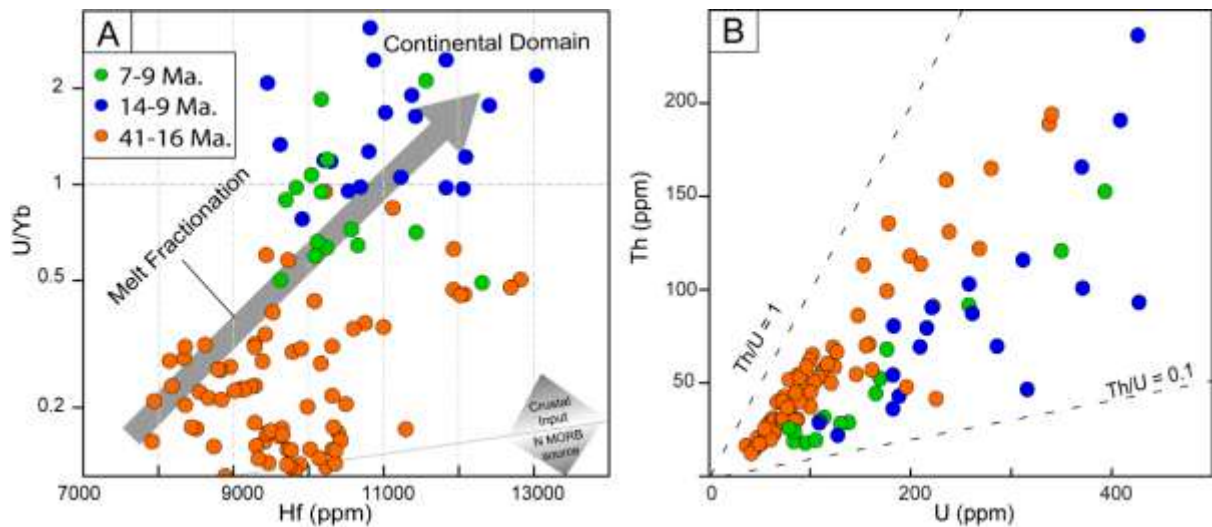


Figure 3.7 Zircon discrimination diagrams. A) U/Yb vs. Hf, following by Grimes et al. (2007) and B) Th vs. U.

The Eu/Eu* ratio (Fig. 3.8) exhibits two distinct increasing trends, rising from approximately 0.3 to 0.7 over time. The LREE/HREE ratio exhibits a sustained increase between 41 and 7 Ma, while the U/Yb ratio also shows a marked positive (enrichment) trend, with an older cluster (41–31 Ma) exhibiting a narrower range of values below 0.5 and a younger second cluster (16–8 Ma) exhibiting a broader range of values between 0.5 and 2.5. Furthermore, Ti-in-zircon temperatures (proposed as a thermometer by Watson & Harrison (2005) assuming an $a\text{TiO}_2 > 0.5$), show a slight decrease of crystallization temperatures from 650 to 800 °C between 41 and 31 Ma to 600–700 °C between 16 and 7 Ma.

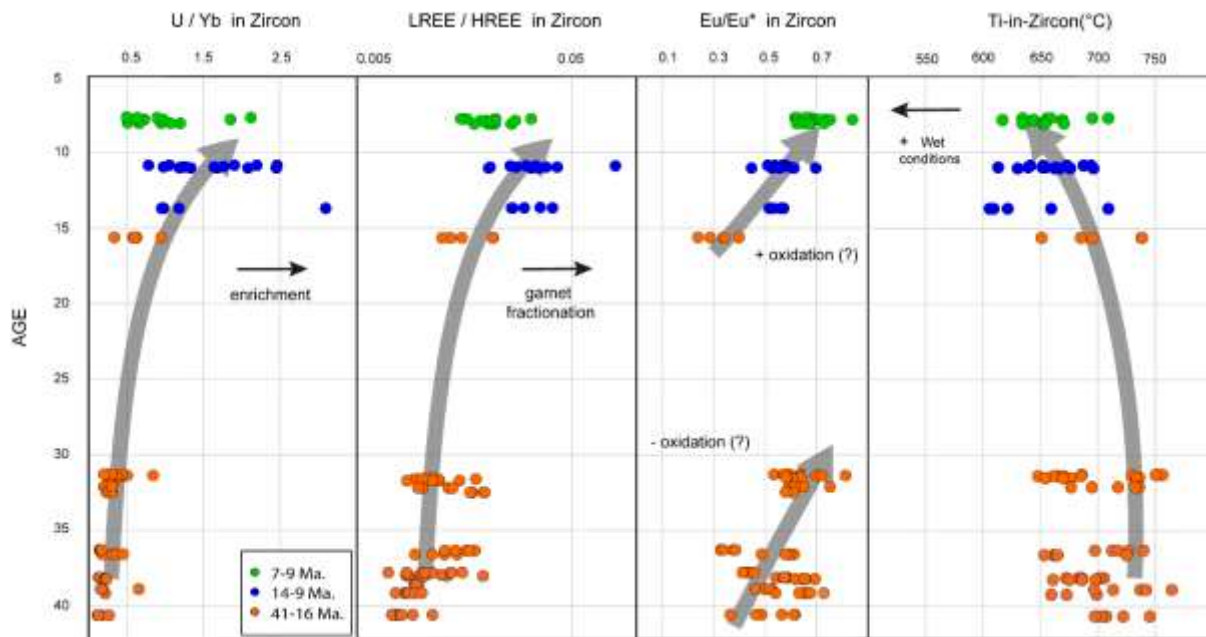


Figure 3.8 Trace elements ratios in zircon.

The analysis of the trace element ratios (Eu/Eu^* vs. Hf , Yb/Gd vs. Th/U , Yb/Gd vs. Hf) can provide insights into pressure-sensitive mineral fractionation (. Indeed, distinct trends emerged across different periods based on this analysis. For example, the lack of correlation between Eu/Eu^* and Hf (Fig. 3.9A) suggests that plagioclase is not a dominant fractionating phase in any period. In contrast, the increase in the Yb/Gd ratio with increasing Hf and decreasing Th/U in the 41–16 Ma period is indicative of amphibole fractionation, a trend that is not observed in the younger periods (Fig. 3.9B, C). Finally, these ratios also provide insights into magmatic differentiation processes. Unlike the 41–16 Ma period, the 14–7 Ma period is characterized by a significant increase in magmatic water content (H_2O) as well as deeper melting and/or increased interaction with magmas generated at greater depths (Fig. 3.9D, E). Zircon trace element analyses are presented in Table 6 in the Supplementary Data.

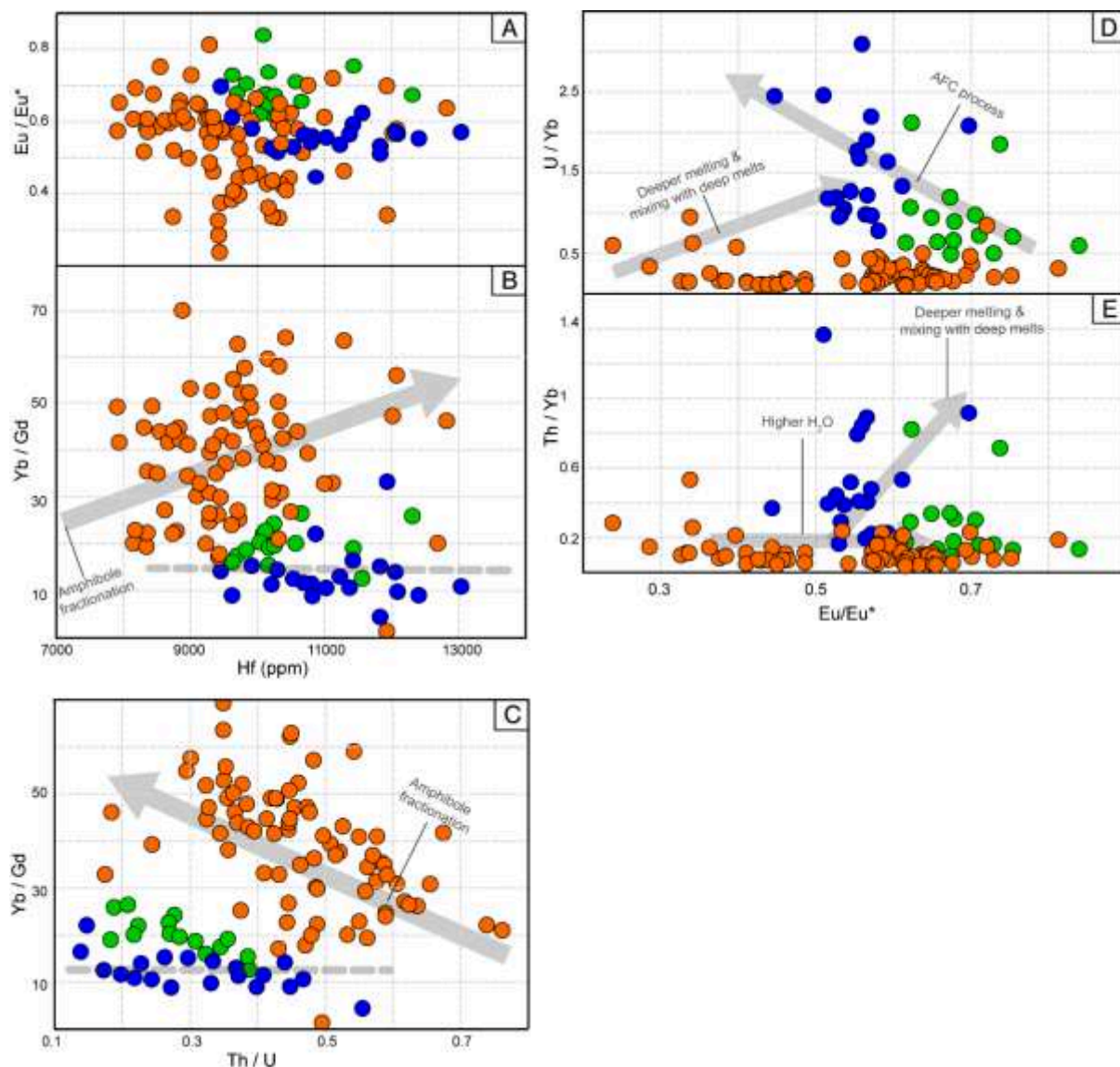


Figure 3.9 Zircon Geochemistry showing: A, B, C) fractionation trends of plagioclase and amphibole; and D, E) discrimination diagrams illustrating magmatic differentiation processes.

3.5 Discussion

3.5.1 New chronologic insights for the Santiago and Apuela Batholiths

The new U-Pb (zircon) dataset presented in this study allows for a redefinition of the spatial distribution of magmatic bodies in the NB. Our study identified zircon U/Pb ages ranging from 40.6 to 38.1 Ma in the region east of the SB; ages ranging from 39.3 to 31.48 (late Paleogene) near the southwestern boundary of the AB, and ages ranging from 37.8 to 36.28 Ma in regions previously mapped as part of the AB (Fig. 3.2). Although whether these new ages redefine the extent of the SB remains uncertain, they clearly provide new insights into the spatial extent of Eocene magmatism in the NB.

Within the AB, our analysis reveals a single age of 15.63 ± 0.86 Ma, close to the hornblende K/Ar age of 16.5 Ma reported by Boland et al. (2000). In the northeast of the NB, near the Colombian border, we obtained Miocene ages ranging from 13.7 ± 0.3 to 7.69 ± 0.29 Ma. Like the Eocene magmatism, while it is not clear whether these new ages redefine the extension of the AB, they certainly redefine the spatial extent of Miocene magmatism in the NB.

The chronological dataset presented here provides a robust framework for the temporal distribution of magmatism in the NB, with two main periods of magmatic activity identified at 41–31 Ma and 16–7 Ma. Whether the gap between these two periods represents a true magmatic gap cannot be determined with the current dataset. Detrital zircons obtained near the NB spanning the ~31–16 Ma interval (e.g., sample NA-12 from Pepper et al., 2016) exhibit highly juvenile $\epsilon\text{Hf}(t)$ values above 13, which is atypical for the central Ecuadorian Andes (Fig. 6; George et al., 2021; Schütte, 2009; Witt et al., 2021). This suggests that these zircons may be sourced from granitoids emplaced in the NB. This evidence, combined with the U-Pb age of 23 Ma for the AB reported by Margirier et al. (2023), would explain the 31–16 Ma gap that has arisen due to a lack of in-situ dating. However, a recent study exploring the evolution of the continental arc in Colombia suggests that ~23 Ma granitoids observed in the southern WC may represent the first products of magmatism after an Oligocene-Miocene magmatic gap, related to highly oblique convergence (Botello et al., 2024 and references therein). Finally, it should be noted that only one inherited zircon was identified across all dated rocks, suggesting a lack of continental crust beneath the NB.

3.5.2 Enrichment trends

The 41–31 Ma magmatic interval is characterized by depleted mantle-like $\epsilon\text{Hf}(t)$ values (Fig. 3.6). Zircon $\delta^{18}\text{O}$ measurements corroborate this observed trend in $\epsilon\text{Hf}(t)$ values. In the 41–16 Ma interval, sub-mantellic $\delta^{18}\text{O}$ values, which are commonly linked to hydrothermally altered oceanic basement rocks, transitioned toward mantle-like $\delta^{18}\text{O}$ values. In contrast, the 14–7 Ma interval is characterized by $\epsilon\text{Hf}(t)$ values that possessed moderately enriched signatures and $\delta^{18}\text{O}$ values that exhibited slightly supracontinental signatures. Consequently, the $\epsilon\text{Hf}(t)$ and $\delta^{18}\text{O}$ values, as well as other whole-rock and zircon trace element contents (e.g., Sr/Y, La/Yb_N, LREE/HREE, and U/Yb), present an enrichment trend from 41 to 7 Ma (Figs. 3.5, 6, and 8) that is strongly suggestive of progressive variations in the magmatic reservoirs.

The SB exhibits a more pronounced yet less widespread juvenile $\epsilon\text{Hf}(t)$ signature compared to rocks north and south of the NB. Specifically, slightly enriched signatures are observed in the Timbiqui Complex (Colombia), while more dispersed signatures are observed in the El Domo deposit (Fig. 3.6; Vallejo et al., 2016; Barbosa-Espitia et al., 2019). The isotopic signatures of the SB are the most primitive signatures observed in both the in situ and detrital record of the Cenozoic Ecuadorian arc (Pepper et al., 2016; Schütte, Chiaradia, Massimo, et al., 2010; Vallejo et al., 2016; Witt et al., 2023).

Barbosa-Espitia et al. (2019) proposed that depleted HREE, intermediate Sr/Y, and the absence of Eu anomalies in the intrusive rocks of the Timbiqui Complex in southern Colombia are indicative of a moderately mature arc, formed at mid-to-shallow crustal levels, with the assimilation of both sediment and deep mafic crust. In contrast, from 41 Ma onwards, the SB exhibits more juvenile $\epsilon\text{Hf}(t)$ signatures, with $\delta^{18}\text{O}$ values typical of gabbroic reservoirs and whole-rock and zircon trace element contents that are characteristic of very immature magmatism (i. e., poorly evolved mantle-derived magmas). Despite these primitive signatures, the whole-rock and zircon trace elements in the SB suggest that the magmatic differentiation occurred in the amphibole stability field, with mid-crustal thickness estimates of about 35 km (see Section 5.3).

Zircon U/Yb and LREE/HREE ratios also indicate significant evolution of the magmatic reservoirs between 41 and 7 Ma, with the most significant change occurring at ~14 Ma and peak values at 12 Ma (Fig. 3.8). These trends may reflect source enrichment via crustal assimilation/melt interaction, or HREE depletion due to fractionation or the presence of residual high-pressure minerals (e.g., garnet, amphibole) in the source, or a combination of both processes (see Section 5.3). Notably, these variations correlate with other enrichment trends (e.g., $\epsilon\text{Hf}(t)$, $\delta^{18}\text{O}$) and crustal thickness markers (see Section 5.3). Our dataset suggests a transition to adakite-like magmas, characterized by low Yb and Y contents, high Sr/Y and La/Yb ratios, and low Rb/Sr ratios (see Fig. 5 and Supplementary Fig. 6). This transition occurred at approximately 14 Ma, which is approximately 5 Ma later than previously proposed for central-southern Ecuador (Chiaradia et al., 2004). Furthermore, this ~14 Ma transition is unlikely to be due to the onset of the subduction of the Carnegie ridge as most estimates place its initiation at 6–2 Ma (Hernández et al., 2020; Margirier et al., 2023; Michaud et al., 2009; Witt et al., 2006). The enrichment of the magmatic reservoirs during the late Miocene via the addition of greater amounts of continental crust melts is also unlikely due to minor $\delta^{18}\text{O}$ enrichment and the lack of inherited zircons across a total of 253 analyzed grains. The limited $\delta^{18}\text{O}$ variation further reflects the low sensitivity of oxygen isotopes to minor crustal input, as

the mantle's large oxygen reservoir tends to buffer these signals. In contrast, a mass balance based on ϵHf , which is more sensitive to small crustal contributions, showed minimal sediment inputs, consistent with the subtle isotopic shifts observed in this study and with other Andean $\epsilon\text{Hf}_{(t)}-\delta^{18}\text{O}$ mixing models (e.g., Jones et al., 2015). Consequently, the most plausible scenario for the enrichment of the magmatic reservoirs involves the subduction of sediments associated with the arrival of the young Nazca plate (see also Section 5.3); this includes those likely resulting from subduction-erosion processes or through the melting of a more enriched oceanic lithosphere compared to the Eocene and Oligocene. The latter mechanism is similar to that proposed by Chiaradia (2009), who proposed that the enrichment of the magmatic reservoirs is the result of the interaction between mantle-derived magmas and the lower or intermediate sections of a thickened juvenile crust.

The majority of markers (e.g., U/Yb, LREE/HREE ratios) suggest a small decrease in enrichment ~ 9 Ma, indicating a change in magmatic reservoir conditions; however, it is difficult to determine whether this is a sustained depletion of the source or simply a minor drop in a global enrichment trend, as there is a lack of younger data in this area.

3.5.3. Crustal thickness constraints and estimates

Whole-rock Sr/Y and La/Yb ratios have been proposed as barometers of magmatic differentiation in intermediate to felsic rocks (SiO_2 between 55 and 68 %). These ratios are based on the differential partitioning of Sr, Y, La, and Yb in the fractionating mineral phases and melts (e.g., Chiaradia, 2015; Profeta et al., 2015; Luffi & Ducea, 2022). Estimates of magmatic fractionation depths are based on the pressure stability fields of plagioclase and garnet, which are diagnostic of thin and thick crust, respectively. In general, Sr is preferentially incorporated into the solid phase at low pressures (<1 GPa) where it strongly fractionates into plagioclase. However, at higher pressures (>1.2 GPa), where plagioclase is less abundant or even absent, Sr is more likely to partition into the liquid phase. Conversely, Y is incompatible at low pressures but becomes increasingly compatible at higher pressures, preferentially partitioning into garnet (and eventually amphibole). Consequently, a higher Sr/Y ratio may be indicative of higher differentiation pressures (or depths), the presence of garnet at the source (e.g., Alonso-Perez et al., 2009), or alternatively the accumulation of Sr-rich plagioclase in lower crust (Brackman and Schwartz, 2022; Carty et al., 2021). A similar process controls the La/Yb ratio (and, consequently, the LREE/HREE ratio): Yb is more compatible with garnet and amphibole

relative to La at higher pressures. Thus, a higher La/Yb ratio is also suggestive of crystallization or differentiation at higher pressures.

However, these barometers require cautious interpretation due to their dependence on tectonic settings and sensitivity to source characteristics, redox states, and magma mixing (Macpherson et al., 2006; Moyen, 2009; Richards and Kerrich, 2007). These complexities can decouple whole-rock compositions from true melt signatures, highlighting the need for complementary proxies such as mineral chemistry. In this study, we address this issue by focusing on zircon geochemistry, which, alongside whole rock data, reveals pronounced HREE fractionation in chondrite-normalized patterns. This strongly suggests that residual or fractionating garnet played a major role in depleting Yb and Y in the parental melts. Furthermore, the samples in this study lack the typical features of plagioclase-rich cumulates, such as high Al_2O_3 contents, positive Eu and Sr anomalies, and high modal plagioclase abundance. For these reasons, we consider it more likely that the high values of these barometers are related to the presence of garnet.

Amphibole fractionation is favored at higher pressures and higher water contents (Davidson et al., 2007). Accordingly, as depth increases, magmatic differentiation is characterized by enhanced amphibole crystallization, with limited to absent plagioclase fractionation. At even higher pressures, garnet fractionation becomes dominant, which can mask amphibole signatures (Ulmer, 2007; Alonso-Perez et al., 2009).

Quantitative estimates using the method proposed by Sundell et al. (2021) suggest a crustal thickness of approximately 28 km during the 41–31 Ma period (average Sr/Y and La/Yb ratios of ~ 20 and ~ 2 , respectively). The estimated crustal thicknesses increase around 14 Ma, reaching a maximum of around 60 km at 12 Ma (average Sr/Y ratio of ~ 95 and La/Yb ratio of ~ 16). During the 8–7 Ma period, the estimated crustal thicknesses decrease to approximately 50 km (average Sr/Y ~ 70 and La/Yb ~ 8), accompanied by a slight depletion of the reservoirs, as reflected in zircon geochemistry (e.g., decreasing U/Yb; see Section 5.2). In general, these estimates are consistent with the current crustal thickness of about 50 km in this part of the WC (Koch et al., 2021).

Additional evidence for crustal thickening at ~ 14 Ma is provided by the low zircon LREE/HREE ratio (~ 0.03 ; Fig. 8), suggesting crystallization from melts under high-pressure conditions within the garnet stability zone. Other proxies for crustal growth in zircon show varying degrees of agreement, with certain proxies agreeing (e.g., Dy/Yb); roughly agreeing (e.g., Ce/Y), or disagreeing (e.g., Eu/Eu*) with these outcomes. It should be noted that Eu/Eu*

ratios are also dependent on other parameters, such as oxidation, oxygen fugacity, and source composition (e.g., Yakymchuk et al., 2023).

Several other whole-rock and zircon geochemical characteristics further support the idea of magmatic evolution occurring within an intermediate to thick crust. Eu/Eu^* in zircon does not exhibit a clear relationship with increased fractionation (i.e., Hf) (Fig. 3.9A), suggesting that magmatic evolution occurred primarily at middle to deep crustal levels, outside the plagioclase stability zone. Claiborne et al. (2010) suggest that the presence of amphibole in the host melt is evidenced by the increase of Yb/Gd in zircon as Hf increases and Th/U decreases; this pattern is particularly prevalent during the 41–16 Ma interval, suggesting that amphibole was a major fractionating phase during this period. Conversely, during the 14–7 Ma period, a relatively constant Yb/Gd ratio (Fig. 3.9B, C) suggests that magmatic evolution occurred in zones where amphibole stability was not as dominant as that of garnet. The presence of garnet is further supported by the more significant fractionation of HREE during this period as well as the decreasing WR ($\text{La}-\text{Gd}$)/Yb ratios with differentiation (see Fig. 3.4E, F).

Zircon trace element ratios (Th/Yb vs. Eu/Eu^* , U/Yb vs. Eu/Eu^* ; Bell & Kirkpatrick, 2021; Reimink et al., 2020) suggest that magmas were the result of deep melting of the crust during the 14–7 Ma period; this was accompanied by assimilation- fractional crystallization (AFC) processes and an increase in H_2O content compared to the 41–16 Ma period, as evidenced by the negative correlation between U/Yb and Eu/Eu^* and the increase of Th/Yb with the increase of Eu/Eu^* (see Fig. 3.9D, E). These findings are corroborated by Zircon Ti thermometry, which reveal lower crystallization temperatures for the Miocene granitoids, indicative of the evolution of melts under water-saturated conditions (Harrison et al., 2007). This process may have been driven by the consumption of hydrated minerals (e.g., amphibole) or increased interaction with slab fluids, as inferred in other settings (Grove et al., 2012).

3.5.4 Regional considerations and geodynamic implications

Crustal thickening can result from tectonic shortening, magmatic inflation, or underplating (Lee et al., 2015). Slab angle fluctuations are among the primary factors that control upper-plate strain and magmatism in subduction settings (Lallemand et al., 2005; Horton, 2018). In general terms, slab rollback, and its associated transition to higher subduction angles, leads to extensional upper-plate strain and a trenchward migration of magmatism, while shallowing subduction angles lead to compressional upper-plate strain and the landward

migration of magmatism. These slab fluctuations, combined with internal orogenic processes (e.g., tectonic thickening and magmatic underplating), provide effective explanations for the evolution of upper-plate tectonics and magmatism in several Andean settings (Horton, 2018; Jara et al., 2021; Savignano et al., 2016).

Continental arcs are among the highest topographic features on Earth, and highlight the strong relationships between magmatism, crustal thickening, and the resulting topographic response. The thicker crust will generate a topographic response in an attempt to maintain an isostatic equilibrium with the underlying mantle (e.g., Lee et al., 2015; Farner and Lee, 2017). Currently, there are no pre-Quaternary estimates of paleoaltitude for the entire Ecuadorian Andes. However, studies focusing on Cenozoic magmatism have highlighted several periods of elevated crustal thickness. For example, the adakitic signatures of the Eocene Macuchi Arc have been interpreted as evidence of a thickened juvenile crust (Chiaradia, 2009), although ~42 Ma massive sulfide deposits in El domo deposit, located at the western foothills of the WC, are indicative of submarine conditions (Vallejo et al., 2016). This study presents evidence that suggests: 1) a thickness estimate of about 35 km from 41 to 31 Ma, which corresponds to a paleoaltitude of about 1.5 km based on global relationships (Lee et al., 2015) as well as an oceanic crust density of 2.8 g/cm³ (Aizprua et al., 2020); and 2) a period of crustal thickness increase at 14–12 Ma, up to a mean of 60 km, accompanied by the enrichment of magmatic reservoirs. A crustal thickness of 60 km and a crustal density of 2.8 g/cm³ represent a mean altitude of ~4 km (Lee et al., 2015).

Thermochronological data, including apatite fission track and apatite (U-Th)/He dating, provide evidence of multiple Miocene- Pliocene phases of arc cooling in the WC (Margirier et al., 2023) as well as in moderately deep detrital rocks in the adjacent forearc (Brichau et al., 2021). The first phase reflects post-magmatic thermal relaxation following the emplacement of Miocene intrusions, evidenced by thermochronological data showing slow cooling rates (~15 °C/Myr) and minimal exhumation rates (<0.1 km/Myr) between 20 and 15 Ma. The second phase, which occurred at ~6–5 Ma in the NB (~7–6 Ma in the rest of the WC), at increased exhumation rates of ~0.5 km/Myr. This phase coincided with uplift along the Coastal Cordillera in the forearc as well as the onset of tectonically controlled crustal thickening and exhumation in the WC and is related to the onset of the subduction of the Carnegie Ridge (Margirier et al., 2023). The geochemical suggests that crustal thicknesses began to increase at ~9 Ma in the central parts of the WC (Chiaradia et al., 2004) and ~ 14 Ma in the NB (this work), at least 3–8 Ma before the arrival of the Carnegie Ridge into the subduction margin (best estimates at 6–5 Ma; see Hernández et al., 2024).

The increase in crustal thickness in the NB could have arisen from two potential mechanisms: 1) Andean compressional stresses associated with either regional overthrusting at mid-low crustal levels and eastward dipping reverse faults, such as those more specifically observed near the Andean piedmont in the WC (Hernández et al., 2024); and 2) magmatic underplating related to the successive build-up of magmatic arcs. Our data reveals that the increase of crustal thickness occurred relatively abruptly around 14–12 Ma: this suggests that compressional tectonic stresses are a more plausible mechanism for crustal thickening compared to long-term magmatic build-up. We also suggest that the crustal thickening in the NB is most likely linked to the arrival of newly formed, buoyant oceanic lithosphere from the Nazca plate beneath the South American margin at ~15–14 Ma (Hey, 1977; Meschede and Barckhausen, 2001). The relatively young and buoyant nature of the oceanic lithosphere would have reduced the subduction angle, leading to increased lithospheric coupling and compressive deformation of the upper plate. This interpretation is further supported by the contemporaneous uplift of the forearc margin (Hernández et al., 2020) and the onset of the first exhumation period in the WC (Margirier et al., 2023).

3.6 Conclusions

Whole-rock geochemistry, coupled with U-Pb geochronology, trace elements, and radiogenic and stable isotopes in zircon, provides an excellent framework for evaluating the Cenozoic tectono-magmatic evolution of the northernmost part of the Ecuadorian arc (Fig. 10). Magmatic rocks in the NB exhibit a compositional shift from basic tonalitic (41–16 Ma) to intermediate-acidic granodioritic magmas (14–7 Ma).

Both whole rock and zircon geochemistry suggest a greater contribution from enriched (i.e., evolved) reservoirs during the Miocene compared to the Eocene–Oligocene period. This is supported by an isotopic pull-down in ϵ_{Hf} values and $\delta^{18}\text{O}$ values (>5.3 ‰) consistent with input from supracrustal altered materials during the Miocene.

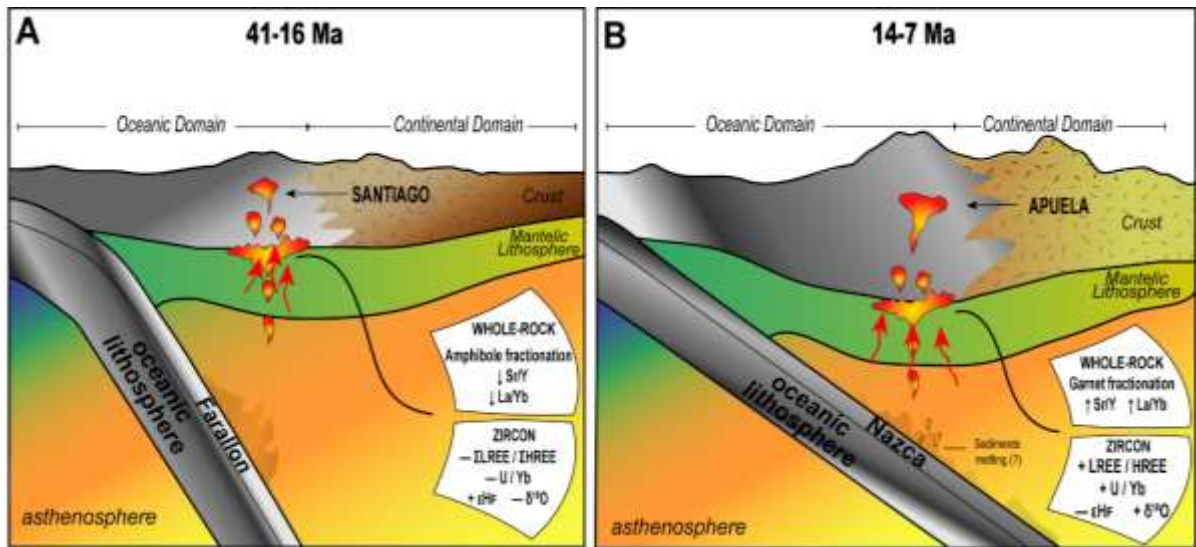


Figure 3.10 Cartoons showing the proposed tectono-magmatic model, A) during the emplacement of the Santiago batholith, B) and during the emplacement of the Apuela batholith.

The increased contribution of evolved materials may be due to the melting of a more evolved oceanic crust as a result of the underthrusting of oceanic plateau fragments or the occurrence of sediment subduction. The predominantly primary origin of zircons suggests that no continental crust was involved in magmatism during the 41–7 Ma interval, indicating that plateau accretion and underplating were the main mechanisms driving the crustal evolution of the WC as proposed by Jaillard (2022).

From the Eocene to the early Miocene (41–16 Ma), juvenile mantle signatures in ϵHf_t , $\delta^{18}\text{O}$, and zircon trace elements (U/Yb, Eu^*/Eu , LREE/ HREE) suggest that magmatic differentiation occurred in zones of increased amphibole stability, indicating interaction with an already thickened crust. Towards the late Miocene (11–7 Ma), evolved signatures in ϵHf and $\delta^{18}\text{O}$, coupled with zircon trace element trends, suggest magmatic evolution in high-pressure differentiation zones within the garnet stability field, indicative of significantly thickened crust. This evolutionary trend reflects fractionation in a thickening crust, with crustal thickness estimates of approximately 35 km at 41–16 Ma, which increased to 60–70 km at 14–9 Ma and 60–50 km at 9–7 Ma.

Our data shows that geochemical enrichment and crustal thickening peaked at around 12 Ma. This timing rules out any direct association between these trends and the subduction of the Carnegie Ridge, the onset of which would have been around 6–5 Ma based on best estimates. Instead, the observed thickening—and potentially the enrichment trend—appear to be related to the arrival of the more buoyant Nazca plate at the South American margin around 15–14 Ma, which would have resulted in a shallower subduction angle and the establishment of a more compressional setting in the northern part of the WC.

A reduction in geochemical enrichment and crustal thickness trends around 9 Ma is evident in all datasets, including whole-rock constraints (e.g., Sr/Y, La/Yb), zircon isotopes ($\delta^{18}\text{O}$, $\epsilon\text{Hf}_{(t)}$) and zircon TE (U/Yb, LREE/HREE); this likely indicates a change in magmatic reservoir conditions. However, it is difficult to determine whether this represents a sustained depletion of the source or simply a minor drop in a broader enrichment trend, as no younger data are currently available for this area.

Acknowledgments

This work was supported by Cornerstone Capital Resources, the Institute National des Sciences de l'Univers (CNRS, France), the VINCI program of the Italian-French University, and the National Polytechnic School through the PIEX-DG-IRD-23 External Project. Elizabeth Bell and an anonymous reviewer, as well as Associate Editor Greg Shellnutt, are kindly thanked for their detailed comments and criticisms that significantly improved our study.

CHAPTER 4: Zircon Chronology and Geochemistry of Cenozoic Subduction-Related Magmatism in the Central Ecuadorian Andes

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Declaration

The objective of this chapter is to present a detailed reconstruction of the Cenozoic magmatic arc in the Central Ecuadorian Andes, with a specific focus on deciphering the mechanisms behind the observed geochemical transitions and the role of crustal architecture by integrating zircon U–Pb geochronology, Hf–O isotopic data, trace-element analyses, and whole-rock geochemistry. This work is still in preparation as further analysis and discussions are needed to improve the interpretation of the results.

Abstract

This study integrates zircon U–Pb geochronology, zircon Hf–O isotopic data, whole-rock geochemistry, and zircon trace-element analyses to reconstruct the tectono-magmatic evolution of the Cenozoic arc in the Central Ecuadorian Andes between. New zircon U–Pb ages refine the magmatic chronology, revealing prolonged pluton emplacement from 39 to 9 Ma. Zircon $\epsilon\text{Hf}_{(t)}$ signatures (+15.6 to +9.9) indicate dominantly juvenile, mantle-derived sources for the plutons emplaced north of the Chimbo-Toachi shear zone, within the Macuchi block, whereas plutons southeast of the CT shear zone record more enriched signatures (+7.9 to +2.3), likely reflecting inputs from subducted sediments or enriched oceanic crust. Whole-rock geochemistry indicates that 39–20 Ma intrusions display typical calc-alkaline features, such as negative Eu anomalies and non-depleted HREE, consistent with magmatic differentiation dominated by plagioclase $\pm$ amphibole at mid- to upper-crustal levels. By contrast, younger intrusions emplaced north of the CT shear zone at ~11 Ma and south of it between 13 and 9 Ma record strong LREE enrichment, pronounced HREE depletion, and the disappearance of Eu anomalies, marking the onset of adakite-like signatures under higher-pressure conditions. Zircon trace-element data, however, demonstrate that this transition was more gradual than whole-rock patterns suggest amphibole involvement is evident during the Eocene–Oligocene, while in the Miocene its progressive weakening reflects a stepwise shift toward garnet stability at depth. Crustal thickness estimates corroborate this trend, increasing from ~15–30 km (39–30 Ma) to ~20–40 km (26–21 Ma), and reaching ~50 km by the Late Miocene, coeval with the strongest expression of adakitic signatures, plausibly linked to the arrival of younger, more buoyant Nazca lithosphere following Late Oligocene (~25 Ma) Farallon plate fragmentation. Collectively, these results underscore the dual control of (1) juvenile oceanic plateau basement composition and (2) overlying crustal architecture in governing arc magmatism. Adakite-like signatures reflect localized, high-pressure differentiation processes superimposed on a mantle-dominated petrogenesis modulated by crustal thickening and evolving subduction dynamics.

4.1 Introduction

The study of magmatism and its underlying geodynamic processes provides a powerful framework for understanding subduction zones, as it reveals how plate interactions generate arc magmas, drive crustal growth and recycling (e.g., Stern, 2002; Ducea *et al.*, 2015). Exploring magmatic arcs by coupling zircon U–Pb geochronology, zircon Hf–O isotopic

signatures, trace-element compositions, and whole-rock geochemistry, provides a powerful approach for reconstructing the tectono-magmatic evolution of continental arcs. This multi-proxy approach offers critical insights into crustal growth and recycling, magma differentiation processes, and the relative contributions of mantle inputs, slab-derived fluids and melts, and crustal assimilation to subduction-related magmatism (e.g., Belousova *et al.*, 2002; Bindeman, 2008; Grimes *et al.*, 2015; Bell and Kirkpatrick, 2021; Sundell *et al.*, 2022), and have been recently successfully applied in the Ecuadorian and Peruvian Andes (e.g., Iglesias *et al.*, 2025; Sandoval-Espinel *et al.* 2026).

The northern Andes are a continental magmatic arc resulting from the subduction of oceanic lithosphere beneath continental crust or accreted oceanic crust. In Ecuador, the oceanic crust accreted in the late Cretaceous forms the basement of the Cenozoic forearc and frontal arc (Western Cordillera-WC; Aizprua *et al.*, 2020), and influences the chemical composition of magmatism (Chiaradia, 2009; Jaillard, 2022; Luzieux *et al.*, 2006; Vallejo *et al.*, 2009). The central segment of the WC (0°-2°S) is primarily composed of two distinct blocks: to the east the Pallatanga block separated from the interandean valley by the Calacalí-Pujilí-Pallatanga Fault (CPPF), and the Macuchi block to the west, separated by the Chimbo-Toachi (CT) shear zone (Fig. 4.1; Hughes and Pilatasig, 2002). The older Pallatanga block comprises a diverse geological record, including an oceanic plateau basement with affinities to the Caribbean Large Igneous Province, a Late Cretaceous volcanic arc, volcanic rocks interlayered with continental red beds, Paleocene–Eocene sedimentary sequences; and Miocene subaerial volcanic and volcanosedimentary sequences (Hughes and Pilatasig, 2002; Vallejo *et al.*, 2019).

In contrast, the younger Macuchi block displays features typical of a submarine volcanic arc system, developed above the overthickened plateau basement (Hughes and Pilatasig, 2002; Vallejo *et al.*, 2019). Together the Pallatanga and Macuchi blocks are intruded by a series of type I calc-alkaline granitoids, of which the main ones are El Corazon, Chazo Juan Telimbela, Echeandia and Undushig (Fig. 4.1), most of which hosting porphyry-type systems and the volcanogenic massive sulfide deposits La Plata, Macuchi and El Domo (McCourt *et al.*, 1997; PRODEMİNCA, 2000; Vallejo *et al.*, 2016). These granitoids, together with the most evolved rocks of the Macuchi arc, andesitic to dacitic high-level intrusions, display adakite-like signatures that may reflect the interaction of mantle-derived melts with intermediate to felsic magmas in the lower to mid-levels of the thickened juvenile crust (Chiaradia, 2009; Vallejo *et al.*, 2016). Alternatively, they could record a temporal evolution from early basaltic magmas undergoing shallow low-pressure fractionation to later melts evolving at deeper crustal levels (Chiaradia, 2009). However, the scarcity of systematic

geochronological data on high-level intrusions emplaced in the Macuchi arc leaves these models weakly constrained, and resolving this uncertainty is essential for understanding the onset and evolution of adakite-like magmatism in the central segment of the Western Cordillera. Despite the central segment of the Western Cordillera being one of the most economically important regions, owing to its porphyry and VMS deposits that have attracted considerable geochronological attention, isotopic constraints remain surprisingly scarce. This contrasts with the proven effectiveness of multi-proxy approaches, integrating zircon U–Pb dating, Hf–O isotopes, and zircon trace-element analyses, for unraveling the tectono-magmatic evolution of continental arcs. To date, only Hf analysis of zircons has been reported for one sample at ~41 Ma (Vallejo et al., 2016), along with a set of Nd isotopic data from whole rock (Chiaradia, 2009; Schütte, Chiaradia, Massimo, et al., 2010). Addressing this gap, the present study provides a robust and comprehensive dataset that combines new zircon U–Pb geochronology, whole-rock geochemistry, and Hf–O isotopic analyses to unravel how tectonic processes (convergence dynamics, slab evolution), crustal thickness, and magmatic differentiation shaped the Cenozoic magmatic arc of the central Ecuadorian Andes. This approach refines magmatic chronology and sources, distinguishing the relative roles of mantle input, slab-derived components, and crustal assimilation.

4.2 Geological background

The basement of the WC of Ecuador consists of oceanic lithosphere accreted to the continental margin during the Late Cretaceous to Eocene, likely through one or multiple tectonic events (Jaillard, 2022; Kerr et al., 2002; Vallejo et al., 2009). Part of this oceanic basement is represented by the Macuchi arc, located between 0° and 2°30'S along the western flank of the WC. Based on geochemical data, it was originally defined as an oceanic island arc active during the Late Eocene (Hughes and Pilatasig, 2002; Kerr et al., 2002). However, Vallejo *et al.* (2016, 2019) proposed an autochthonous origin, with the arc developing on a thickened oceanic plateau crust and remaining active during the Late Eocene (42–38 Ma). The Macuchi arc comprises mainly basaltic to andesitic volcanic and volcanosedimentary sequences, including pillow lavas, hyaloclastites and breccias (Hughes and Pilatasig, 2002; Vallejo et al., 2019). It also hosts undeformed calc-alkaline I-type granitoids of granodioritic to tonalitic composition (McCourt et al., 1997). These intrusions belong to the Cenozoic magmatic arc, a transitional arc constructed on oceanic crust north of ~3°S and on continental crust to the

south, formed by the eastward subduction of the Farallon/Nazca plate beneath the South American plate.

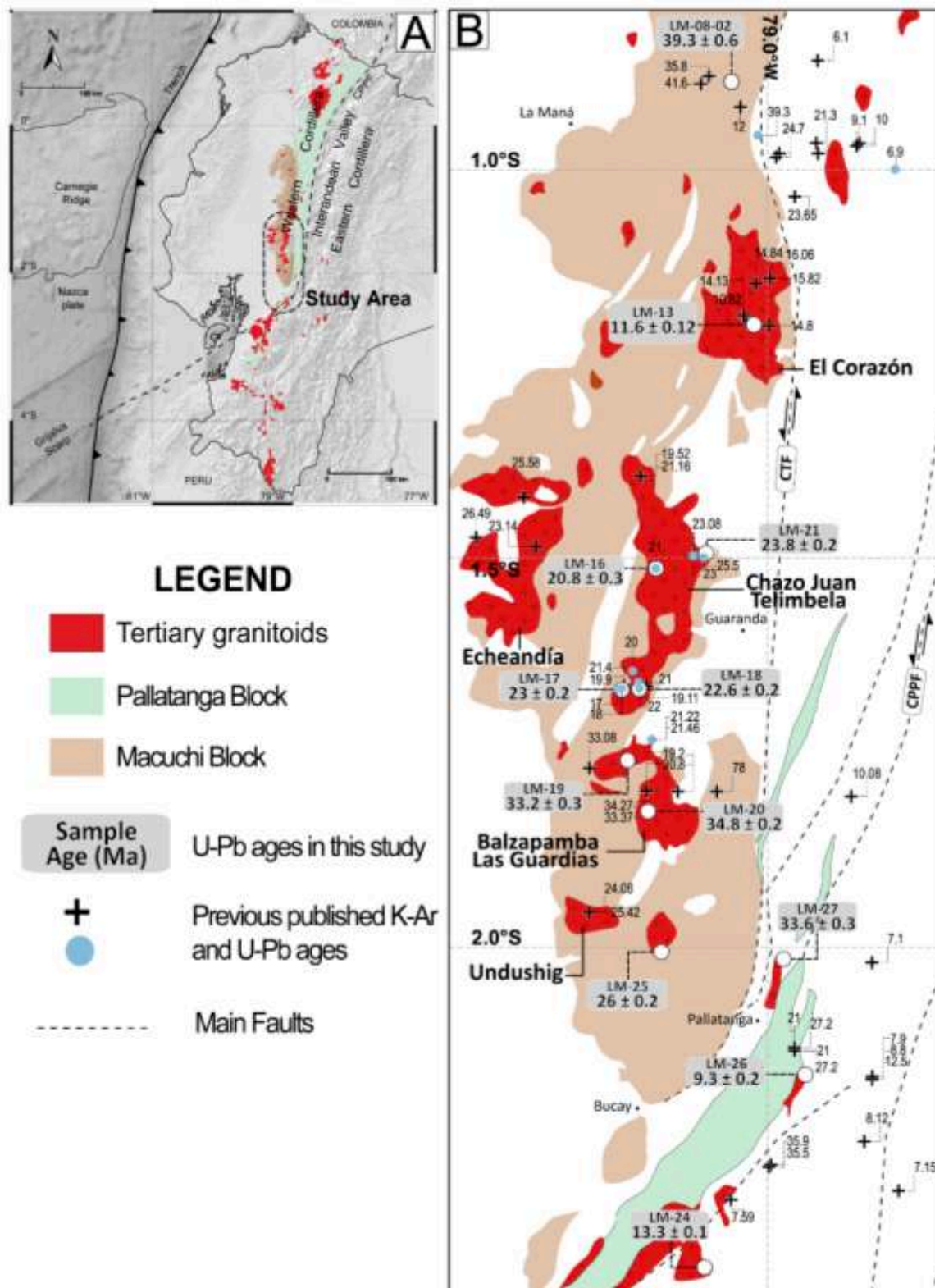


Figure 4.1 Geological map of the study area in central Ecuador, showing sample locations and zircon U–Pb ages obtained in this study, and labelled at each sample location (white circles). Blue dots indicate previously published K–Ar and U–Pb ages from Henderson (1979), Kennerly (1980), Pichler & Aly (1983), Barberi *et al.* (1988), Lavenue (1992), Liu *et al.* (2023), PRODEMİNCA (2000), Schütte *et al.* (2010), Margirier *et al.* (2023), George *et al.* (2021). Major faults, including the Calacali–Pallatanga–Pujilí Fault (CPPF) and Chimbo–Toachi Fault (CTF), are marked with dashed lines. The inset map shows the regional context and location of the study area within the Northern Andes.

Prominent plutonic bodies in the study area include the El Corazón, Echeandía, Chazo Juan–Telimbela, and Balzapamba–Las Guardias plutons, along with several smaller intrusive bodies. McCourt *et al.* (1997) suggested that the minor plutons may represent apophyses of the major bodies and potentially indicate the existence of a composite batholith beneath the arc. Most geochronological data from the region are based on K–Ar dating of minerals (hornblende, biotite, plagioclase) or whole-rock samples. From north to south, reported ages are 16–14 Ma for El Corazón, 27–23 Ma for Echeandía, 21–15 Ma for Telimbela–Chazo Juan, and 34–30 Ma for Balsapamba–Las Guardias (e.g., Boland *et al.*, 2000; Eguez, 1986; PRODEMİNCA, 2000; Kennerly, 1980; McCourt *et al.*, 1997). U–Pb zircon dating conducted on the Telimbela–Chazo Juan and Balzapamba–Las Guardias plutons, constrain their emplacement ages to between 25 and 17 Ma (H. Liu *et al.*, 2023; Margirier *et al.*, 2023; Schütte, Chiaradía, Massimo, *et al.*, 2010).

4.3 Analytical Methods

Twelve representative samples were collected north and south of the CT shear zone, from major plutons such as El Corazon, Telimbela -Chazo Juan, and Balsapamba-Las Guardias, along with minor plutons, targeting if possible fresh, unaltered samples. Sample preparation, including washing, crushing, sieving, grinding, and density separation, was conducted at the Department of Geology, Escuela Politécnica Nacional (Quito, Ecuador), following the protocol of Malusà and Fitzgerald (2019). Zircon grains were handpicked and mounted in epoxy resin holders and imaged by optical cathodoluminescence, at the University of Lille (France), to characterize internal zoning and structures, and guide domains selection for analyses. After analysis, high-resolution cathodoluminescence was conducted at the Geo-Ocean laboratories in Grenoble (France) (Supplementary Figure. 3).

Whole-rock geochemistry was performed using ICP-AES (Ultima 2, Jobin Yvon) at the Geo-Ocean laboratory (PSO – Pôle de Spectrométrie Océan, University of Brest, France).

Zircon U–Pb dating was conducted at the GeOHeLiS analytical platform (OSUR, University of Rennes 1, France) using an ESI NWR193UC excimer laser coupled to an inductively coupled plasma mass spectrometry Agilent 7700x quadrupole ICP-MS with a dual pumping system to improve sensitivity (Paquette et al., 2014). Concordia diagrams were generated with IsoplotR (Vermeesch, 2018).

Trace element and Lu–Hf isotopic analyses in zircon were performed at the Geosciences Laboratory, University of Montpellier (France), using a Thermo Finnigan Neptune+ inductively coupled mass spectrometer (MC-ICP-MS) coupled to a Photon Machine Analyte G2 laser. Standards 91500, Plešovice, and GJ-1 were used to monitor analytical accuracy and reproducibility. ϵHf_t and initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios were calculated following Söderlund *et al.* (2004) and Bouvier *et al.* (2008). Zircon trace elements were analyzed using a Teledyne G2 193 nm ArF excimer laser coupled to a Thermo Finnigan Element XR sector-field ICP-MS, using a repetition rate of 6 Hz, spot size of 50 μm , and an energy density of 4.51 J/cm². Calibration was performed with NIST SRM 612 glass, and data reduction was performed using GLITTER software (van Achterberg et al., 2001).

Oxygen isotope analyses in zircon were conducted at the Centre de Recherches Pétrographiques et Géochimiques (CRPG, Université de Lorraine, Nancy, France) using a secondary ion mass spectrometer Cameca IMS 1270 SIMS using a 2.5 nA, 10 kV Cs⁺ beam in FC/FC detection mode. Instrumental mass fractionation was corrected using the 91500-zircon standard ($\delta^{18}\text{O}$ range: 4.41‰–6.42‰). Additional methodological details are available in Iglesias *et al.* (2025), Sandoval-Espinel *et al.* (2025), Witt *et al.* (2017) and Witt *et al.* (2023).

4.4 Results

The samples are dominantly diorites and granodiorites with holocrystalline, hypidiomorphic textures of medium grain size, occasionally displaying microgranular or porphyritic features. The mineral assemblage is primarily composed of plagioclase (50–60%), quartz (30–40%), and minor biotite and amphibole ($\leq 10\%$). Accessory phases include magnetite, titanite, and apatite. Plagioclase appears as tabular to subtabular crystals with Carlsbad and polysynthetic twinning and occasional zoning. Chlorite is locally present, likely as an alteration product of biotite or amphibole. Biotite, when observed, forms subhedral lamellar crystals with characteristic brownish green pleochroism. The mineralogy of microcrystalline samples and groundmass in porphyritic textures reflects a similar paragenesis. (Supplementary Fig. 2).

The location, rock type, and zircon U-Pb ages for all samples are summarized in Table 1 and Figure 4.1. Detailed analytical results, including zircon U-Pb geochronology, whole-rock geochemistry, zircon trace-element concentrations, and zircon Hf and O isotope ratios, are provided in Tables 2–5 (Supplementary Data).

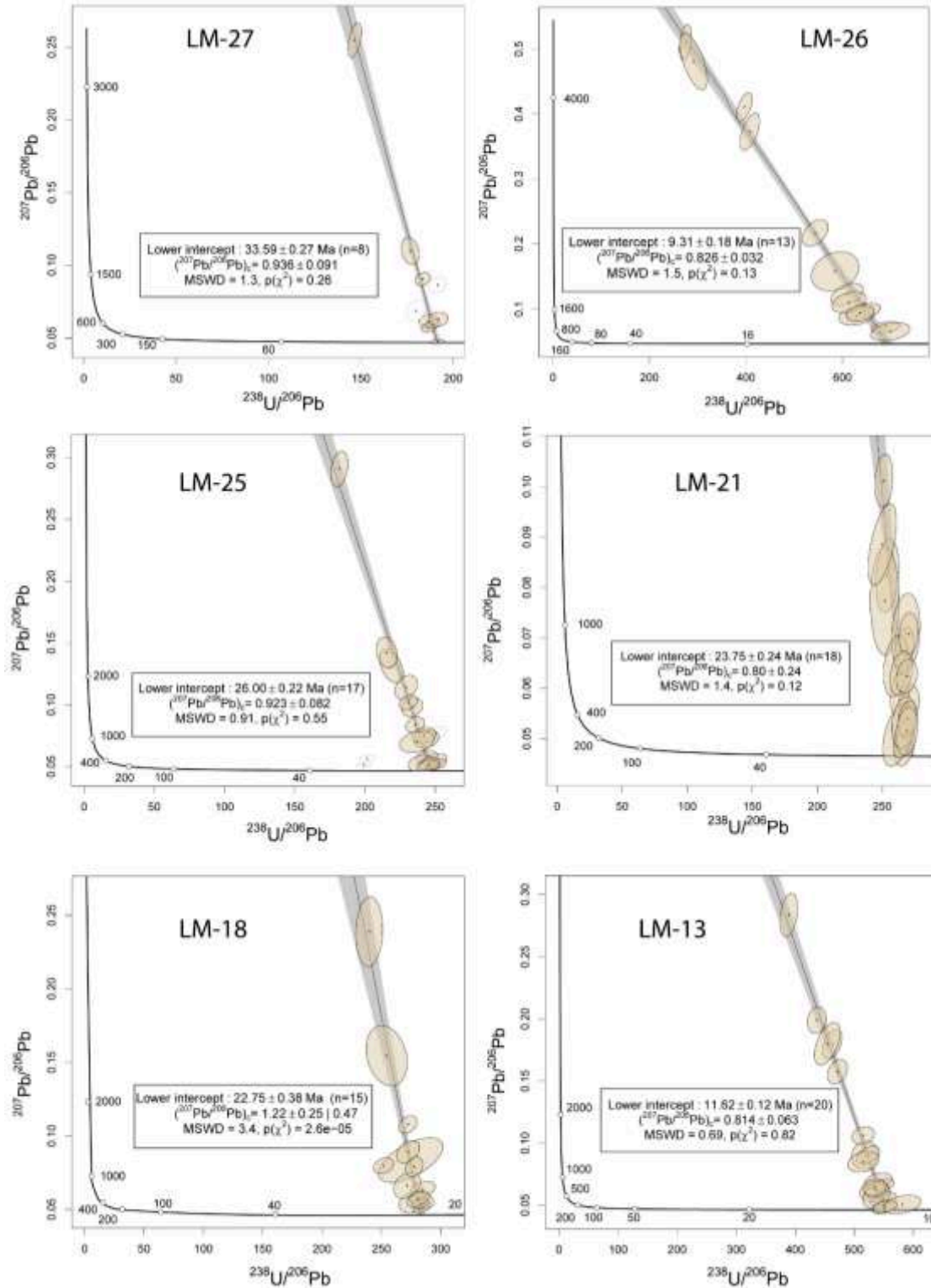


Figure 4.2 Tera-Wasserburg diagrams showing the lower interception ages for representative samples.

Table 4.1 Sample location and U-Pb ages.

Sample	Latitude	Longitude	U-Pb Age	2s
LM-08-02	-0.89	-79.03	39.2	0.6
LM-13	-1.2	-79	11.62	0.12
LM-16	-1.51	-79.13	20.75	0.25
LM-17	-1.67	-79.17	23.03	0.18
LM-18	-1.67	-79.15	22.63	0.21
LM-19	-1.76	-79.16	33.2	0.3
LM-20	-1.83	-79.14	34.79	0.2
LM-21	-1.49	-79.06	23.75	0.24
LM-24	-2.41	-79.07	13.27	0.12
LM-25	-2.01	-79.12	26	0.22
LM-26	-2.16	-78.94	9.31	0.17
LM-27	-2.02	-78.96	33.59	0.27

4.4.1 Zircon U-Pb Geochronology

Zircon U–Pb analyses from the 12 samples ($n = 195$) reveal three main age groups based on lower intercept ages from reverse concordia (Tera–Wasserburg) diagrams (Fig. 4.2). All analyzed zircon populations display clear discordance between the $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{235}\text{U}$ systems, most likely related to Pb loss. This open-system behavior produces linear arrays in Tera–Wasserburg space, from which the lower intercepts are interpreted as the most reliable estimates of zircon crystallization ages and, thus the timing of magmatic events. Eocene ages range from 39.2 ± 0.6 Ma (LM08-02) to 34.8 ± 0.2 Ma (LM20). Oligocene intrusions yield ages of 33.6 ± 0.3 Ma (LM27), 33.2 ± 0.3 Ma (LM19), 26.0 ± 0.2 Ma (LM25), and 23.8 ± 0.2 Ma (LM21). Meanwhile the Miocene ages are 23.0 ± 0.2 Ma (LM17), 22.6 ± 0.2 Ma (LM18), 20.8 ± 0.3 Ma (LM16), 13.3 ± 0.1 Ma (LM24), 11.62 ± 0.1 Ma (LM13), and 9.3 ± 0.2 Ma (LM26).

The El Corazón pluton yields an age of 11.62 ± 0.1 Ma ($n = 20$). The Telimbela–Chazo Juan pluton exhibits ages of 23.8 ± 0.2 Ma ($n = 20$), 23.0 ± 0.2 Ma ($n = 22$), 22.6 ± 0.2 Ma ($n = 15$), and 20.8 ± 0.3 Ma ($n = 22$). The Balzapamba–Las Guardias pluton yields ages of 34.8 ± 0.2 Ma ($n = 17$) and 33.2 ± 0.3 Ma ($n = 13$). The pluton located to the east of the Undushig pluton gives an age of 26.0 ± 0.2 Ma ($n = 20$).

An intrusive body north of El Corazón, in the La Maná sector, records an Eocene age of 39.2 ± 0.6 Ma ($n = 7$). In the sector south-southeast of the CT shear zone, intrusive bodies yield lower intercept ages of 33.6 ± 0.3 Ma ($n = 10$), 13.3 ± 0.1 Ma ($n = 16$), and 9.3 ± 0.2 Ma ($n = 13$). Complete analytical data and inverse concordia plots are provided in Supplementary Table 2.

4.4.2 Whole-rock geochemistry

Major and trace elements concentrations of 12 samples are summarized in Supplementary Table 3. Based on the TAS classification diagram of Middlemost (1994) (Fig. 4.3A), the rocks range in composition from gabbro-diorites and diorites to predominantly granodiorites. SiO_2 contents span a wide range, from 52.36 to 75.71 wt.%, accompanied by variable TiO_2 (0.40–0.77 wt.%), Al_2O_3 (14.85–20.69 wt.%), MgO (0.03–4.83 wt.%), CaO (0.16–9.56 wt.%), and FeOt (2.86–7.14 wt.%). K_2O contents are low and relatively uniform (0.04–2.36 wt.%), as are Na_2O and P_2O_5 contents (Supplementary Figure 1). Most samples belong to the medium-K calc-alkaline series (Fig. 4.3B).

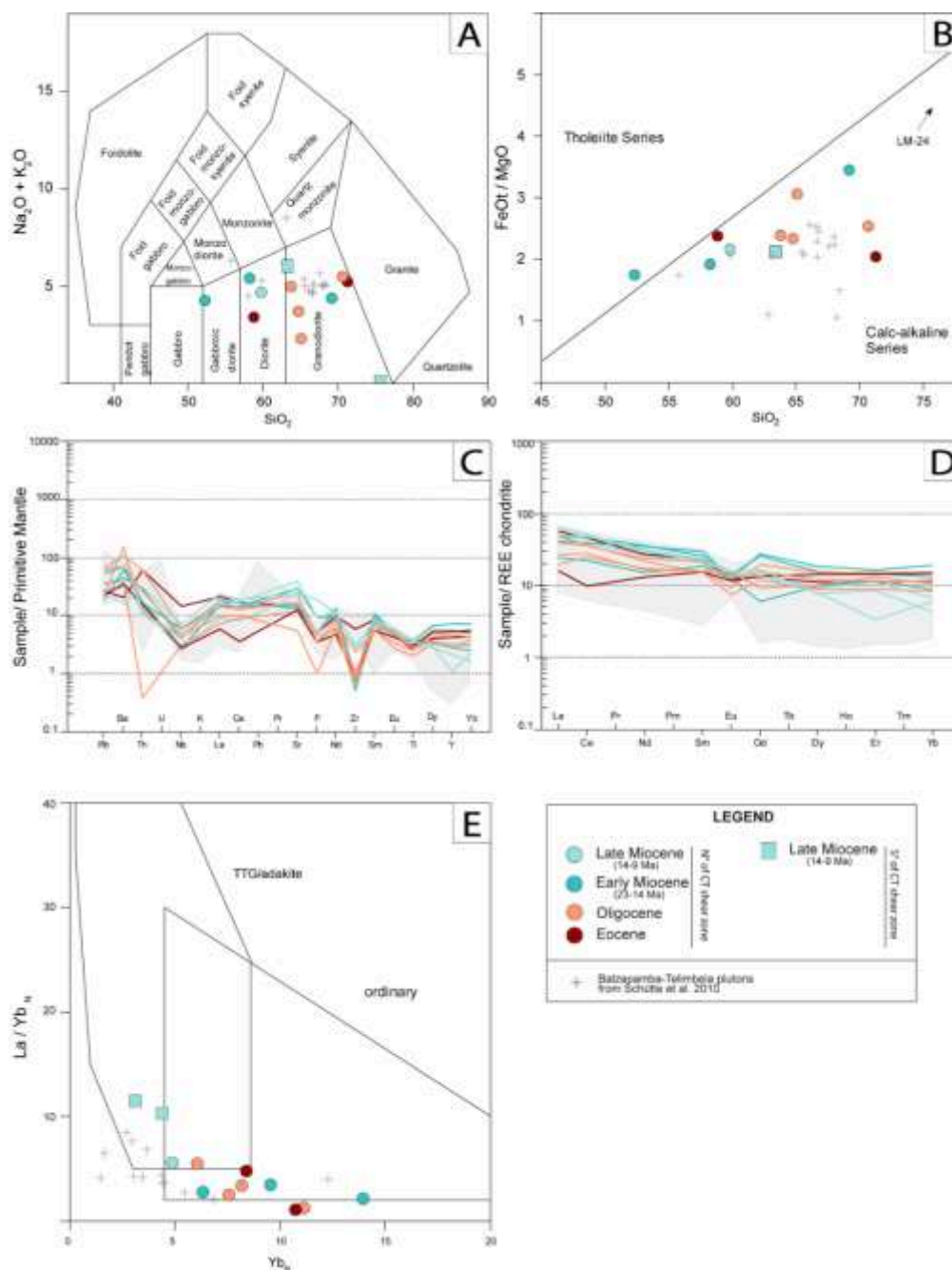


Figure 4.3 Geochemical characteristics of studied plutons. (A) Classification TAS diagram (Middlemost, 1994). (B) FeO_t/MgO vs. SiO_2 diagram distinguishing calc-alkaline from tholeiitic affinities. (C) Primitive mantle-normalized multi-element diagram. (D) Chondrite-normalized REE patterns. (E) La/Yb_N vs. Yb_N diagram (after Defant and Drummond, 1990).

Primitive mantle-normalized multi-element patterns exhibit typical arc-related signatures, including pronounced depletion in Nb, Ti, and P, and enrichment in Rb, Ba, and Sr (Fig. 3C). Chondrite-normalized rare earth element (REE) patterns of the 39–20 Ma samples display pronounced negative Eu anomalies, null to moderate LREE enrichment relative to HREE ($\text{La}_N/\text{Yb}_N = 1.06\text{--}5.58$), low to moderate LREE enrichment relative to MREE ($\text{La}_N/\text{Sm}_N = 1.12\text{--}5.89$), and flat MREE–HREE trends ($\text{Sm}_N/\text{Yb}_N = 1.05\text{--}1.98$). La_N/Yb_N values below 5.58 are consistent with normal calc-alkaline magmatism. In contrast, the younger samples, 11.6, 13.3, and 9.3 Ma, the latter two located south-southeast of the CT shear zone, exhibit strong LREE enrichment relative to HREE ($\text{La}_N/\text{Yb}_N = 5.64\text{--}11.68$) and to MREE ($\text{La}_N/\text{Sm}_N = 5.95\text{--}12.93$), moderate MREE enrichment relative to HREE ($\text{Sm}_N/\text{Yb}_N = 3.12\text{--}5.43$), and no negative Eu anomalies (Fig. 4.3D). These progressively higher La_N/Yb_N ratios, coupled with the absence of Eu anomalies, point to the development of adakitic-like signatures in the youngest intrusions (Fig. 4.3E).

4.4.3 Zircon Hf–O isotopes

A total of 74 zircon grains were analysed to determine initial $^{176}\text{Hf}/^{177}\text{Hf}$ isotope ratios and corresponding age-corrected $\epsilon\text{Hf}_{(t)}$ values. Complete results are presented in Supplementary Table 5 and illustrated in Figure 4.4. Samples emplaced within the Macuchi arc yield $\epsilon\text{Hf}_{(t)}$ values between +15.6 and +9.9, indicative of a predominantly depleted to juvenile magmatic source. In contrast, two samples located south-southeast of the CT shear zone (LM-26, LM-24) exhibit slightly more evolved $\epsilon\text{Hf}_{(t)}$ signatures, ranging from +7.9 to +2.3. These lower values suggest a minor contribution from reworked or evolved crustal material.

Fifty-eight zircons were analyzed for oxygen isotopes. $\delta^{18}\text{O}$ values from plutons north of the CT shear zone are generally mantle-like, averaging $5.3 \pm 0.6\text{‰}$, except for two samples that show a slight shift toward a supracrustal signature, with values reaching $\sim 7\text{‰}$. In contrast, plutons south of the CT shear zone display a stronger supracrustal influence, with $\delta^{18}\text{O}$ values reaching up to 8‰ .

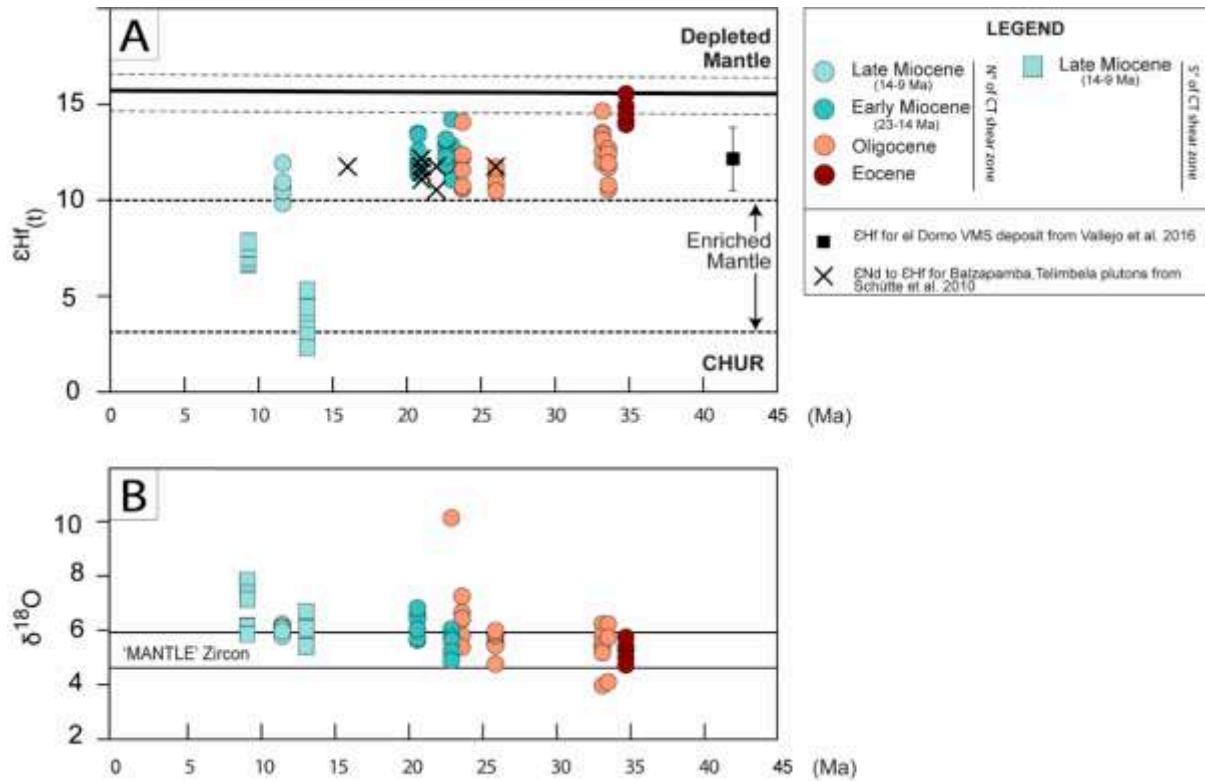


Figure 4.4 (A) $\epsilon\text{Hf}_{(t)}$ vs. crystallization age, and B) $\delta^{18}\text{O}$ vs. crystallization age for the studied zircons.

4.4.4 Zircon trace-elements

A total of 69 zircon grains were analysed for zircon trace element compositions. They are characterized by depleted light rare earth elements (LREE), enriched heavy rare earth elements (HREE), positive Ce anomalies, and negative Eu anomalies (Fig. 4.5A). These element compositions and ratios confirm their magmatic origin. Most samples have U/Yb ratios ranging from 0.1 to 0.4, close to the average value for primitive arc basalts (i.e., 0.3; Fig. 4.5B; Rudnick and Gao, 2003).

Zircon LREE/HREE ratios remain consistently low (<0.02), with a slight increase around ~11 Ma in plutons north of the CT shear zone, reflecting the strong compatibility of HREE in zircon and the limited incorporation of LREE. In contrast, values increase south of the CT shear zone, reaching up to 0.035 (Fig. 4.5C). Eu/Eu* values span a broader range (0.15–0.7) and display distinct spatial and temporal patterns. Most zircons emplaced within the Macuchi arc, north of the CT shear zone, record values <0.4 , consistent with plagioclase fractionation, except for two samples. Conversely, zircons south-southeast of the CT shear zone, along with the two older exceptions (35 Ma in the Balsapamba pluton and 26 Ma in the

pluton east of the Undushig pluton), yield higher values (>0.4), indicating crystallization under relatively oxidizing conditions (Fig. 4.5D). Nb/Ta ratios range from 1.8 to 4.6, suggesting derivation from mafic melts with limited influence of residual or fractionating rutile. Most samples north of the CT shear zone yield values generally between 2 and 3, with a slight increase around 11 Ma. Samples from south of the CT shear zone show slightly higher values of 2–4 (Fig. 4.5E). Dy/Yb ratios vary from ~ 0.09 to 0.4. North of the CT shear zone, values mainly fall between 0.1 and 0.3, which is consistent with zircon late crystallization and relatively shallow depths. South of the CT shear zone, values increase to 0.2–0.4, consistent with crystallization at shallow to moderate depths (Fig. 4.5F).

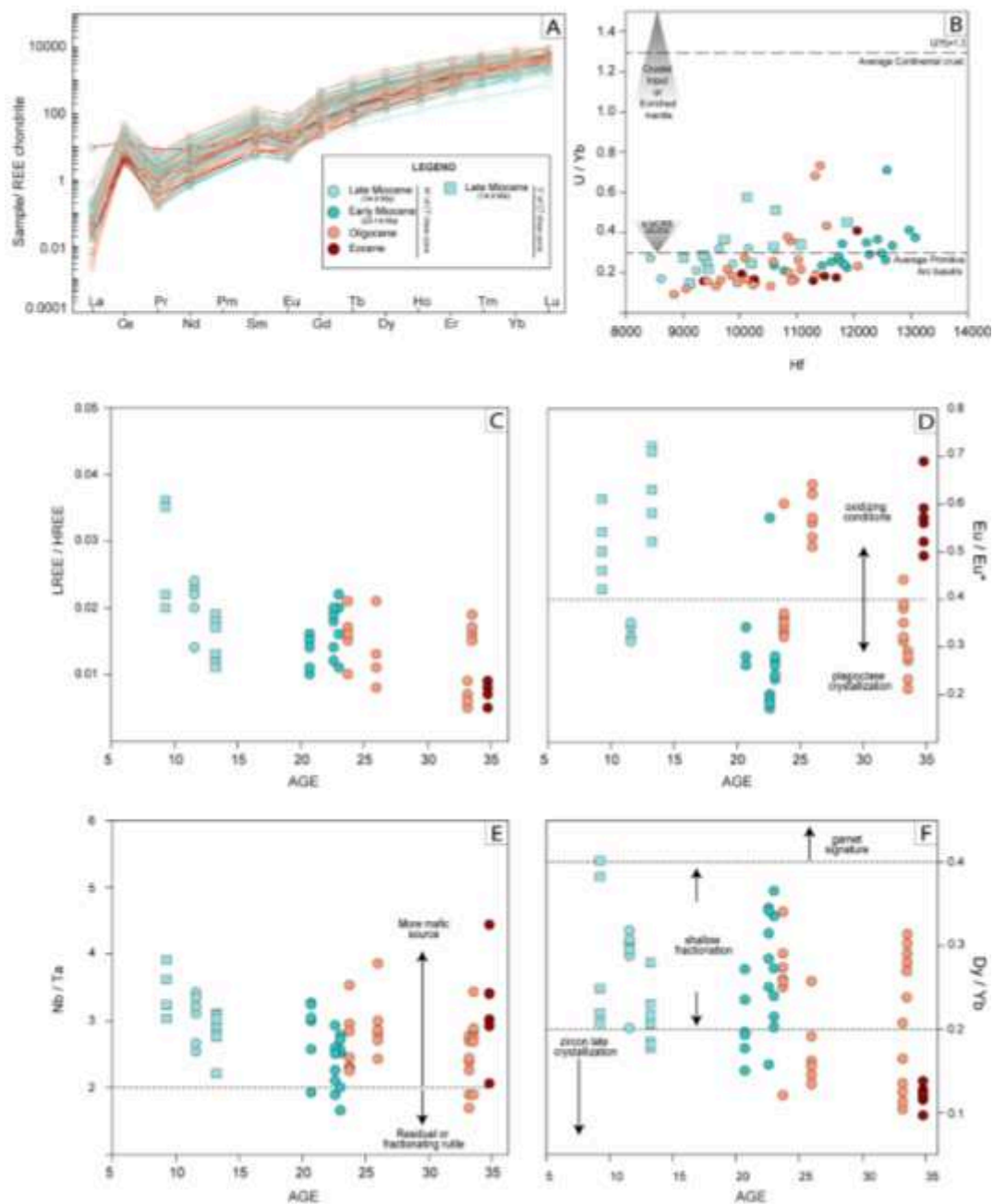


Figure 4.5 Trace element concentrations in zircons from the analyzed plutons. (A) Chondrite-normalized REE patterns. (B) U/Yb versus Hf. (C) LREE/HREE ratios. (D) Eu/Eu* anomalies. (E) Nb/Ta ratios. (F) Dy/Yb ratios.

4.5 Discussion

4.5.1 Geochronology

The new U–Pb zircon ages considerably extend the existing U–Pb geochronological record in the study area, reinforcing and broadening its spatial coverage. The results confirm a protracted magmatic history between ~39 and ~9 Ma, which is broadly consistent with previous K–Ar constraints. However, they also provide improved accuracy and resolution. By enlarging the U–Pb dataset available for this region, this study provides a more comprehensive framework for understanding the temporal and spatial evolution of magmatism in the central segment of the Western Cordillera.

This study reports the first U–Pb zircon age for the El Corazón pluton, yielding 11.62 Ma which falls within the previously established range of 16–11 Ma defined by hornblende and biotite K–Ar ages (PRODEMINCA, 2000). For the Telimbela–Chazo Juan pluton, the new ages of 24–20 Ma align well with earlier U–Pb zircon results (25–17 Ma; Schütte *et al.*, 2010a; Margirier *et al.*, 2023; Liu *et al.*, 2023), and K–Ar hornblende and biotite ages ranging from 21 to 15 Ma (PRODEMINCA, 2000). However, the 23 Ma age obtained here from the southwestern sector of the pluton raises questions, though does not conclusively refute, the westward younging trend proposed by Liu *et al.* (2023), who reported a 17 Ma age at the southwestern margin. The current dataset highlights the need for denser chronological coverage to better resolve potential younging patterns within this pluton. The Balsapamba–Las Guardias pluton yields ages of 34.8–33.2 Ma, significantly older than the ca. 21 Ma U–Pb ages previously reported by Schütte *et al.* (2010a), but consistent with earlier hornblende K–Ar ages of 34–33 Ma (PRODEMINCA, 2000), except for two anomalously younger hornblende K–Ar ages of 25.7 and 19.8 Ma (Kennerley, 1980; McCourt *et al.*, 1997). Finally, this study provides the first U–Pb age for the pluton east of the Undushig pluton, yielding 26 Ma which is comparable to the 25.4 Ma K–Ar hornblende–biotite date reported by McCourt *et al.* (1997).

5.5.2 Petrogenesis

Zircon $\epsilon\text{Hf}_{(t)}$ values obtained in this study establish a spatially and temporally extensive isotopic record for the central Western Cordillera. Plutons emplaced within the Macuchi block,

north of the CT shear zone, yield $\epsilon\text{Hf}_{(t)}$ values between +15.6 and +9.9, confirming a dominantly depleted mantle source and reinforcing the juvenile isotopic signature previously recognized by Vallejo *et al.* (2016) and consistent with values recalculated from $\epsilon\text{Nd}_{(t)}$ data by Schütte *et al.* (2010a) (Fig. 4.4A). The maximum value of +15.6 significantly extends the known $\epsilon\text{Hf}_{(t)}$ range toward more juvenile compositions, highlighting a stronger mantle contribution than previously recognized. These depleted mantle-derived $\epsilon\text{Hf}_{(t)}$ signatures are accompanied by $\delta^{18}\text{O}$ values that are predominantly mantle-like, with only minor excursions toward slightly supracontinental compositions. Such isotopic patterns suggest interaction with a juvenile crustal component, most plausibly the oceanic plateau-type crust that underlies the Macuchi block. This basement is characterized by Pb–Sr–Nd isotopic compositions and $\epsilon\text{Nd}_{(t)}$ values of +5 to +7 (Vallejo *et al.*, 2006; Chiaradia, 2009), consistent with a juvenile origin. At the base of such a plateau-type crust, magmas could have evolved within a melting, assimilation, storage, and homogenization (MASH) zone, where depleted mantle-derived inputs interacted with this juvenile basement, producing the combined $\epsilon\text{Hf}_{(t)}$ – $\delta^{18}\text{O}$ signatures recorded in zircon.

Zircon trace-element systematics from these plutons north of the CT shear zone also record temporal variations. U/Yb ratios show values around 0.2 in the Eocene-Oligocene, while towards the Miocene the ratios exhibit a slight increase, reaching values of up to 0.4, indicative of a slightly more enriched magmatic source. LREE/HREE ratios remain consistently low (<0.02), reflecting an unfractionated mantle-dominated source, with a slight increase above 0.02 at ~11 Ma marking the appearance of a more enriched component. Dy/Yb ratios remain relatively uniform (<0.3), indicating crystallization at shallow crustal levels, as also evidenced by Eu/Eu*. Nb/Ta ratios stay above the rutile control threshold (~2; Drabon *et al.*, 2024; Tang *et al.*, 2019) and below ~3, consistent with a mantle-dominated source. A subtle increase in Nb/Ta values at ~11 Ma may reflect enhanced contributions from younger, more mafic mantle inputs. Collectively, these isotopic and trace-element records define a robust juvenile mantle signature for the plutons within the Macuchi block and reveal modest but progressive changes in magma sources and fractionation processes through time.

In contrast, plutons south-southeast of the CT shear zone record lower $\epsilon\text{Hf}_{(t)}$ values (+7.9 to +2.3) and $\delta^{18}\text{O}$ values reaching up to 8‰, pointing to a more enriched mantle-derived magmatic source. Such enrichment is more plausibly attributed to the incorporation of subducted sediments or a more enriched oceanic crust (i.e., Pallatanga basement) rather than

crustal recycling, as evidenced by the absence of inherited zircons. Overall, the $\epsilon\text{Hf}_{(t)}$ variations appear to be primarily controlled by spatial differences in the underlying basement.

Together these geochemical and subtle isotopic patterns point to a slight variation in magma sources and differentiation conditions around ~11 Ma. This transition marks the shift from moderately fractionated mantle-dominated sources toward slightly more enriched mantle reservoirs, plausibly linked to modification in subduction dynamics, potentially the arrival of younger, more buoyant segments of the Nazca plate, which would have enhanced mantle melting and modified the composition of slab-derived components feeding the arc, as has been documented in the Cenozoic magmatism in the north-western Ecuadorian Andes (Iglesias et al., 2025). The contemporaneous emergence of adakite-like signatures at ~11 Ma, especially pronounced south of the CT shear zone (Fig. 4.3E), further supports a shift toward higher-pressure magmatic differentiation. These signatures, characterized by depleted zircon and whole-rock HREE patterns and the disappearance of negative Eu anomalies, signal plagioclase destabilization and the stabilization of amphibole $\pm$ garnet as residual or fractionating phases.

Although Dy/Yb ratios in zircon remain below the typical threshold for garnet stability (~0.4; Fig. 4.5), but this does not necessarily preclude garnet involvement. Amphibole fractionation can decrease Dy/Yb ratios (Macpherson et al., 2006), partially masking the garnet signal. Evidence for amphibole involvement, increasing Yb/Gd ratios together with decreasing Th/U and increasing Hf in zircon (Claiborne et al., 2010; Drabon et al., 2024), is present during the Eocene–Oligocene but absent in the Miocene (Supplementary Fig. 4), which could suggest the destabilization of amphibole under progressively higher-pressure conditions. The absence of adakitic signatures between 39 and 20 Ma and occurrence at ~11 Ma contrasts with previously reported adakitic signatures in the more evolved rocks of the Macuchi arc (Eocene). This adakitic signatures have been interpreted as the result of mixing between mantle-derived basaltic magmas and intermediate–felsic hybrid magmas generated by partial melting of both deep crustal components and a juvenile oceanic plateau source (Chiaradia, 2009; Vallejo et al., 2016). An alternative model proposed for the most evolved rocks of the Macuchi arc, though not fully constrained due to the lack of precise geochronology at the time, possibly involves a temporal shift in magmatic processes, from early shallow-level fractionation to later deep-crustal evolution that produced adakite-like signatures (Chiaradia, 2009). Additional adakitic features have also been reported in the Telimbela and Balsapamba plutons (Schütte et al., 2010b). These authors point out that the Telimbela and Balzapamba plutons are characterized by magmatic differentiation at the shallow crustal level, and by high-pressure differentiation, respectively, and that the adakitic signatures are the result of a strong depletion of Y, which

could be due to a greater fractionation of the accessory titanite phase, or to anomalies in the subducting lithosphere that promote greater stability of amphibole and garnet.

Whole-rock data between 39 and 20 Ma, characterized by slight LREE enrichment, non-depleted HREE, and negative Eu anomalies, indicate magma evolution dominated by plagioclase $\pm$ amphibole fractionation at mid- to upper-crustal levels, consistent with La/Yb and Dy/Yb trends versus SiO₂ (Davidson et al., 2007). Around ~11 Ma, adakitic signatures appear, marked by depleted HREE and the disappearance of Eu anomalies, pointing to plagioclase destabilization and the stabilization of amphibole + garnet under higher-pressure conditions. Zircon data, however, reveal an earlier and more gradual transition: Eocene–Oligocene compositions show evidence of amphibole involvement, increasing Yb/Gd, decreasing Th/U, and increasing Hf (Bell and Kirkpatrick, 2021; Claiborne et al., 2010), but these features are absent in the Miocene, suggesting a progressive shift from amphibole to garnet control on magma differentiation.

Crustal thickness estimates from Sr/Y and La/YbN ratios (Sundell et al., 2021) indicate a progressive thickening of the crust over time. Plutons emplaced north of the CT shear zone, within the Macuchi block during the 39–30 Ma interval record crustal thicknesses of ~15–30 km, reflecting magma ascent through relatively thin crustal sections. Between 26 and 21 Ma, estimated crustal thicknesses increase to ~20–40 km, marking a transition toward mid- to upper-crustal magma evolution. The greatest thicknesses, reaching ~50 km, are recorded at ~11 Ma and in intrusions south–southeast of the CT fault, indicating significantly thickened crustal conditions by the Late Miocene. These temporal variations in crustal thickness are consistent with the observed granitoid mineral assemblages and are further supported by zircon trace-element ratios, which collectively indicate magma evolution within the plagioclase $\pm$ amphibole stability field during the Eocene–Oligocene, with a possible transition to amphibole + garnet fractionation conditions in the Miocene.

4.5.3 Geodynamic Implications

Previous models provide important constraints on the geodynamic evolution of the Cenozoic Ecuadorian arc. Adakitic signatures documented in the more evolved magmas of the Paleocene-Eocene Macuchi arc may have originated from deep crustal magmatic evolution in a crust progressively thickened by successive arc overlapping and associated underplating (Chiaradia, 2009; Jaillard et al., 2005). These authors also suggested that coupling between the subducting and overriding plates facilitated the development of adakite-like signatures, which

continued intermittently alongside normal calc-alkaline magmatism until the present day. In their model, the initiation of subduction of the aseismic Carnegie Ridge at ~9 Ma increased slab–arc coupling, enhancing magma evolution at deeper crustal levels and producing transient adakitic signatures, although the timing of Carnegie Ridge subduction remains debated (e.g., Gutscher *et al.*, 1999; Margirier *et al.*, 2023), with best estimates suggesting an onset at 6–5 Ma (Hernández *et al.*, 2024).

Additional evidence from Schütte *et al.* (2010b) indicates that high-pressure magmatic differentiation developed progressively from the Late Oligocene to the Late Miocene, with the most pronounced adakitic signatures appearing in the younger intrusions. Their results highlighted that in the Balsapamba–Telimbela granitoids, anomalous volatile input (e.g., H₂O) or enhanced fractionation of accessory phases promoted the early development of adakitic signatures already during the Early Miocene, suggesting that high-pressure differentiation, favorable for porphyry formation, can occur locally even before crustal thickening reaches a regional maximum.

This volatile contribution model is consistent with the interpretation of Aizprua *et al.* (2020), who proposed that serpentinization of the lower crust or the underlying mantle lithosphere of the oceanic plateau may have provided water-rich components essential for generating fertile magmas in Late Eocene–Oligocene porphyry–epithermal systems (e.g., Balsapamba, Chazo Juan, La Plata). Likewise, Liu *et al.* (2023) proposed that variations in magmatic flux at Telimbela pluton may reflect changes in the convergence rate of the Farallon–Nazca plate system, based on the plate convergence history proposed by Somoza (1998). This model involves an acceleration of subduction at ~28 Ma, coeval with increased magmatic activity in the Ecuadorian arc during the Late Oligocene–Miocene, followed by a slowdown at ~20 Ma.

Our new results indicate a progressive geochemical shift from moderately fractionated Eocene–Oligocene magmas toward more enriched, and possibly more direct, mantle-connected sources after ~11 Ma. This transition likely reflects changes in subduction dynamics, plausibly linked to the arrival of younger and more buoyant segments of the Nazca plate, resulting from the fragmentation of the Farallon plate in the Late Oligocene (~25 Ma; Meschede and Barckhausen, 2001), which would have enhanced mantle melting and modified the composition of slab-derived components feeding the arc. Such tectonic reorganization has also been invoked for the northern segment of the Cenozoic Ecuadorian arc, where the arrival of the younger Nazca plate has been linked to deeper magmatic differentiation (Iglesias *et al.*, 2025).

While whole-rock Sr/Y and La/Yb ratios indicate that adakitic signatures emerge north of the CT shear zone at ~11 Ma, zircon trace-element data reveal that this transition was more gradual than previously recognized. The progressive weakening of the amphibole residual signature during the Early Miocene suggests that the conditions favouring high-pressure differentiation, marked by the destabilization of plagioclase, and increasing involvement of amphibole $\pm$ garnet, began earlier and evolved stepwise throughout the Miocene. An additional line of evidence comes from crustal thickness estimates, which show maximum values (>50 km) attained in the Late Miocene, coinciding with the emergence of adakite-like signatures.

This model does not exclude earlier proposals emphasizing the role of changes in plate convergence direction and velocity in driving magmatic and tectonic changes. However, whereas Maloney *et al.* (2013) documented relatively constant convergence velocities (~4 cm/yr) and less oblique convergence since at least 40 Ma, contrasting with earlier reconstructions, the arrival of progressively younger and more buoyant Nazca lithosphere at ~11 Ma likely triggered crustal shortening and deepening of magma evolution levels, peaking during the Late Miocene. This interpretation is supported by the observed decrease in the age of the subducting plate after ~10 Ma (Maloney *et al.*, 2013), coeval with the thickest crustal estimates and the most pronounced adakitic signatures in our dataset.

4.6 Conclusions

New zircon U–Pb geochronology, whole-rock geochemistry, zircon Hf–O isotopes, and trace-elements data from the Central Ecuadorian Andes refine the temporal, and tectono-magmatic evolution of the Cenozoic magmatic arc between ~39 and 9 Ma. The new U–Pb ages provide a more robust geochronological record.

Isotopic and trace-element data reveal that magmatism north of the CT shear zone within the Macuchi block was dominated by juvenile, depleted mantle sources interacting with plateau-type basement, while plutons emplaced south of the CT shear zone reflect more enriched mantle reservoirs. Whole-rock geochemical patterns indicate a transition at ~11 Ma, when magmas began to record adakite-like signatures linked to higher-pressure differentiation. This shift coincides with subtle but progressive changes in mantle inputs, the destabilization of plagioclase, and the increasing role of amphibole $\pm$ garnet. Zircon data reveal that this transition was more gradual than previously recognized, with evidence for amphibole involvement during the Eocene–Oligocene. In the Miocene, however, the progressive reduction of amphibole participation indicates that magmatic evolution was gradually shifting toward the garnet stability field at greater depths, reflecting a stepwise deepening of differentiation conditions.

Crustal thickness estimates further support this interpretation, showing a progressive thickening from ~15–30 km in the Eocene–Oligocene to ~50 km by the Late Miocene, when the adakitic signatures appear. Together, these observations highlight a two-stage evolution: (1) an early phase of moderately fractionated, mantle-dominated magmatism, and (2) a younger Miocene phase, characterized by increasingly enriched and higher-pressure differentiation with notable adakitic signatures at ~11 Ma, linked to crustal thickening and geodynamic reorganization.

These changes are interpreted as the result of evolving subduction dynamics, particularly the arrival of younger and more buoyant segments of the Nazca plate following Farallon plate fragmentation. Such tectonic reconfiguration likely enhanced mantle melting, modified slab-derived components, and promoted crustal shortening, ultimately driving the deepening of magmatic differentiation levels. It is therefore suggested that the Late Miocene represents the peak of a long-term transition when maximum crustal thickening and the strongest expression of adakitic signatures recorded the dynamic interplay between magmatism and tectonics in the central Western Cordillera.

CHAPTER 5: Petrogenesis and Tectonic Evolution of Cenozoic Magmatism in the Southernmost Northern Andes: Insights from Zircon Petrochronology

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Declaration

This chapter aims to refine the temporal and spatial framework of magmatism in the Southern Northern Andes (SNA) from ~65 to 6 Ma by integrating new zircon U–Pb geochronology with zircon $\varepsilon\text{Hf}(t)$ – $\delta^{18}\text{O}$ isotopic data and whole-rock geochemistry to demonstrate that magma composition is governed by pre-existing crustal architecture and spatial controls rather than simple temporal trends. The author contributions for this work are as follows: **Iglesias, J.** led the Conceptualization, Formal Analysis, Writing – Original Draft, and Visualization; Witt, C. provided Supervision, acquired Funding, and contributed to Writing – Review & Editing; Formal Analysis was performed by Poujol, M., Bruguier, O., Ventalon, S., and Liorzou, C.; Writing – Review & Editing was conducted by Sandoval, C., Zattin, M., Poma, O., Hernandez, M.J., Seyler, M., Bosch, D., and Chanier, F.

Abstract

New zircon U–Pb geochronology, integrated with zircon $\epsilon\text{Hf}_{(t)}$ – $\delta^{18}\text{O}$ isotopic data and whole-rock geochemistry, refines the temporal and spatial framework of magmatism in the Southern Northern Andes (SNA) from ~65 to 6 Ma. Four main batholiths, San Lucas, Catamayo, Portachuela, and Gonzanamá, along with Late Miocene intrusions, reveal emplacement patterns primarily governed by pre-existing crustal architecture. Early San Lucas magmatism (65–63 Ma) intruded thick continental crust (~60 km) and exhibits enriched isotopic signatures ($\epsilon\text{Hf}_{(t)}$: -5 to +5 and $\delta^{18}\text{O}$: 6 to 12‰), whereas later pulses (54–49 Ma) intruded thinner crust (~30 km) and show less enriched compositions ($\epsilon\text{Hf}_{(t)}$: +4.3 to +6.5 and $\delta^{18}\text{O}$: 5 to 6.5‰). West of the Las Aradas Fault, the Catamayo (36–32 Ma) and Gonzanamá (21–17 Ma) batholiths display juvenile signatures ($\epsilon\text{Hf}_{(t)}$: +7 to +14 and $\delta^{18}\text{O}$: 3.7 to 6‰), reflecting emplacement into thin, oceanic-type basement. East of the fault, the early pulse of the Catamayo batholith (39 Ma) intruded thicker crust (~60 km) and records more evolved signatures ($\epsilon\text{Hf}_{(t)}$: +4.7 to +7). Portachuela magmatism (~32–16 Ma) derives from enriched mantle sources, possibly influenced by limited sediment subduction ($\epsilon\text{Hf}_{(t)}$: -1.3 to +6.7 and $\delta^{18}\text{O}$: 3.5 to 6.7‰). Some Late Miocene intrusions (13–6 Ma) show adakitic signatures as well as high-pressure fractionation, and isotopic enrichment ($\epsilon\text{Hf}_{(t)}$: +0.7 to +7 and $\delta^{18}\text{O}$: ~4 to 6.7‰) that are consistent with crustal thickening. Collectively, these results reveal that magma composition in the SNA is primarily governed by spatial controls. Isotopic patterns define at least two distinct magmatic reservoirs separated by the Aradas Fault: to the west, a juvenile source related to extensional tectonics and oceanic basement; to the east, a more enriched source likely influenced by subduction processes, including sediment subduction. Together, these findings challenge prevailing models of large-scale arc migration and highlight the interplay of mantle input, inherited basement heterogeneity, and variable crustal thickness in shaping SNA magmatism.

5.1 Introduction

Continental magmatic arcs are key settings for understanding the processes associated with plate tectonic. Unravelling their chronological and petrogenetic evolution provides crucial insights into tectonic and geodynamic processes. In particular, the geochemical evolution of continental arcs, in conjunction with their spatial and temporal development in subduction zones, reflects complex interactions between slab dynamics, crustal thickness, and the architecture of crustal domains, among other controlling factors.

Andean type arcs are continental magmatic arcs that develop through the subduction of oceanic lithosphere beneath continental or accreted oceanic crust. The Andes represent the world's most extensive orogenic subduction system, with a long-lived and nearly continuous subduction history since at least the Jurassic (e.g., Horton, 2018; Jaillard et al., 2000; Somoza, 1998). In the southernmost Northern Andes (SNA; 3°–5°S), the Cenozoic magmatic arc roughly coincides with the Huancabamba deflection, a major geotectonic feature marking the transition between the Northern and Central Andes. In this region, the continental arc is thought to be emplaced on an autochthonous basement composed mainly of Paleozoic metamorphic rocks and Triassic intrusions (Aspden et al., 1992; Sandoval-Espinel et al., 2025; Witt et al., 2017).

Very few works dealt with the Cenozoic magmatism in southern Ecuador (e.g., Chiaradia et al., 2004; Schütte et al., 2010). Although these works offered valuable insights into the evolution of Cenozoic magmatism in southern Ecuador, they are frequently constrained by limited temporal and spatial resolution. As a result, the lack of chronological and geochemical data has hindered an accurate understanding of the origin, petrogenesis and tectonic significance of magmatism, which remains insufficiently explored and have yet to be comprehensively contextualised within the geodynamic framework of the northern Andes.

Zircon U-Pb chronology, integrated with petrography, whole-rock analyses, zircon trace element analysis, and isotopic data (ϵHf_t and $\delta^{18}\text{O}$), represents a robust tool for investigating the spatio-temporal evolution of magmatic reservoirs and differentiation and assimilation processes. This information can provide critical constraints on tectonic and geodynamic interpretations (Attia et al., 2020; Grimes et al., 2015; Iglesias et al., 2025; Jara et al., 2021; Jones et al., 2015; Witt et al., 2023).

This study presents 28 new zircon U-Pb ages, along with whole-rock and zircon geochemical analyses obtained from major batholiths (San Lucas, Portachuela, Gonzanamá, Catamayo) to minor stocks (Late Miocene plutons) in southern Ecuador. This study significantly improves the knowledge of the temporal and spatial evolution of the Cenozoic magmatic arc in the SNA and yields significant information about the evolution of magmatic reservoirs, the crustal segmentation, and possible recent variations in crustal thickness. This study underscores the importance of Mesozoic geodynamic events resulting in the formation of new oceanic crust, thereby exerting a primary control on subsequent arc geochemistry.

5.2 Geological background

5.2.1 The geodynamic context of the Cenozoic magmatic arc

The Ecuadorian Northern Andes margin has a complex subduction history marked by the accretion of oceanic lithosphere to the continental margin. The most accepted accretion period took place during the Late Cretaceous at ~72 Ma, involved plateau rocks of the Caribbean plate and resulted in a compressive setting leading to a major increase of crustal thickness (George et al., 2021; Jaillard, 2022; Vallejo et al., 2009; Witt et al., 2023). Accreted rocks underlie both the forearc basin and the Western Cordillera and constitute the basement into which the Cenozoic arc is emplaced (Aizprua et al., 2020; Hernández et al., 2024; Iglesias et al., 2025). In contrast, south of 3°S the arc is thought to be emplaced within autochthonous continental crust, composed mainly of Paleozoic metamorphic rocks intruded by Triassic granitoids (Spikings et al., 2015; Witt et al., 2017).

Regional studies have provided first-order insights into the evolution of the arc in the Ecuadorian Andes. North of 3°S, Chiaradia et al. (2004) identified a shift from non-adakitic to adakitic-like magmatism during the Late Miocene, driven by crustal thickening associated with a transition to a compressional regime, thought to be triggered by the onset of Carnegie Ridge subduction. Iglesias et al. (2025) described a transition from juvenile, mantle-derived magmatism to more evolved sources at ~14 Ma, reflecting progressive crustal thickening linked to the arrival of the buoyant Nazca plate and the onset of a compressional regime.

South of 3°S, Schütte (2009) and Schütte et al. (2010) documented a Late Oligocene–Early Miocene magmatic flare-up linked to accelerated convergence rates and reduced subduction obliquity. They also reported a progressive along-arc broadening during the Mid- to Late Miocene, attributed to shallow slab subduction. Furthermore, Cenozoic forearc detrital zircons derived from southern Ecuador record the arc evolution, marked by high isotopic variability resulting from crustal recycling, coincident with the major ~72 Ma accretion, and transitioning to mantle-dominated magmatism, possibly related to alternating compressional–extensional tectonic regimes (George et al., 2021; Witt et al., 2023).

North of ~3°S the modern volcanic arc is active, associated with ongoing subduction of the Nazca plate beneath the South American plate. In contrast, the arc becomes inactive in southern Ecuador, where no Quaternary volcanism is recorded, and the youngest evidence of magmatism (dated at ~3.6 Ma) is adakitic in nature and has been linked to the last episodes of magmatism resulting from slab flattening (Beate et al., 2001). This north-south contrast reflects

variations in subduction dynamics, crustal structure, and possibly slab geometry, highlighting the complex geodynamic segmentation along the SNA margin.

Northern Peru (3°–15°S) is characterized by flat-slab subduction, shaped by the geometry and timing of Nazca Ridge and Inca Plateau subduction (Margirier et al., 2015; Rosenbaum et al., 2005). Variations in convergence rates are linked to episodic forearc deformation and increased magmatic activity (Jaillard, 2025; Schütte et al., 2010; Espurt et al., 2018). The tectonic framework of the region reflects Cenozoic accretion of crustal and sedimentary units (Espurt et al., 2018), with detrital zircon data revealing a strong continental basement signature (Witt et al., 2017, 2019, 2023). Globally, isotopic shifts in Tertiary magmas are primarily attributed to crustal contamination rather than mantle source variation, particularly during the 30–7 Ma interval between 13° and 18°S (Mamani et al., 2010).

5.2.2 The Cenozoic continental arc in southern Ecuador

The continental arc in southern Ecuador is outlined by several intrusive and volcanic bodies located between the Eastern Cordillera and the Amotape terrane (Fig. 5.1).

The Amotape terrane, a key crustal block in the southern Northern Andes, is bounded to the south by the Celica-Lancones Basin and consists of metamorphic rocks intruded by Triassic granitoids (Aspden et al., 1995; Bosch et al., 2002; Riel et al., 2013; Witt et al., 2017). It is interpreted either as the equivalent of the eastern Ecuadorian Cordillera and the Peruvian Olmos terrain (Aspden et al., 1992; Witt et al., 2017), or as an allochthonous terrane accreted in the Permian or Early Cretaceous (Mourier et al., 1988; Ramos, 2009; Winter et al., 2010). Its current position likely results from an initial ~110° clockwise rotation during the Late Carboniferous, evidenced by paleomagnetic data (Mourier et al., 1988), and is associated with the Late Cretaceous formation of the Lancones basin (Witt et al., 2017). The oceanic nature of the basin basement is further supported by regional models in which high-gravity anomalies indicate high crustal density and a thin continental crust (Mamani et al., 2009).

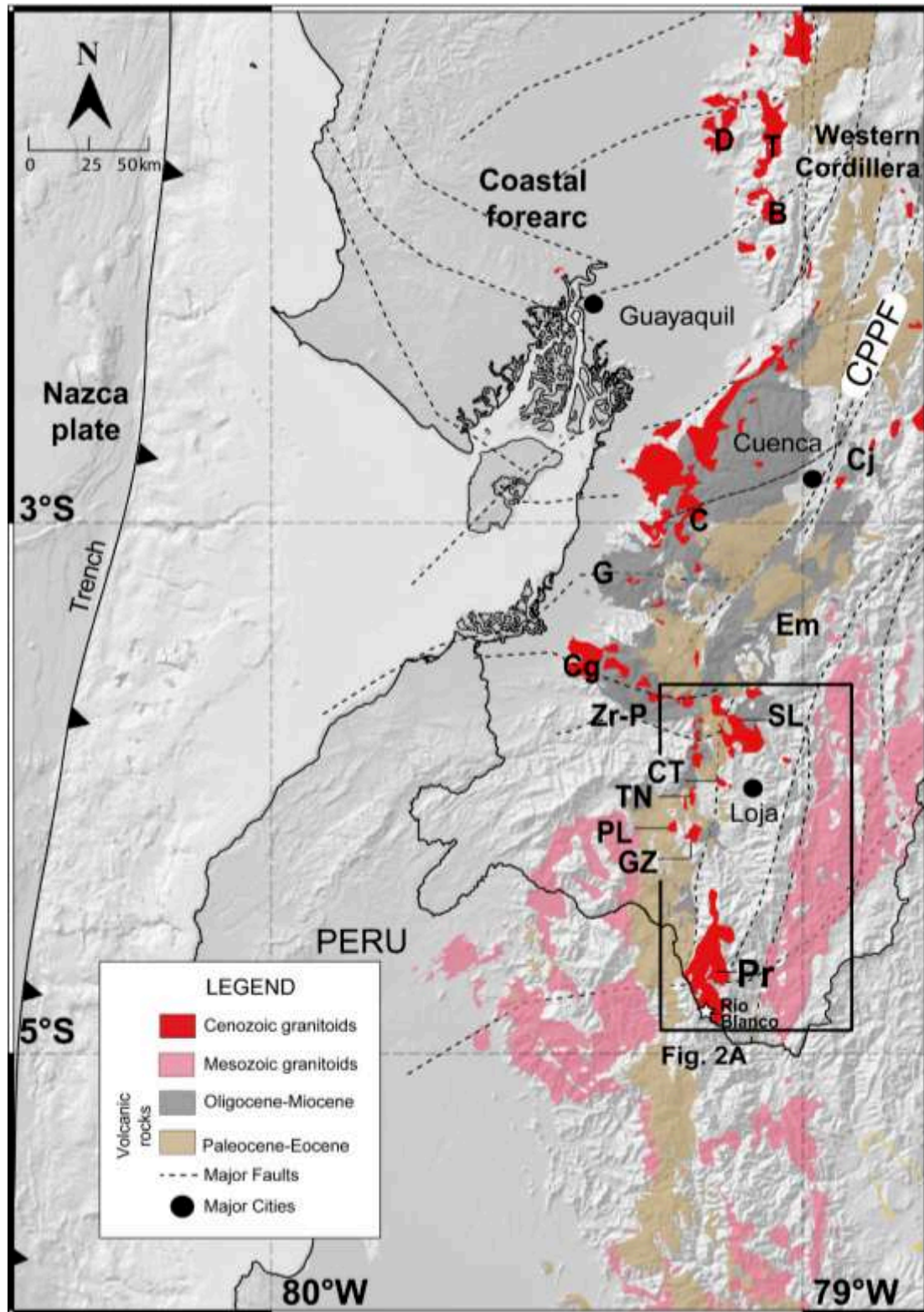


Figure 5.1 Regional geological map of the southernmost Northern Andes, showing the distribution of Cenozoic arc-related plutons, associated volcanic rocks, and major fault systems. The letters correspond to the main intrusive bodies: D – Domo, T – Telimbela, B – Balzapamba, Cj – Cojitambo, C – Chaucha, G – Gaby, Cg – Cangrejos, Em – El Mozo, Zr-P – Zaruma Portovelo, SL – San Lucas, CT – Catamayo, TN – El Tingo, PL – Palo Blanco, GZ – Gonzanama, Pr – Portachuela. The location of the Río Blanco porphyry is also indicated. The boxed region marks the area enlarged in Figure 2A.

The Cenozoic magmatic arc in the SNA is mainly defined by the San Lucas and Portachuela batholiths, along with other smaller intrusive bodies, here defined as the Catamayo and Gonzanama batholiths, together with additional minor intrusions collectively referred to as Late Miocene intrusives (Fig. 5.2). These igneous bodies show no evidence of deformation, although they are roughly aligned along a prominent N-S trend, parallel to the NNE-striking Aradas fault system (Fig. 5.2), which is thought to have played a key role in controlling their emplacement (Aspden et al., 1992; Chiaradia et al., 2004, this work). Additionally, the main volcanic deposits correspond to the Early Eocene-Paleocene Sacapalca Formation and the Oligocene-Early Miocene Saraguro Group (BGS and CODIGEM, 1999).

The San Lucas batholith is characterized by multiple mineralogical facies, including hornblende granodiorites, biotite granodiorites, and granites (Kennerley, 1980), with biotite and hornblende K-Ar ages ranging from 68 Ma to 51 Ma (Aspden et al., 1992; Bristow and Hoffstetter, 1977). The Portachuela batholith, located on the Ecuador-Peru border, intrudes Paleozoic to Triassic metamorphic rocks and consists of tonalitic, dioritic and granodioritic compositions, with biotite-hornblende K-Ar ages ranging from 24 to 17 Ma and zircon U-Pb ages of 14 and 12 Ma (Chen, Meng, et al., 2022; Litherland et al., 1994).

Smaller batholiths, less defined in regional maps, are here defined as the Catamayo and Gonzanama batholiths. The Catamayo batholith, comprises several plutons, notably the El Tingo pluton, a granodiorite located west of Catamayo (Fig. 5.2), with hornblende and biotite K-Ar ages ranging from 50 Ma to 45 Ma (Bristow and Hoffstetter, 1977; Kennerley, 1980). Also included within this batholith are the La Toma and Catamayo plutons, located west of Loja, both classified as granodiorites, with biotite K-Ar ages of 57.6 and 57–58 Ma, respectively (Aspden et al., 1992; Litherland et al., 1994), as well as, the Palo Blanco pluton, located northwest of the Gonzanama locality, which yields whole-rock and plagioclase K-Ar ages of 21 and 26 Ma (Jaillard et al., 1996).

The Gonzanama batholith is mainly composed of what is referred to here as the Gonzanamá pluton, located north of the town of Gonzanama. Also included within this batholith are smaller plutons located in the Cariamanga area. Finally, the Late Miocene intrusives comprise smaller intrusive bodies located within the Portachuela batholith and to the north-northwest of the San Lucas batholith (Fig. 5.2).

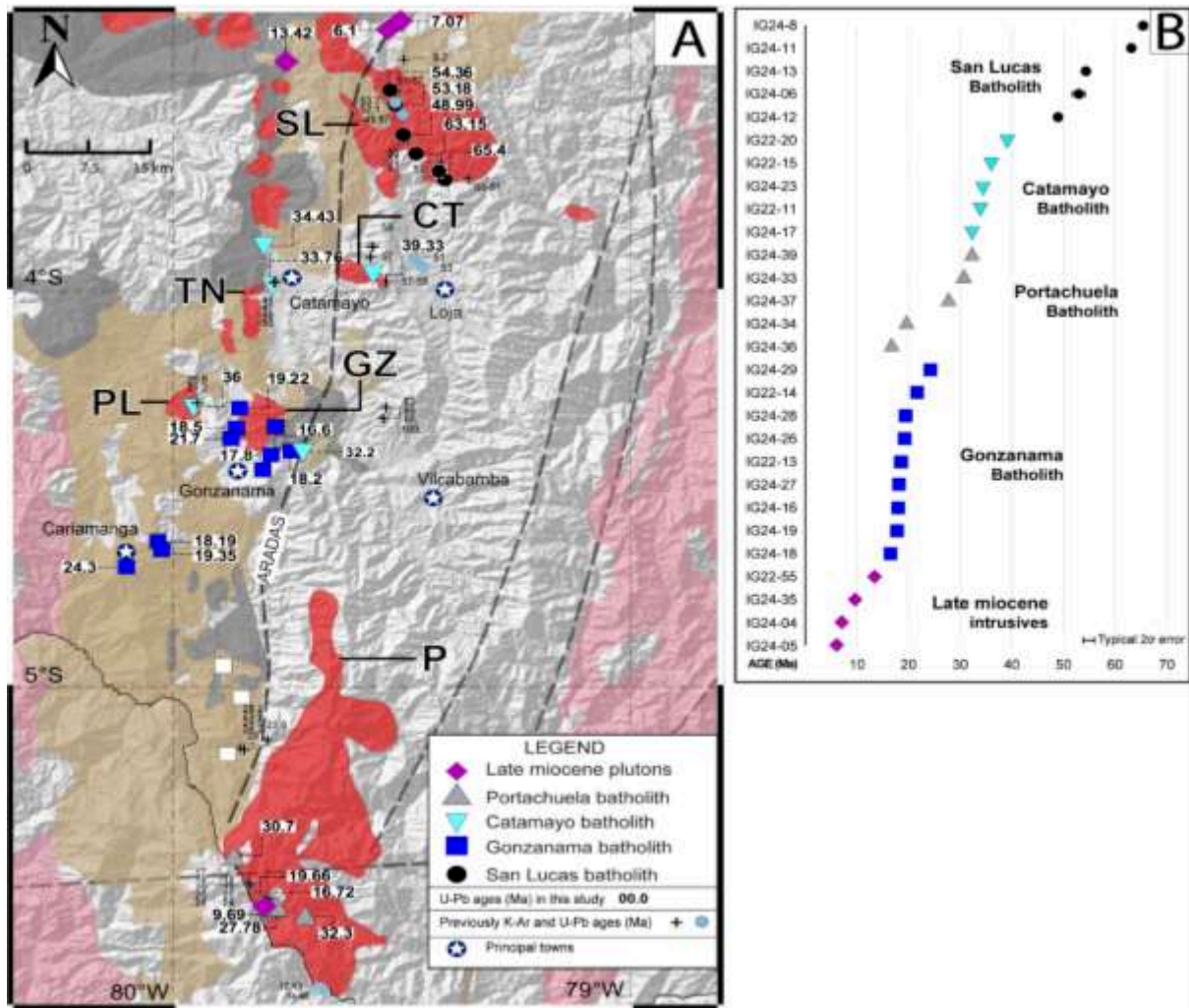


Figure 5.2 (A) Detailed geological map of the Catamayo–Loja–Gonzanamá region, showing the spatial distribution of five intrusive assemblages: the San Lucas Batholith, Catamayo intrusives, Portachuelo Batholith, Gonzanamá intrusives, and the younger Upper Miocene plutons. (B) U–Pb zircon crystallization ages obtained in this study for the various intrusive units, highlighting their temporal relationships.

5.3 Methods

A total of 28 samples were collected along a N–S corridor bounded primarily by the San Lucas batholith to the north and the Portachuela batholith to the south, as well as other smaller intrusions such as the Catamayo, El Tingo and Palo Blanco plutons, located in the center of this corridor, east and west of the Aradas Fault. Sampling locations were selected based on accessibility and outcrop suitability (Fig. 5.2A, Table 1). Least altered samples were prioritized; however, some altered specimens were also included, as zircon’s resistance to secondary alteration makes it a reliable source of geochronological and geochemical information.

Table 5.1 Sample Location and U-Pb Age

	Sample	Latitude	Longitude	Age	2s
1	IG24-5	-3.67	-79.27	6.1	0.3
2	IG24-4	-3.66	-79.25	7.1	0.2
3	IG24-35	-4.78	-79.40	9.7	0.3
4	IG22-55	-3.71	-79.32	13.4	1.0
5	IG24-18	-4.21	-79.39	16.6	0.4
6	IG24-19	-4.23	-79.40	17.8	0.5
7	IG24-16	-4.21	-79.37	18.1	0.5
8	IG24-27	-4.32	-79.52	18.2	0.2
9	IG22-13	-4.18	-79.43	18.5	0.2
10	IG24-26	-4.15	-79.43	19.2	0.3
11	IG24-28	-4.33	-79.52	19.4	0.1
12	IG22-14	-4.19	-79.44	21.7	0.4
13	IG24-29	-4.35	-79.55	24.3	0.4
14	IG24-36	-4.78	-79.39	16.7	0.4
15	IG24-34	-4.78	-79.41	19.7	0.2
16	IG24-37	-4.78	-79.39	27.8	0.2
17	IG24-33	-4.72	-79.44	30.7	0.3
18	IG24-39	-4.79	-79.36	32.3	0.3
19	IG24-17	-4.79	-79.36	32.3	0.3
20	IG22-11	-4.00	-79.39	33.8	0.3
21	IG24-23	-3.95	-79.40	34.4	0.5
22	IG22-15	-4.15	-79.48	35.7	0.3
23	IG22-20	-3.98	-79.28	39.3	0.9
24	IG24-12	-3.80	-79.25	49.0	0.3
25	IG24-6	-3.77	-79.26	53.2	1.2
26	IG24-13	-3.75	-79.27	54.2	0.3
27	IG24-11	-3.83	-79.24	63.2	0.6
28	IG24-8	-3.86	-79.21	65.4	0.8

Sample preparation, including washing, crushing, sieving, grinding, and density separation was carried out in the laboratories of the Department of Geology (National Polytechnic School of Quito, Ecuador). Whole-rock major and trace elements were analysed via inductively coupled plasma atomic emission spectroscopy (ICP-AES, Ultimate 2 - Jobin Yvon) at the Geo-Ocean laboratory (PSO – Pôle de Spectrométrie Océan, University of Brest, France).

Zircon separation was performed following conventional magnetic and density techniques (Malusà & Fitzgerald, 2019; and references therein). Zircons were mounted in epoxy resin holders, polished to expose cores, and initially imaged by optical cathodoluminescence (CL) at the Lille university to examine their internal structures and select

suitable zones for dating. Subsequently, high-resolution scanning electron microscope cathodoluminescence (SEM-CL) was performed at Geo-Ocean laboratories in Grenoble (France) to reveal detailed textures of the dated zircons (Supplementary Fig. 1).

Zircon U-Pb dating was performed on three different laboratories by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). In the GeOHeLiS analytical platform (OSUR, University of Rennes, France) using an ESI NWR193UC excimer laser coupled to an Agilent 7700x quadrupole ICP-MS with a dual pumping system to improve sensitivity (Paquette et al., 2014) for 13 samples. At the Geosciences Montpellier Laboratory (University of Montpellier, France) using a Teledyne G2 excimer laser (193 nm) coupled to a single collector Element XR (ThermoScientific) ICP-MS equipped with a dual pumping system to improve sensitivity (Edwards 80 m³/h) for 7 samples. At the Magmas and Volcans Laboratory (Clermont Ferrand, France) using a Resonetics/M-50E excimer laser (193 nm) coupled to a single collector Element XR (ThermoScientific) ICP-MS for 6 samples. Data acquisition parameters are given in the Supplementary Table 2.2, 2.3, and 2.5. Data were processed with Isoplot R (Vermeesch, 2018) to generate concordia diagrams (Fig. 5.3).

Trace elements and Lu-Hf isotope analyses in zircon were carried out at Geosciences Laboratory (University of Montpellier, France). Lu-Hf isotopes were measured using a Thermo Finnigan Neptune+ inductively coupled mass spectrometer (MC-ICP-MS) coupled to a Photon-Machine Analyte G2 excimer laser. Standards 91500, Plešovice, and GJ-1 were analysed to check data quality and reproducibility. ϵ_{Hf} values and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios were calculated using parameters from (Söderlund et al., 2004) and Bouvier et al. (2008).

Trace elements in zircon were examined using a laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS) with a 193 nm ArF excimer laser (Teledyne G2) coupled to a Thermo Finnigan Element XR mass spectrometer, enhanced for sensitivity with an Edwards primary pump in the interface. The laser was set with a repetition rate of 6 Hz, with a 50 μm spot size and a 4.51 J/cm² energy density. NIST 612 was used for external calibration (Pearce et al., 2007), and standards (91500, GJ1, and Plešovice) ensured accuracy and long-term reproducibility. Data reduction was performed using Glitter (van Achterberg et al., 2001).

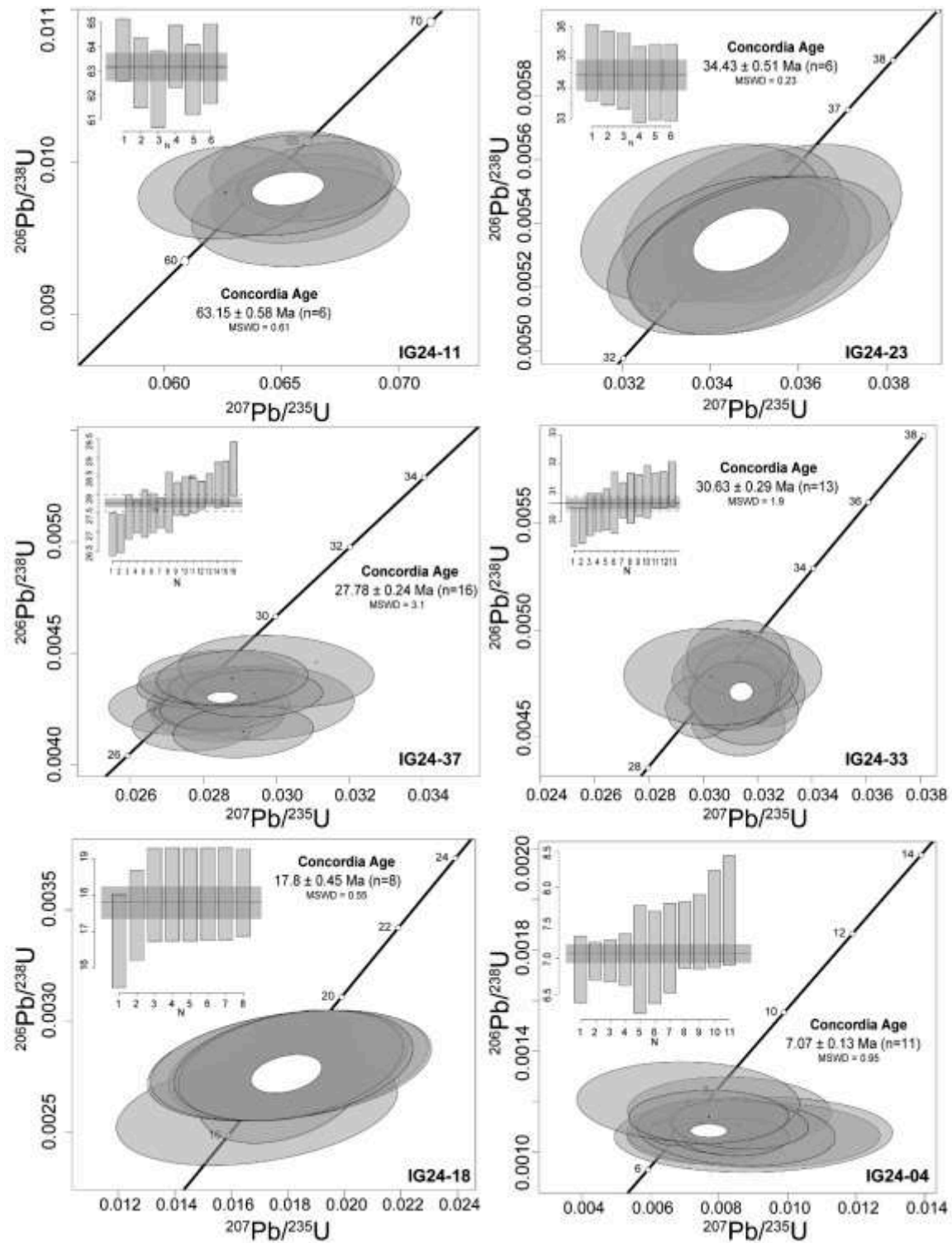


Figure 5.3 Representative zircon U–Pb dates and associated Concordia diagrams, including 2σ error margins. Weighted mean age plots based on the Concordia dates are also presented.

Oxygen isotopes were performed at the Centre de Recherches Pétrographiques et Géochimiques (CRPG, Université de Lorraine, Nancy, France). A Cs⁺ primary ion beam (2.5 nA, 10 kV) with a secondary ion mass spectrometer Cameca IMS1270 in FC/FC detection mode was used. Instrumental mass fractionation was improved using reference material 91500-

zircon ($\delta^{18}\text{O}$: 4.41‰–6.418‰). Other technical aspects as well as method descriptions can be found in Sandoval-Espinel et al. (2025) and Witt et al. (2023, 2017).

5.4 Results

5.4.1 Geochronology

Zircon U-Pb dating was performed on 28 samples (Fig. 5.2), comprising 332 zircon grains. The zircons occur as subhedral to euhedral crystals, typically 50–250 μm in size, displaying magmatic oscillatory zoning and core–rim structures (Supplementary Fig. 1). For analyses with 90–105% concordance, no filtering of the youngest or oldest dates was applied; concordia ages were calculated and reported at the 95% confidence level (2σ), both numerically and graphically (error bars and ellipses). These ages, interpreted as crystallization ages, were plotted on Wetherill concordia diagrams. For samples with partially discordant zircon analyses, weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages or lower-intercept ages from discordia regressions were calculated, providing robust estimates of crystallization ages consistent within analytical uncertainty. Age results are presented in concordia and Tera–Wasserburg diagrams to facilitate interpretation of discordance and age distribution across the sample set. Full zircon U-Pb data are presented in the Supplementary Table 2, 2.2, and 2.4.

The San Lucas batholith yields ages ranging from 65.4 ± 0.5 to 48.9 ± 0.3 Ma, based on 28 concordant analyses from five samples. The Catamayo Batholith records ages of 39.2 ± 0.9 to 32.3 ± 0.3 Ma from 39 concordant analyses from five samples. The Portachuela Batholith has ages between 32.3 ± 0.3 to 16.7 ± 0.4 Ma, constrained by 61 concordant analyses from five samples. The Gonzanama Batholith has a narrow set of ages ranging from 21.6 ± 0.4 to 17.8 ± 0.5 Ma from 54 concordant analyses from nine samples. The youngest intrusive bodies identified in this study, referred to as Late Miocene intrusions, yield ages from 13.4 ± 1.0 to 6.1 ± 0.3 Ma, based on 8 concordant analyses and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages from four samples.

5.4.2 Petrography and whole-rock data

Major and trace element analyses were performed on 21 samples, with results presented in Supplementary Table 3. Our sample set consists of compositions ranging mainly from tonalites to granites on the basis of the meso-normative Q'-ANOR diagram (Streckeisen and Le Maitre, 1979; Fig. 5.4A). The San Lucas batholith comprises tonalite, granodiorite, and monzogranite, whereas the Portachuela batholith exhibits a broader compositional range, including quartz gabbro, granodiorite, and monzo-syenogranite (Fig. 5.4A). The Catamayo

batholith is mainly tonalitic to granodioritic, while the Gonzanama batholith intrusives range from quartz gabbro to tonalite. An exception is sample IG24-18, which initially plotted within the alkaline feldspar granite field. However, due to visible macroscopic alteration, this sample was reclassified as diorite/gabbro using the immobile element classification scheme (Nb/Y vs. Zr/TiO₂) of Vry et al. (2010). Younger intrusive bodies display a broader composition, including quartz diorite, tonalite, and granite. The rocks are generally composed of variable proportions of quartz, plagioclase feldspar, K-feldspar, and minor hornblende and biotite.

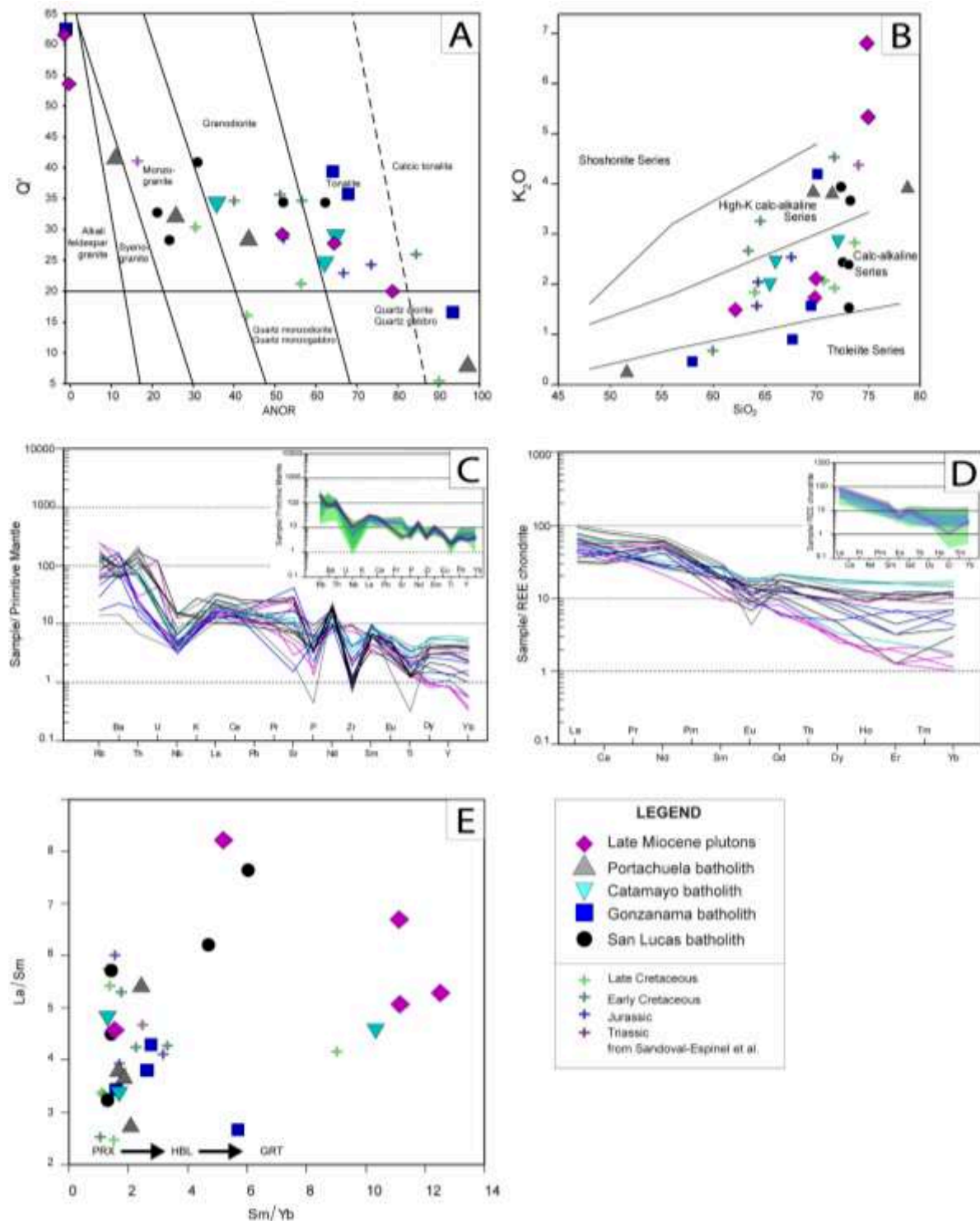


Figure 5.4 Whole-rock geochemistry diagrams. (A) Q–ANOR diagram for classification of granitoid types. (B) K₂O vs. SiO₂ diagram showing magma series classification after Peccerillo & Taylor (1976). (C) Primitive mantle–normalized multi-element diagram. (D) Chondrite-normalized rare earth element (REE) patterns. (E) La/Sm vs. Sm/Yb diagram illustrating fractionation trends, with vectors indicating mineral control (PRX = pyroxene, HBL = hornblende, GRT = garnet).

The samples predominantly exhibit holocrystalline, medium-grained, hypidiomorphic textures, with occasional microgranular textures (Supplementary Fig. 2). The mineral assemblages are as follows: San Lucas batholith—Qz (50–60%) + Plg (30–40%) + amph–K-fds–bt ($\leq 10\%$); Catamayo batholith—Qz (40%) + Plg (35–40%) + K-fds (10%) + amph (10%) + bt; Gonzanama batholith—Qz (40%) + Plg (35–40%) + prx (10%) + amph–bt; Portachuela batholith—Qz (35%) + Plg (30%) + K-fds (15%) + bt (15%) + amph; and younger intrusives—Plg (35–40%) + Qz (30%) + K-fds (15%) + amph (15%) + bt. Accessory minerals include magnetite, titanite, epidote, apatite, and zircon. Plagioclase occurs as tabular, zoned crystals with Carlsbad twinning, often altered to sericite. Chlorite is occasionally present, likely as an alteration product of biotite or amphibole. Biotite, when present, forms subhedral platy crystals with brownish green pleochroism.

The chemical composition of the analysed plutons is characterized by SiO₂ contents ranging from 51.64 – 78.76 wt.%, recalculated volatile-free. The magnesium number (#Mg) of the dataset ranges generally between 31 to 59.6, with three samples below this rank. In terms of major oxides, all the samples exhibit roughly linear negative (Al₂O₃, FeO_T, MgO, MnO, CaO, P₂O₅, TiO₂), positive (K₂O), or constant trends (Na₂O), in relation with SiO₂ (Supplementary Fig. 3). Overall, the samples from all groups are mainly peraluminous and exhibit a calc-alkaline to high-K calc-alkaline affinity, however two samples from the Gonzanama intrusives and one from the Portachuela batholith have tholeiitic affinity (Fig. 5.4B).

All the samples, show characteristics of arc magmatism like enrichment in Rb, Ba, Sr, and depletion in like Nb, Ti and P, in the primitive mantle normalized multi-element diagram (Fig. 5.4C). Chondrite normalized REE values display moderate to high enrichments in light rare elements (LREE) relative to heavy rare elements (HREE) with La_N/Yb_N values ranging from 2.15 to 49.86, and flat to marked MRE–HREE sections with Sm_N/Yb_N values ranging from 1 to 13.69 (Fig. 5.4D).

Kay et al. (1991) defined stability fields for pyroxene, amphibole, and garnet fractionation based on La/Sm and Sm/Yb ratios. Most samples from the Portachuela batholith, Gonzanama batholith, and several from the San Lucas batholith, Catamayo batholith, and

younger plutons fall within the pyroxene stability field ($\text{Sm}/\text{Yb} = 0.9\text{--}2.8$; $\text{La}/\text{Sm} = 2.8\text{--}5.7$). A subset of samples from the San Lucas batholith and younger intrusives plot within the amphibole field ($\text{Sm}/\text{Yb} = 4.6\text{--}5.9$; $\text{La}/\text{Sm} = 6.3\text{--}8.2$). Additionally, three younger plutons and one Catamayo sample fall within the garnet stability field ($\text{Sm}/\text{Yb} = 10.7\text{--}12.6$; $\text{La}/\text{Sm} = 4.5\text{--}6.8$; Fig. 5.4E).

La_N/Yb_N ratios in the Portachuela and Gonzanama batholiths, as well as in certain samples from the Catamayo batholith and younger intrusives cluster within a narrow range (2.8–8.9), consistent with normal arc magmas. In contrast, higher values (19.7–49.9) in several younger intrusives, two San Lucas samples, and one from Catamayo reflect adakitic signatures. Sr/Y ratios mirror a similar trend but span a broader range, reinforcing the distinction between typical arc and adakitic magmatism (Fig. 5.5).

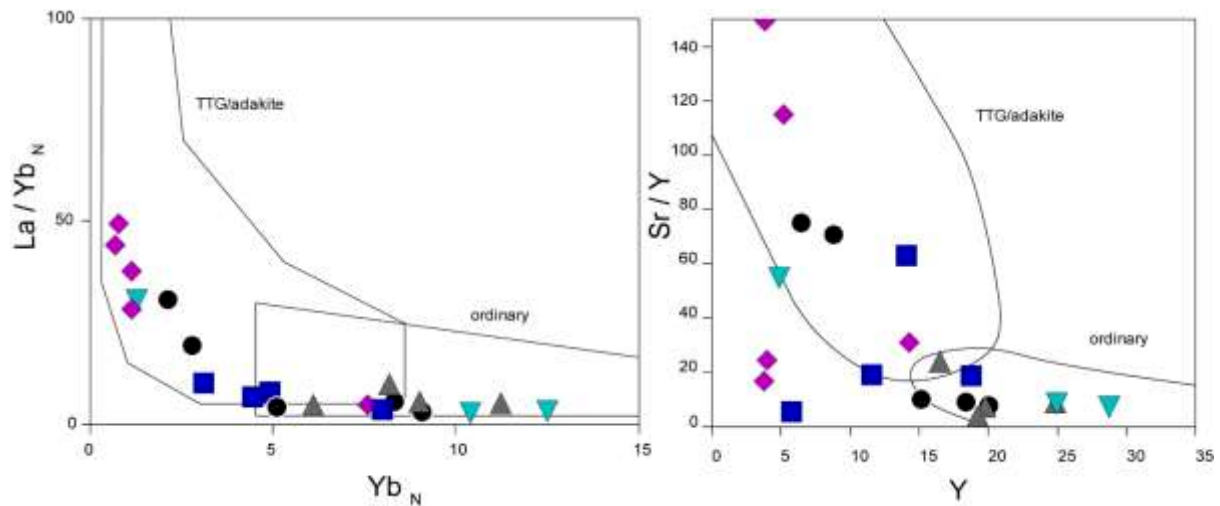


Figure 5.5 Adakite discrimination diagrams: Sr/Y vs. Y and $(\text{La}/\text{Yb})_N$ vs. Yb_N .

5.4.3 Isotopic ($\epsilon\text{Hf} + \delta^{18}\text{O}$) constrains

Age-corrected $\epsilon\text{Hf}_{(t)}$ values (Fig. 5.6) for the San Lucas and Portachuela batholiths, as well as for the Late Miocene intrusives, show more enriched values compared to the Catamayo and Gonzanama batholiths. The San Lucas batholith has a range of ϵHf values between -5.4 and $+5.4$ between 65–63 Ma; and a well-defined range of values between $+6.5$ and $+4.3$ between 54–49 Ma. The Portachuela Batholith exhibits a stable ϵHf trend, ranging from -1.3 to $+3.6$ at approximately 30 Ma, with a slight shift to less enriched values, reaching up to $+6.7$ around 20 Ma. The Catamayo batholith displays ϵHf values comparable to those of the San Lucas Batholith at ~ 39 Ma, followed by a range of $+7.1$ to $+13.8$ between 37 and 32 Ma. This range is similar to that of the Gonzanama batholith, which represent the most juvenile signatures, closely resembling a depleted mantle source. The Late Miocene intrusives exhibit

enriched ϵ_{Hf} values, ranging from +2.8 to +5.3 at ~13 Ma and from +2.6 to +6.3 between 7 and 6 Ma.

The $\delta^{18}\text{O}$ values (Fig. 5.6) of the San Lucas batholith (~50-65 Ma) shows a wider range, with some analyses significantly exceeding typical mantle like zircon values ($\sim 5.3 \pm 0.6 \text{ ‰}$).

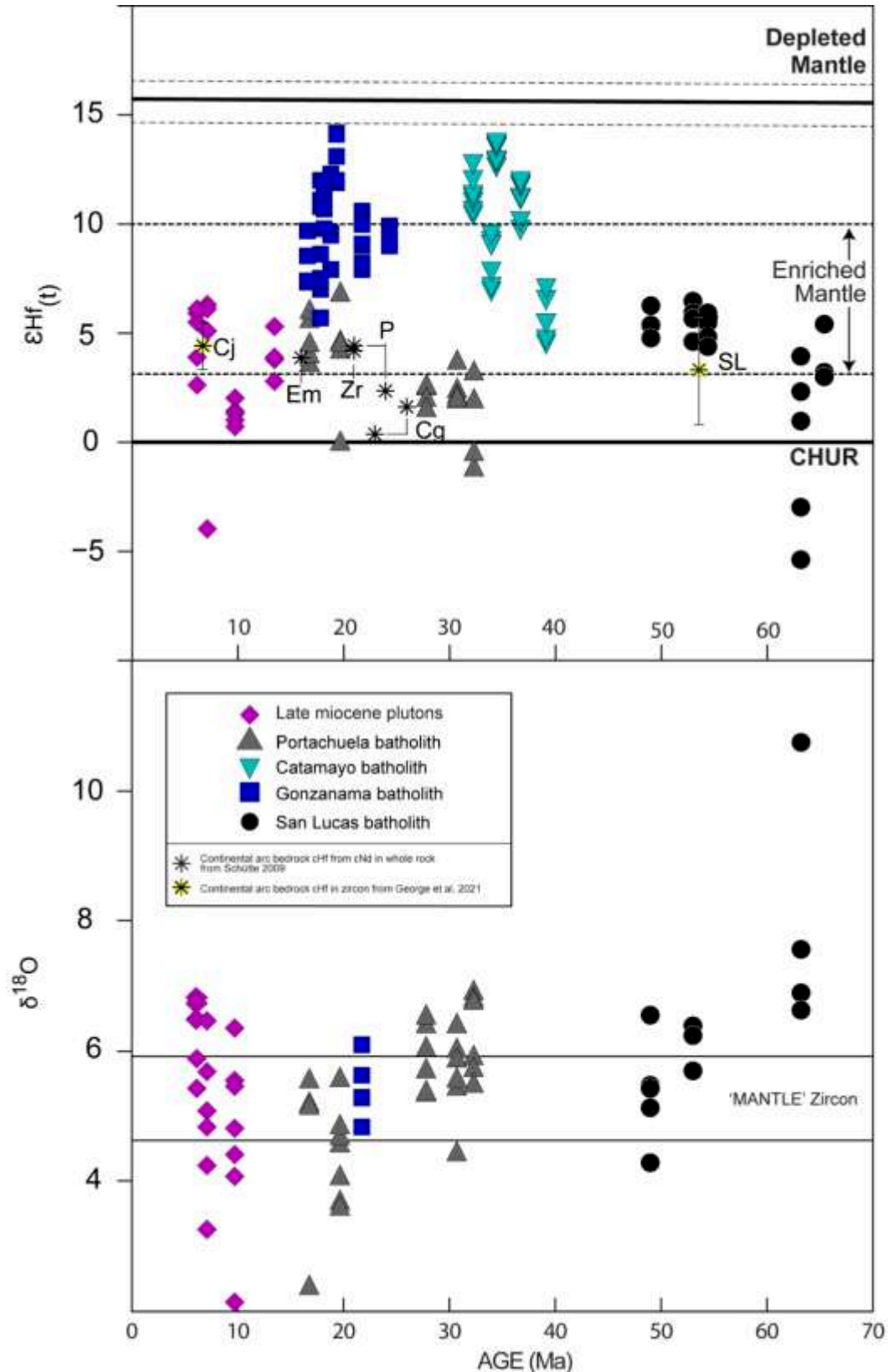


Figure 5.6 Plots showing ϵ_{Hf} and $\delta^{18}\text{O}$ vs. crystallization age for the studied zircons.

This suggests a greater crustal contribution during the early stages (63–65 Ma), which became more limited in the later phases of the batholith. The Portachuela and Gonzanama batholiths (~15–39 Ma) show $\delta^{18}\text{O}$ values (~4–6 ‰) closer to those of the mantle, suggesting a more primitive or less altered mantle magmatic source. Furthermore, this period is characterized by the lowest $\delta^{18}\text{O}$ variability, suggesting a more homogeneous magmatic reservoir, potentially reflecting a tectonically stabilized setting with limited crustal assimilation. In contrast, Late Miocene intrusions exhibit a subtle but noticeable increase in $\delta^{18}\text{O}$ values from around 10 Ma onwards, suggesting a stronger renewed, though still limited, crustal contribution to the magmatic sources.

5.4.4 Zircon trace-elements

Zircon trace element concentrations and their ratios (e.g., U/Yb, U/Nb, Nb/Yb) provide key insights into the tectonic-magmatic setting. These data also indicate the presence or absence of pressure-sensitive minerals during melt fractionation or in the residuum, such as plagioclase (Eu/Eu*), rutile (Nb/Ta), amphibole (Yb/Gd), and garnet (Dy/Yb), which are considered as proxies for crustal thickness, as well as magma oxidation state (e.g., Ce/Ce*, Ce/Y) (Bell and Kirkpatrick, 2021; Grimes et al., 2015; Tang et al., 2024, 2019; Zhong et al., 2019). In addition, Ti concentrations in zircon provide crystallization temperature estimates that complement the pressure and redox constraints inferred from other trace element proxies (Harrison et al., 2007; Watson and Harrison, 2005).

All analysed zircons show characteristics of igneous zircons in the rare earth diagram, such as enrichment in HREE accompanied by depletion in LREE, and positive and negative anomalies in Ce and Eu, respectively (Fig. 5.7A). Zircons from the San Lucas and Portachuela batholiths and Late Miocene intrusives fall mostly in the continental domain fields defined by Grimes et al. (2015). In contrast, zircons from the Catamayo batholith plot between the continental and oceanic domains, while those from the Gonzanama batholith fall entirely within the oceanic domain (Fig. 5.7B).

These zircons possess U/Yb values between 0.08 and 3.2 (Fig. 5.7C), with those from the San Lucas, Portachuela, Catamayo batholiths and Late Miocene intrusives between lower and upper crustal values (0.13 and 1.35, respectively; Rudnick and Gao, 2003), and only zircons from the Gonzanama batholith with values below 0.1 suggesting a depleted mantle source (Grimes et al., 2007, 2015). U/Nb values range from 33 to 546, and in contrast to all groups with arc signatures, only zircons from the Gonzanama batholith show mantle signatures (Fig. 5.7D).

Nb/Ta ratio in zircon, a proxy for source composition, tectonic setting, and melting depth (Drabon et al., 2024; John et al., 2011; Tang et al., 2019), predominantly range from 1 to 4 across all samples. Values indicative of rutile fractionation or its presence in the residual phase (Tang et al., 2019), are observed only in the early phase of the San Lucas batholith (~62 Ma). In contrast, the Gonzanama, Catamayo, and Portachuela batholiths, as well as the Late Miocene intrusives, display Nb/Ta ratios that do not clearly reflect the presence of rutile (Fig. 5.8A). Dy/Yb ratios range from 0.14 to 0.35. These values remain, below the threshold (>0.4) typically associated with garnet fractionation (Fig. 5.8B). However, it has been proposed that amphibole fractionation or its presence in the residue prior to zircon crystallization may result in lower Dy/Yb values, even in association with garnet (Drabon et al., 2024).

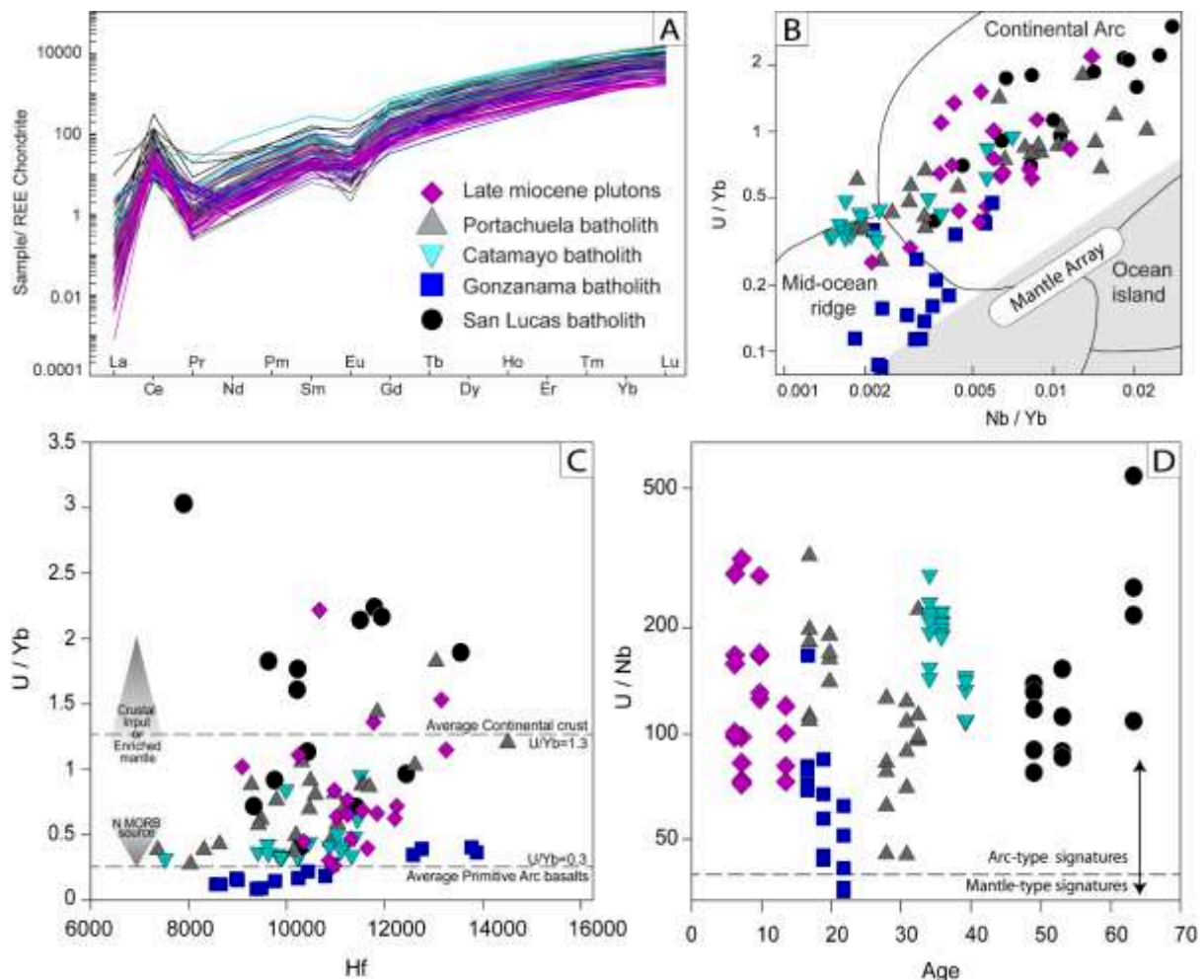


Figure 5.7 Zircon tectonic discrimination diagrams. (A) Chondrite-normalized rare earth element (REE) patterns, normalizing values from Sun & McDonough (1989). (B) U/Yb vs. Nb/Yb tectonic setting discrimination, fields for continental Arc, mid-Ocean ridge, mantle Array, ocean island from Grimes et al. (2015). (C) Crustal input indicators comparing average continental crust (U/Yb = 1.3) and primitive arc basalts (U/Yb = 0.3). (D) U/Nb vs. Age distinguishing arc-type and mantle-type signatures.

Light to heavy rare earth elements ratio (LREE/HREE) ranges from 0.006 to 0.03, with a tightened range toward the Late Miocene intrusives compared to other batholiths. This trend suggests an increasing enrichment of the magmatic reservoirs during this period (Fig. 8C). The Eu/Eu* values vary mainly between 0.1 and 0.7, with the values above 0.4, indicative of oxidizing conditions, appearing in the early phase of the San Lucas batholith (~62 Ma), as well

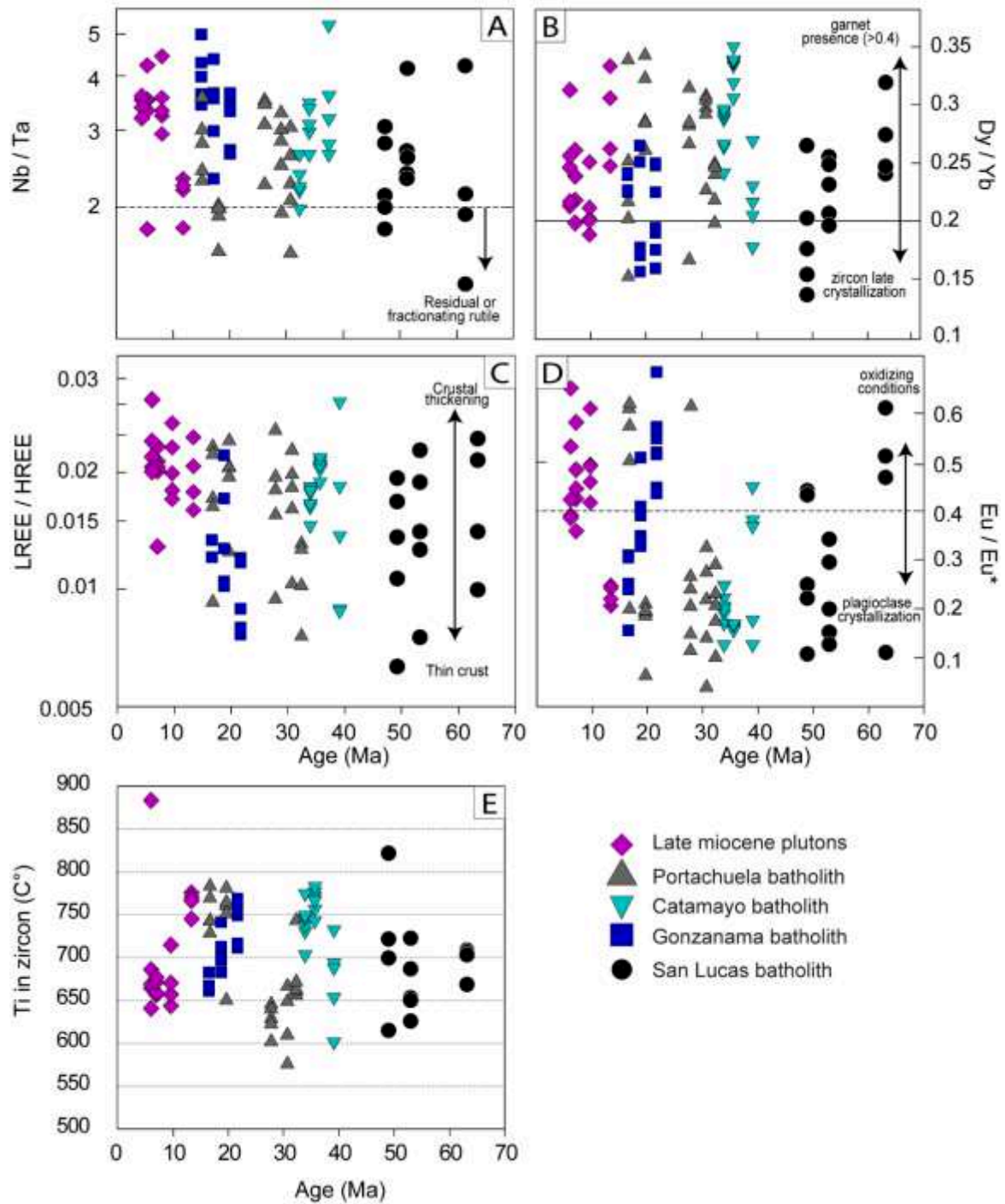


Figure 5.8 Zircon geochemical proxies tracking melt evolution, crustal thickness variations, and magmatic oxidation state through time. (A) Nb/Ta ratio vs. Age (rutile stability indicator). (B) Dy/Yb ratio vs. Age (garnet fractionation proxy for crustal thickness). (C) LREE/HREE ratio vs. Age (melt enrichment/depletion trends). (D) Eu/Eu* anomaly vs. Age (plagioclase and redox indicator). (E) Ti-in-zircon temperature vs. Age.

as from ~20 Ma onward in the Gonzanamá batholith, the youngest intrusion of the Portachuela batholith, and the Late Miocene intrusives, except for one intrusive body located west of the Aradas Fault (Fig. 5.8D).

Moreover, based on the Ti-in-zircon thermometer proposed by Watson and Harrison (2005) assuming an $a_{\text{TiO}_2} > 0.5$, crystallization temperatures range from ~600 °C to 770 °C. The San Lucas batholith records 600–720 °C, Catamayo and Gonzanamá 660–770 °C, and Portachuela 600 at ~30 Ma and 770 °C around 16 Ma. Late Miocene intrusions show a decrease from 770 °C at 13 Ma to 660 °C at <10 Ma (Fig. 5.8E).

5.5 Discussion

5.5.1 Chronology of emplacement

The new zircon U-Pb dating results presented here redefines the temporal and spatial characteristics of magmatism in the SNA. The San Lucas batholith frames the earliest phase of post-accretionary magmatism within the arc. The ages obtained for the San Lucas batholith ($65.35 \pm 0.5 - 48.99 \pm 0.3$ Ma) broaden the previously reported U-Pb age range for this batholith (53.7, 52.1, and 49.87 Ma; George et al., 2021; Guerrero Tamayo, 2020) and are consistent with the previously published K-Ar ages (Hbl, Bt, Plg: 68 to 51 Ma; Aspden et al., 1992; Litherland et al., 1994). Additionally, ages for samples ECU21-40 and ECU21-41 were inferred based on their co-location with dated samples IG24-5 and IG24-6 and their similar whole-rock geochemical signatures. The age range of the Portachuela batholith obtained in this study (32.3 ± 0.3 Ma to 16.72 ± 0.4 Ma) is significantly broader than the previously reported zircon U-Pb ages (14.48–12.43 Ma; Chen et al., 2022b), and extends beyond the earlier K-Ar age range of 24 to 12 Ma (Hbl, Bt, Plg; Aspden et al., 1992). The ages obtained for the Catamayo batholith, which includes El Tingo, La Toma, Palo Blanco, and Catamayo plutons, range from 39.2 ± 0.9 to 32.3 ± 0.3 Ma. These ages differ considerably from previously published K-Ar ages (Hbl, Bt, Whole-rock), which range from 45 to 50 Ma for El Tingo, 57.6 Ma for La Toma, 21.2–26.6 for Palo Blanco, and 57–58 Ma for Catamayo (Aspden et al., 1992; Bristow and Hoffstetter, 1977; Jaillard et al., 1996; Kennerley, 1980; Litherland et al., 1994). Finally, the Gonzanama batholith, dated here for the first time, has ages ranging from 21.6 ± 0.4 to 17.8 ± 0.5 Ma. Furthermore, although the apparent age gap between approximately 50

and 40 Ma could be interpreted as a magmatic hiatus, this interpretation appears unlikely. This reduced magmatic activity during the Eocene–Early Oligocene has also been documented by Schütte et al. (2010). However, detrital zircon records from this interval (George et al., 2021; Witt et al., 2023), though discrete, are consistently present and more likely reflect a decrease in the intensity of magmatic activity rather than a complete cessation (Supplementary Fig. 4). Further work is needed to better constrain the magnitude and spatial extent of this possible magmatic lull.

Schütte et al. (2010) proposed a latitudinal, and likely longitudinal arc migration, between the Oligocene and middle–late Miocene. The late Miocene latitudinal migration is evidenced by progressively younger minimum ages toward the north, from the Portachuela batholith to $\sim 2.5^\circ\text{S}$. The longitudinal migration involved: 1) a Late Oligocene westward frontal arc migration and broadening, attributed to slab stepping or trench retreat; 2) a possibly Mid-Miocene eastward frontal arc migration, leading to arc narrowing; and 3) a late Miocene eastward migration of both the frontal and rear arc, attributed to slab shallowing combined with erosion–subduction processes.

However, the U-Pb ages presented in this study, ranging from 65 to 6 Ma and spanning latitudes between 3° and 5°S and longitudes between 79.2° and 79.6°W , challenge these proposed models of both latitudinal and longitudinal migration. Concerning the arc broadening the new U-Pb ages here presented (ranging ~ 39 – 32 Ma) for the Catamayo batholith ($79^\circ 16'\text{W}$ – $79^\circ 28'\text{W}$), challenge this interpretation. Further evidence against large-scale (50 km) migration comes from the San Lucas batholith ($79^\circ 20'\text{W}$ – $79^\circ 8'\text{W}$), emplaced during the Paleocene–Eocene, indicating that the arc was inherently wider than proposed.

Although our data substantially refine the chronological framework of the SNA continental arc, the current constraints on its spatial extent, magmatic tempo, and compositional variations are still insufficient to support robust geodynamic interpretations of its evolution, especially because large areas of the Eastern cordillera, believed to have been affected by Cenozoic magmatism (Eguez et al., 2017), remain unexplored.

5.5.2 Petrogenesis

The magmatic pulse at 53 Ma from the San Lucas batholith, along with the 32–31 Ma pulses of the Portachuela batholith and several late Miocene intrusions, located east of the Aradas fault, display the most evolved calc-alkaline geochemical signatures in the region. Petrographically, the Late Miocene intrusions are distinguished by granite facies containing K-feldspar, indicating a high degree of magmatic differentiation. In contrast, west of the fault

system, the Gonzanama batholith together with some pulses of the Catamayo batholith (dated between 36 and 32 Ma), represent the least differentiated pulses. These are characterized by tholeiitic to transitional cal-alkaline signatures and exhibit the most mafic compositions in the region. Their geochemical signatures suggest a mantle-derived origin with minimal crustal assimilation.

Zircon $\epsilon\text{Hf}_{(t)}$ and $\delta^{18}\text{O}$ isotopic compositions provide robust constraints on magma sources, enabling discrimination between mantle and crustal contributions. These isotopic systems, when integrated, shed light on magma evolution, crustal recycling, and help delineate the tectonic environment of magmatic activity. During the early magmatic phase, the San Lucas batholith exhibits intermediate enriched $\epsilon\text{Hf}_{(t)}$ values from -5.4 to +5.4 at 65–63 Ma, and slightly enriched from +6.5 to +4.3 at 54–49 Ma (Fig. 9A shows the spatial distribution of $\epsilon\text{Hf}_{(t)}$ values). This trend is accompanied by inherited zircons and peak supracrustal $\delta^{18}\text{O}$ values reaching up to 12‰ between 65 and 63 Ma, followed by mantle-like $\delta^{18}\text{O}$ values ranging from 5 to 6.5‰ and the absence of inherited zircons around 50 Ma. This shift indicates a transition from a predominantly enriched magmatic source to a less enriched magmatic source that was initially modified by crustal assimilation. The early stage likely reflects interaction with a thickened continental crust formed during the main Late Cretaceous accretion event (George et al., 2021; Witt et al., 2023). In the later stage, the system evolved toward a dominantly mantle-derived magmatic source possibly influenced by sediment subduction, a process already documented in southwestern Ecuador (Witt and Bourgois, 2010).

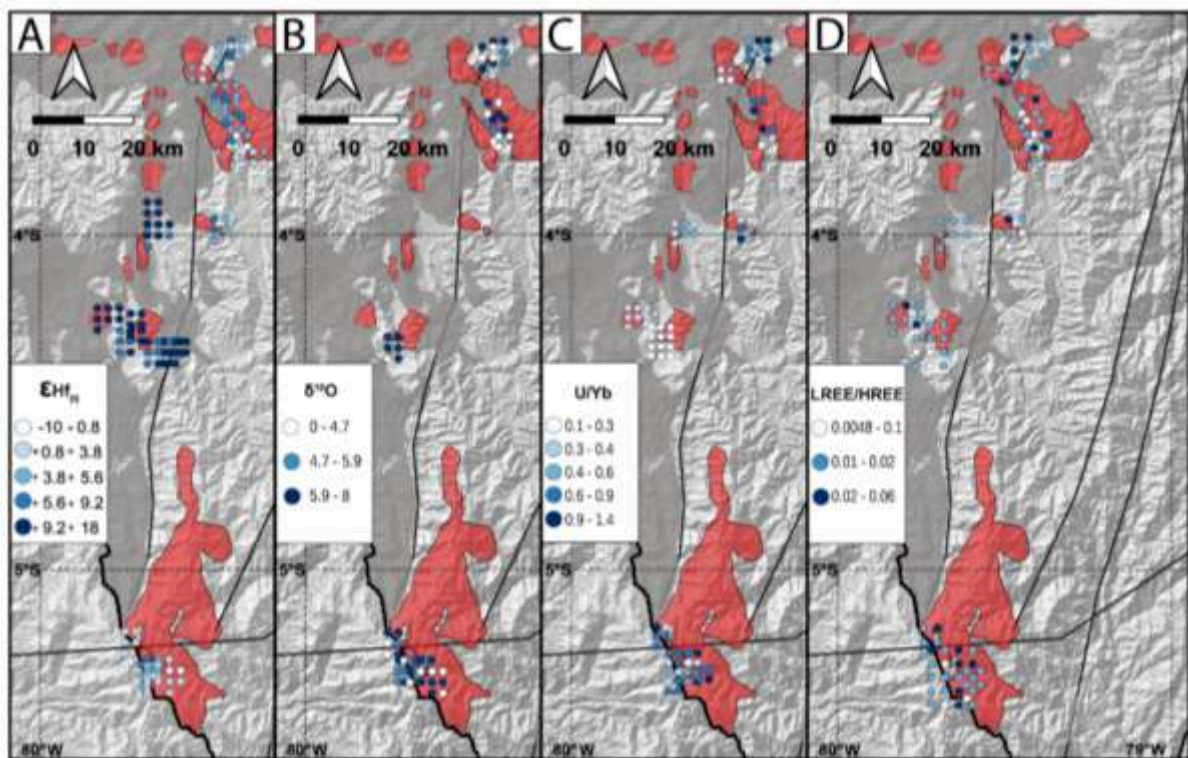


Figure 5.9 Spatial distribution maps of zircon geochemical proxies: (A) ϵHf_t (crustal vs. mantle sources), (B) $\delta^{18}\text{O}$, (C) U/Yb, (D) LREE/HREE.

The Portachuela batholith also shows enriched to mildly enriched ϵHf_t values (−1.3 to +6.7), with a gradual decrease in enrichment toward 20 Ma. This trend parallels a shift from slightly supracrustal to mantle $\delta^{18}\text{O}$ values (from ~7 to 3.5‰), suggesting mantle-derived magmas with diminishing crustal interaction. Similarly, the Late Miocene intrusions display moderately enriched ϵHf_t values coupled with a wide range of $\delta^{18}\text{O}$ values, mostly mantle-like but including some slightly supracrustal (>6‰) and others below 5‰. These lower $\delta^{18}\text{O}$ values likely reflect interaction with hydrothermally altered rocks influenced by meteoric water (Bindeman, 2008), and overall point to a mantle source with limited crustal contamination.

East of the Las Aradas Fault, the Catamayo batholith exhibits slightly enriched ϵHf_t values around 39 Ma, similar to those observed in the more differentiated stage of the San Lucas batholith. In contrast, more juvenile ϵHf_t signatures occur between 36 and 30 Ma, west of the fault. Also, the Gonzanama batholith, located west of the fault, display juvenile to near mantle-depleted ϵHf_t values along with mantle-like $\delta^{18}\text{O}$ signatures, indicating a predominantly mantle-derived source. This signature most likely reflects magma interaction with lithologies of oceanic affinity, which are recognized in several tectonic settings within the Ecuadorian arc. For instance, the Triassic Peltetec ophiolites, represent oceanic lithosphere formed in a back-arc extensional environment (Villares et al., 2021). Similarly, the Raspas

Complex in southwestern Ecuador, part of the Amotapes Massif, comprises MORB-derived eclogites, seamount-type blueschists, and peridotites metamorphosed at high pressure around 130 Ma, and is interpreted as an exhumed oceanic lithosphere (John et al., 2010; Riel et al., 2013).

Oceanic lithologies are also identified in the back-arc Celica–Lacones Basin, formed by trench-parallel extension during the Early Cretaceous, resulting in a rifted arc environment (Jaillard et al., 1999; Riel et al., 2014). The eastern domain of the basin, the Celica arc, consists of calc-alkaline to tholeiitic volcanic and plutonic rocks (Jaillard et al., 1996; L. S. Winter, 2008), while the western domain features deep-marine sedimentation and bimodal volcanism, including tholeiitic basalts and rhyolites indicating high heat-flow and crustal thinning (L. S. Winter, 2008).

Furthermore, very recent works suggest that by the middle Cretaceous (~110 Ma), the arc migrated westward from the current Sub-Andean zone to the western flank of the SNA, probably due to slab rollback, which coincided with the formation of the Celica-Lancones Basin (Sandoval-Espinel et al., 2026). Although our isotopic data confirm magma interaction with an oceanic basement, they do not conclusively identify which juvenile domain was involved.

In addition to isotopic evidence, zircon trace element concentrations further constrain magmatic differentiation processes, melting depth, redox state, and crystallization temperatures. Nb and Ta fractionation in zircon, is influenced by their similar ionic radius and charge with Zr (Foley et al., 2002). Zircon typically crystallizes in the late stages of magmatic evolution from evolved melts, which often exhibit low Nb/Ta ratios due to the presence of rutile in the residue or by its earlier fractionation (Müntener et al., 2018; Tang et al., 2019). The predominantly high Nb/Ta ratios (>2 ; Fig. 8A) recorded in most batholiths suggest melting conditions with negligible or absent rutile involvement, either as a fractionating or residual phase. This signature is consistent with mildly to shallow, mantle-dominated crustal sources or prior rutile depletion. In contrast, the lowest Nb/Ta values restricted to the early San Lucas phase point to deeper melting conditions with enhanced crustal influence, as independently supported by the ϵHf_t and $\delta^{18}\text{O}$ isotopic signatures.

It is worth noting, however, that amphibole fractionation may also contribute to low Nb/Ta ratios in continental crustal settings, due to its preferential incorporation of Nb over Ta ($D_{\text{Nb}}/D_{\text{Ta}} > 1$; Chen et al., 2021; Li et al., 2017), and its presence is further supported by low Dy/Yb ratios (0.14–0.35). These Dy/Yb values lie below the threshold typically associated with garnet fractionation (>0.4 ; Fig. 5.8B), suggesting zircon crystallization out of the garnet

stability field, consistent with amphibole-rich residual assemblages or fractionation at mid-crustal depths (Davidson et al., 2007).

In contrast to the broad LREE/HREE ratios observed in most batholiths, the narrower range in the Late Miocene intrusions suggests progressive melt homogenization and slight increasing source enrichment. Eu/Eu^* values greater than 0.4, typically indicative of suppressed plagioclase crystallization, possibly due to crustal thickening or elevated magma oxidation states (Drabon et al., 2024; Grimes et al., 2015; Sundell et al., 2022; Tang et al., 2024), characterize the early phase of the San Lucas batholith, as well as one sample from the Gonzanamá batholith, the youngest intrusion of the Portachuela batholith, and several Late Miocene intrusions. Among these possibilities, elevated oxidation is the most likely driver, as Chen et al. (2022b) reported oxidation conditions and associated mineralizing cycles around 11 Ma in the Río Blanco porphyry, emplaced within the Peruvian prolongation of the Portachuela batholith (Fig. 5.1). This timing aligns with the occurrence of Eu/Eu^* values above 0.4, particularly in the Late Miocene intrusions. These observations highlight the potential of Eu/Eu^* as a tool for improving exploration targeting in the region. In contrast, lower Eu/Eu^* values in the late phases of the San Lucas, Catamayo, and Portachuela batholiths, plus one Late Miocene intrusion, point to lower oxidation, consistent with zircon crystallization within the plagioclase stability field.

The highest Ti-in-zircon crystallization temperatures, around 750 °C, are recorded in the Gonzanamá batholith, in the pulses of the Catamayo batholith west of the Aradas Fault, in the youngest phase of the Portachuela batholith, and in the 13 Ma Late Miocene intrusion west of the same fault. These elevated temperatures are roughly consistent with hotter magmas derived from mantle-derived magmatic sources.

Overall, the integration of isotopic and trace element data reveals a primarily spatial, rather than purely temporal, pattern in magmatic evolution. Magmatism across the region is broadly mantle-derived, with the crust playing a subordinate to negligible role in its generation. Intrusions emplaced east of the Aradas Fault reflect mildly to shallow crustal levels with a modest but recognizable crustal contribution. In contrast, those west of the fault show higher crystallization temperatures, more juvenile isotopic signatures, and trace element patterns consistent with mantle-derived sources and limited crustal assimilation.

5.5.3. Crustal thickness estimates

Whole-rock Sr/Y and $\text{La}_\text{N}/\text{Yb}_\text{N}$ ratios provide first-order estimates of crustal thickness (Sundell et al., 2021). East of the Aradas fault, the earliest San Lucas pulse (65-60 Ma), the 39 Ma Catamayo pulse, and several Late Miocene intrusions (10-6 Ma) yield the highest Sr/Y and $\text{La}_\text{N}/\text{Yb}_\text{N}$ ratios (Fig. 5.5), indicating average crustal thickness of ~60 km, as estimated following the method of Sundell et al. (2021). Two Late Miocene intrusions show high La/Yb ratios coupled with low Sr/Y values, negative Eu anomalies, and elevated Rb/Sr ratios, signature consistent with extensive plagioclase fractionation. This process selectively removes Sr and Eu from the melt, while exerting minimal influence on heavy rare earth elements and Y (Moyen, 2009). In contrast, the late phase of the San Lucas batholith (53-49 Ma) to its west, together with the Gonzanama batholith, the Catamayo batholith pulse (36-32 Ma) and the late Miocene intrusion at 13 Ma, located west of the Las Aradas fault, show on average crustal thicknesses of 30 km.

These crustal thickness estimates are also corroborated by zircon geochemistry. In the Catamayo batholith, the contrast in crustal thickness between the 39 Ma and 36–32 Ma pulses is mirrored by variations in zircon trace element signatures. High U/Yb values east of the Aradas Fault indicate a continental arc setting underlain by thick crust, whereas lower U/Yb values to the west reflect more mantle-like compositions, consistent with magmatism in an oceanic ridge environment within a thinner crustal domain (Fig. 5.7).

Despite the east–west contrast observed in the San Lucas batholith, where the early southeastern pulse reflects a thickened crust and the later northwestern pulse a thinned one, the high zircon U/Yb ratios typical of continental arc (Fig. 5.7), together with moderately enriched $\epsilon\text{Hf}_\text{t}$ values (Fig. 5.6) throughout the batholith point to a magmatic source predominantly mantle-derived, with varying but overall limited degrees of crustal interaction. This reinforces the notion of a strong spatial control on magma composition in the SNA, rather than a purely temporal evolution.

These estimates contrast with crustal thickness values derived exclusively from zircon Eu/Eu^* ratios from detrital zircons thought to be sourced from the SNA, which suggested thicknesses of 70–55 km for the 45–65 Ma interval and 61–48 km for the 10–20 Ma interval (Witt et al., 2023). However, these earlier interpretations were based on the limited geochemical constraints available at the time. Subsequent studies (Roberts et al., 2024; Tang et al., 2024) have shown that the Eu/Eu^* proxy is strongly influenced by redox conditions,

pressure, and magmatic water content, complicating its use for tracking variations in crustal thickness.

5.5.4 Tectonic and geodynamic implications

The geochronological, geochemical, and isotopic data presented in this study provide new insights into the tectonic architecture and geodynamic evolution of the SNA. The magmatic record from ~65 to 6 Ma spans significant crustal and mantle processes, reflecting both regional-scale convergence dynamics and local crustal architecture.

Following the main Late Cretaceous accretion (~72 Ma; Jaillard, 2022; Witt et al., 2023), a local accretion event likely occurred in southwestern Ecuador during the Paleocene, resulting in the re-establishment of the trench and in crustal thickening to approximately 55–70 km, like the thickening observed during the main accretion (Aizprua et al., 2019; George et al., 2021; Jaillard, 2022; Witt et al., 2019).

As previously discussed in Section 5.3, whole-rock and zircon geochemical proxies suggest that the early southeastern phase of the San Lucas batholith (65–63 Ma) was emplaced into a thickened crust (~60 km), while the later northwestern phase (54–49 Ma) reflects magma ascent through a thinner crust (~30 km). Although this evidence is sparse, largely due to the absence of other coeval intrusions, it can still be integrated with the spatial geochemical variability. Together, these observations suggest that the San Lucas magmatism records a transition from crustal thickening to crustal relaxation or foundering, possibly driven by gravitational collapse (e.g., Garzione et al., 2017) or by emplacement into a pre-thinned marginal domain, such as the one during the Late Cretaceous related to the opening of the Celica–Lancones basin.

Despite this temporal and along-strike variability in crustal thickness, the moderately to strongly enriched zircon $\epsilon\text{Hf}_{(t)}$ and $\delta^{18}\text{O}$ signatures observed throughout the San Lucas batholith, along with mid-enriched isotopic signatures in the detrital zircon record (60–55 Ma) and in situ at 54 Ma (George et al., 2021; Witt et al., 2023), point to a predominantly mantle-derived source variably enriched by crustal inputs throughout its 65–49 Ma evolution.

Zircon geochemistry and isotopic data from the Catamayo batholith reveal juvenile signatures best explained by the spatial influence of the underlying basement on magma composition. Specifically, $\epsilon\text{Hf}_{(t)}$ variations reflect magma interaction with oceanic basement rocks west of the Aradas Fault and more evolved continental basement to the east (Fig. 9).

Although the emplacement of the Catamayo batholith (39–32 Ma) coincides with a period likely linked to limited extension driven by slab rollback (George et al., 2021; Witt et al., 2023), our results suggest that this tectonic interpretation should be reconsidered in light of the basement control documented here.

The emplacement of the Portachuela (~32–16 Ma) and Gonzanama (~21–17 Ma) batholiths falls within the magmatic flare-up interval defined by Schütte et al. (2010) for the Late Oligocene to Early Miocene. These authors attributed the flare-up to increased convergence rates and reduced obliquity between the Farallon/Nazca and South American plates, which they linked to a high flux of mantle-derived magmatism. However, Maloney et al. (2013), show that convergence velocities, absolute overriding plate velocities, and subducting slab ages display no clear relationship with the timing of magmatic events. High-flux magmatic events are commonly associated with transient shifts toward more evolved isotopic signatures (pull-downs), although such transitions are not diagnostic of flare-ups alone (Ducea, 2001; Barton, 2007; DeCelles et al., 2009). Notably, no such abrupt isotopic shifts are observed in any of the batholiths examined in this study.

The Gonzanamá batholith, located west of the Aradas Fault, exhibits juvenile zircon $\epsilon\text{Hf}_{(t)}$ and $\delta^{18}\text{O}$ values suggestive of emplacement within a ~30 km-thick oceanic basement derived from the Celica–Lancones Basin (or, less likely, the Raspas complex or Peltetec ophiolites). In contrast, the Portachuela batholith, located east of the Aradas fault, shows isotopic signatures of medium-enriched mantle reservoirs (Supplementary Fig. 4). The absence of inherited zircons combined with limited $\delta^{18}\text{O}$ enrichment suggests minimal continental crustal input. Instead, the isotopic compositions are more consistent with sediment subduction, a process well documented in southwestern Ecuador (Witt and Bourgois, 2010). This interpretation aligns with the detrital zircon record from this 30–10 Ma interval presented by Witt et al. (2023), which also shows mantle-like $\delta^{18}\text{O}$ values and intermediate $\epsilon\text{Hf}_{(t)}$ signatures indicative of a partially enriched mantle source (Supplementary Fig. 4). Although the presented data do not rule out the occurrence of a magmatic flare-up during this interval, they emphasize that the isotopic signatures indicate a stronger spatial control linked to basement composition rather than a purely temporal or flare-up-driven pattern.

Late Miocene intrusions (13–6 Ma) exhibit high Sr/Y, La_N/Yb_N (adakitic), Dy/Yb ratios, coupled with zircon $\epsilon\text{Hf}_{(t)}$ and $\delta^{18}\text{O}$ enriched compositions and crustal-thickness estimates of 50–75 km. Their isotopic continuity with older magmas rules out a new slab source (Fig. 6); instead, high-pressure fractionation during crustal thickening is favoured. Chen et al. (2022a, 2022b) also reported similar increases in Sr/Y, La_N/Yb_N , and Dy/Yb ratios, along with enriched

isotopic compositions from ~12 Ma onward in the porphyritic rocks of Río Blanco, hosted by the Portachuela Batholith. They classified these as "continental adakites" following the criteria of Moyen (2009) and linked their origin to enhanced compressional stress and crustal thickening driven by the flat subduction of the Inca oceanic plateau (Beate et al., 2001; Chiaradia et al., 2004; Michalak et al., 2016). These rocks are interpreted to have formed in garnet–amphibole stability fields during Miocene compression. Furthermore, Maloney et al. (2013) propose that plateau uplift and initiation of thin-skinned fold-and-thrust belts around 11 Ma in the SNA were driven by trench-normal convergence rates exceeding 4 cm/yr, together with a decrease in the age of the subducting Nazca plate, conditions that would have favoured crustal thickening and higher elevations along the Andes. A comparable scenario is observed north of Ecuador, where the ~14 Ma transition from intermediate crustal thickness to a thicker crust was likely driven by the arrival of the young, buoyant Nazca plate at the South American margin, promoting a shallowing of the subduction angle, increased compressional stresses, and the melting of evolved oceanic crust (Iglesias et al., 2025).

Regardless of whether the Inca Plateau hypothesis or the compression hypothesis holds true, our results confirm both the isotopic enrichment and the shift toward adakitic signatures. This pattern aligns with the Late Miocene convergence dynamics proposed by Jaillard (2025), who associates this period with a compressional continuum marked by near-orthogonal Farallón/Nazca–South America convergence, stronger interplate coupling, and widespread upper-plate shortening in the SNA. Such conditions would have promoted deep magma storage, garnet stability, and rapid surface uplift, processes supported by the high exhumation rates reported by Eude et al. (2015), Hungerbühler et al. (2002), and Wipf (2006). Notably, from ~10 Ma onward, sedimentary records in basins south of the equator document a shift from marine–tidal–estuarine to fully continental depositional environments (Hungerbühler et al., 2002; Steinmann et al., 1999).

5.6 Conclusions

This study refines the temporal, geochemical, and isotopic framework of magmatism in the SNA from ~65 to 6 Ma, revealing that its evolution is primarily governed by spatial variations in crustal architecture rather than by large-scale arc migration or purely temporal trends (Fig. 9). Zircon U-Pb dating expands and defines the emplacement history of the San Lucas, Catamayo, Portachuela, Gonzanamá batholiths, as well as minor Late Miocene intrusions.

Integrated zircon $\epsilon\text{Hf}_{(t)}$ – $\delta^{18}\text{O}$ isotopic data, coupled with whole-rock and trace-element geochemistry, indicate that magmatism across the SNA was broadly mantle-derived, with variable but generally limited crustal assimilation. Contrasts in isotopic signatures across the Las Aradas Fault reflect emplacement into distinct crustal domains: more evolved continental crust to the east, and thinner, juvenile oceanic basement to the west.

The San Lucas batholith records a first magmatic pulse between 65 and 63 Ma, characterized by enriched $\epsilon\text{Hf}_{(t)}$ and $\delta^{18}\text{O}$ values and adakitic signatures, indicating a mantle-derived magma significantly modified by a thick continental crust (~60–70 km). A later pulse (54–49 Ma) shows evidence of emplacement through thinner crust (~30 km). Despite these differences, zircon isotopic data and detrital records suggest a long-lived, moderately enriched mantle reservoir variably influenced by crustal assimilation in the earlier phase and possibly sediment subduction in the later phase.

The Catamayo and Gonzanamá intrusives (~36–17 Ma), emplaced west of the Aradas Fault, display juvenile $\epsilon\text{Hf}_{(t)}$ and mantle-like $\delta^{18}\text{O}$ signatures, consistent with limited crustal input and intrusion into a thin, oceanic-type basement. In contrast, contemporaneous magmatism east of the fault (e.g., Catamayo 39 Ma pulse) reflects a thicker, continental margin (>60 km), emphasizing the role of the Aradas Fault as a long-lived lithospheric boundary controlling magma–crust interaction.

Isotopic signatures of the Portachuela batholith (~32–16 Ma) suggest an enriched mantle source, possibly due to sediment subduction, rather than melting of continental crust, as indicated by low $\delta^{18}\text{O}$ enrichment and the absence of inherited zircons.

Late Miocene intrusions exhibit geochemical and isotopic characteristics that point to high-pressure fractionation during a pronounced thickening of the crust. Magmatism reflects a compressional tectonic regime that favored deep magma storage, garnet-amphibole stability, and rapid uplift. These processes are consistent with regional exhumation patterns and sedimentary changes after ~10 Ma, marking a significant phase of crustal growth and topographic uplift in the SNA.

Overall, the magmatic record of the SNA reflects a dynamic interplay between mantle input, inherited basement heterogeneity, and variations in crustal thickness, offering refined constraints on the tectonomagmatic evolution of the northern Andean margin. These results challenge earlier interpretations of large-scale arc migration and underscore the importance of integrating slab-scale geodynamics with the influence of pre-existing crustal architecture when reconstructing Andean magmatic histories

CHAPTER 6: General Conclusions and Perspectives

This research has addressed the chronology, geochemistry, and geodynamic implications of Cenozoic magmatism in the Ecuadorian Andes, with particular emphasis on the role of crustal architecture and its relationship with arc evolution in the context of ongoing subduction. Through a multidisciplinary approach integrating zircon U–Pb geochronology, whole-rock geochemistry, and zircon trace element and Hf–O isotopic analyses, the timing and nature of magmatism were characterized in northern, central, and southern Ecuador. The results presented here reveal that the temporal and compositional evolution of the arc reflects the interplay between mantle inputs, crustal architecture, and records the influence of both internal parameters of the arc, such as progressive crustal thickening, and external parameters, such as variations in subduction geometry. This final chapter synthesizes the main findings from this study, integrates them into a broader regional framework, and outlines perspectives for future research.

6.1 Geochronology: Refining the temporal framework of the Ecuadorian Cenozoic arc

Zircon U–Pb dating carried out in this thesis provides one of the most robust chronologic frameworks to date for the Ecuadorian Cenozoic arc. The results reveal a protracted magmatic evolution spanning from the Paleocene (~65 Ma) to at least the Late Miocene (~6 Ma). The new results refine the timing, duration, and spatial extent of magmatism across northern and central Western Cordillera (Chapters 3 and 4, respectively) and southern Ecuador (Chapter 5). The spatial distribution of U–Pb ages highlights recurrent magmatic activity, with the southern domain preserving the oldest intrusions (~65–50 Ma) and younger magmatic events recorded across all three segments since at least ~41 Ma.

Historically, the chronologic framework of the Ecuadorian Cenozoic arc has relied primarily on K–Ar ages from hornblende, biotite, and whole-rock. One of the most significant contributions to this framework resulted from the collaborative program between the British Geological Survey (BGS) and the Geological and Mining Research and Development Corporation (CODIGEM), which produced datasets of mainly K–Ar, Sm–Nd, Rb–Sr ages from rocks of the Western and Eastern Cordilleras (e.g., Aspden et al., 1992; Boland et al., 2000; McCourt et al., 1997). Although K–Ar datasets are often carefully screened to exclude disturbed ages, K–Ar chronometers remain susceptible to isotopic resetting through processes

such as hydrothermal alteration or excess argon retention, which can deviate it from true crystallization ages (Kelley, 2002). While K–Ar ages provide a valuable first-order proxy for regional magmatic trends and, in some cases overlapping with zircon U–Pb ages, their precision decreases significantly when used to resolve local-scale interpretations (Schütte, 2009a). Consequently, the U–Pb dataset presented here therefore represents a more robust and reliable record for assessing local magmatic histories and spatial correlations along the arc.

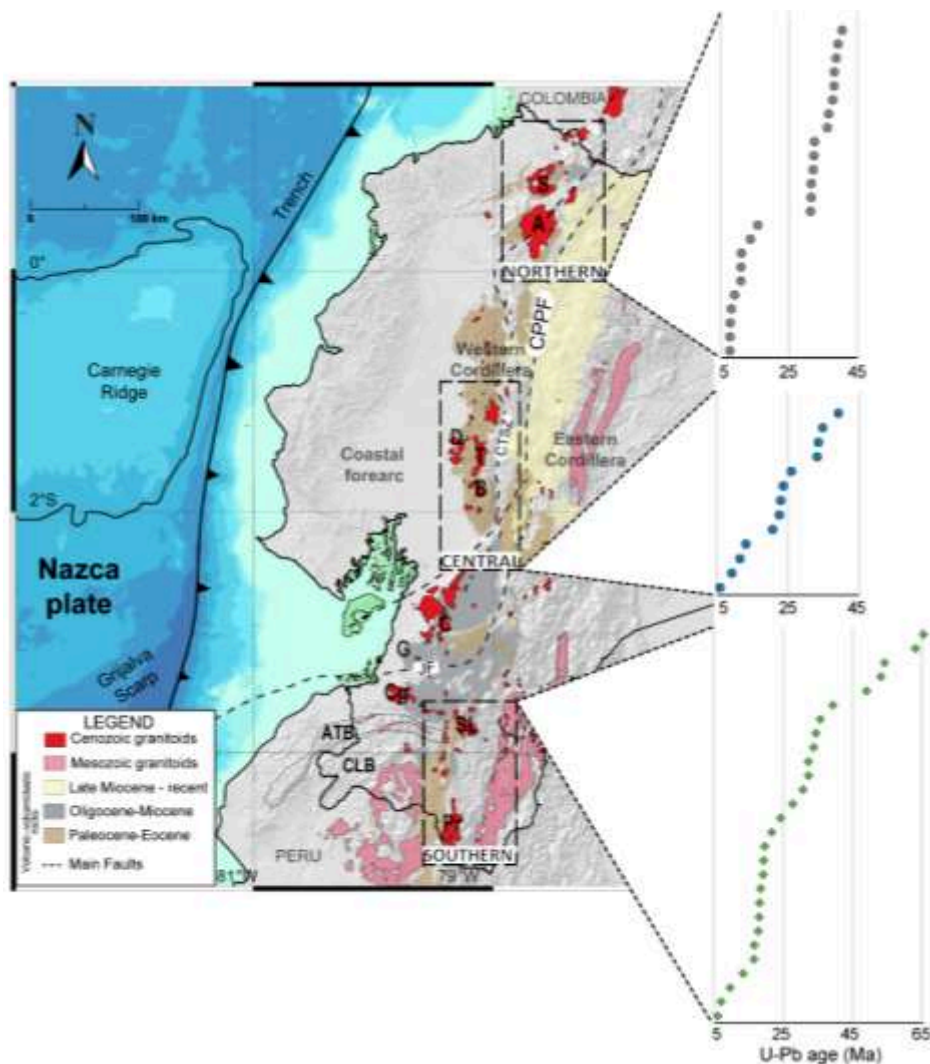


Figure 6.1 Geodynamic sketch of Ecuador showing the distribution of zircon U–Pb ages for Cenozoic granitoids along the northern, central, and southern segments of the magmatic arc. CPPF–Calacali-Pujili-Pallatanga Fault; CTSZ–Chimbo Toachi Shear zone; JF–Jubones Fault.

In the southern Ecuadorian Andes, magmatism initiated as early as the Paleocene, with the emplacement of the San Lucas batholith between 65 and 49 Ma. This intrusion ranks among the earliest magmatic bodies emplaced in the aftermath of oceanic terrane accretion. Although no equivalent intrusions have been defined in the WC, the detrital record of the central

Ecuadorian forearc reveals significant magmatic activity, significantly more juvenile than that of the San Lucas batholith, around 60 Ma (Witt et al., in prep.)

Subsequently, the magmatic record documents nearly continuous pulses of activity along the entire arc between ~41 and 6 Ma. In the northern segment, two main periods of magmatism are identified: one between 41–31 Ma and another between 16–7 Ma. The apparent ~15 Ma gap between them is bridged by detrital and in situ zircon evidence at 23 Ma from northern Ecuador and adjacent southern Colombia (Fig. 6.1; Fig. 4.6; Botello et al., 2024; Echeverri et al., 2015; Margirier et al., 2023; Pepper et al., 2016). This evidence implying possibly that arc magmatism did not cease, but continued, albeit at reduced intensity or exposure, into the Late Miocene, consistent with temporal patterns observed across the other arc segments.

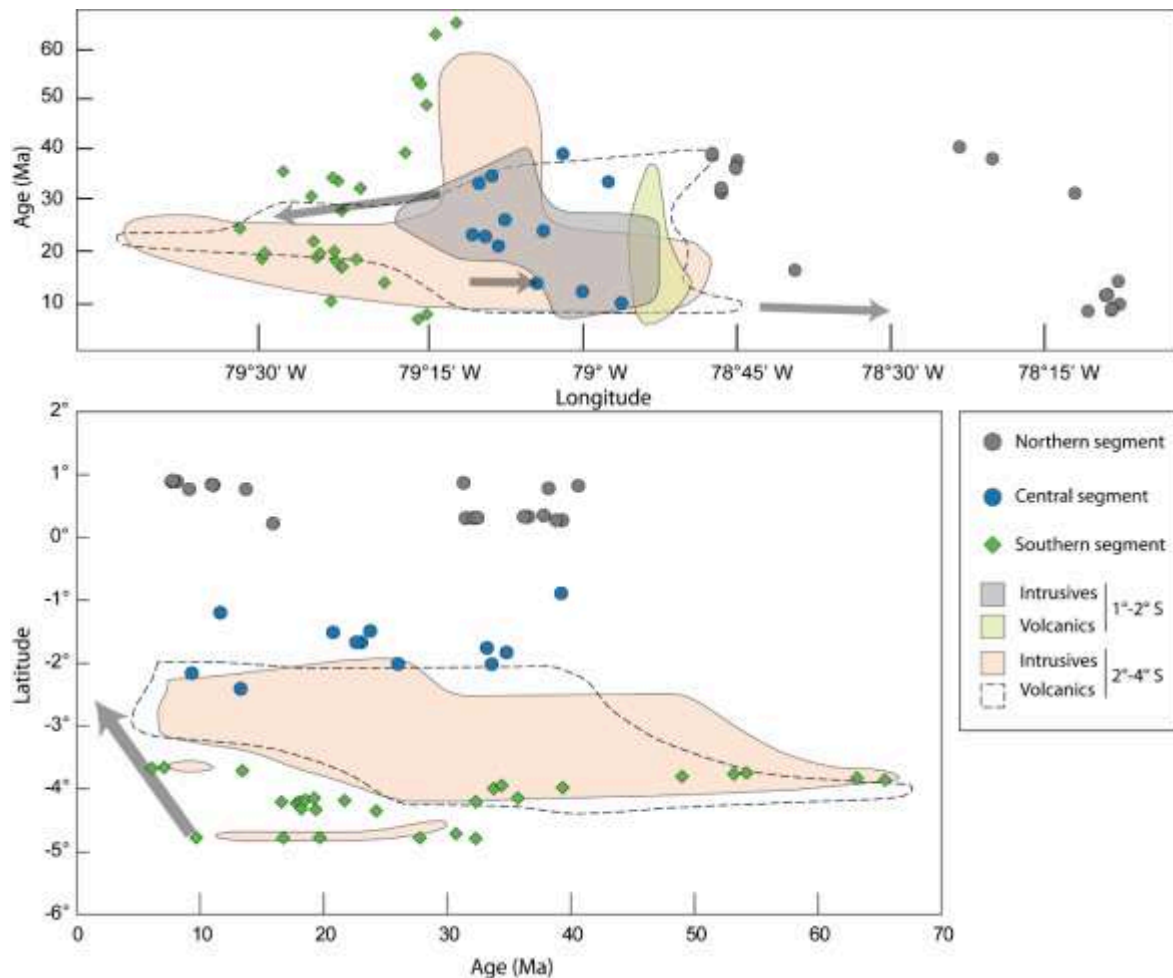


Figure 6.2 Latitude (top) and longitude (bottom) versus age (Ma) for the northern, central, and southern segments, showing the data from this study. Fields defined by Schütte et al. (2010) and references therein are shown for volcanic rocks (dashed lines) and intrusive bodies (shaded areas). Gray arrows indicate possible arc migration processes according to Schütte et al. (2010).

George et al. (2021) reconstructed the regional positions of the Ecuadorian arc (Fig. 1.6), migrating east–west, from the Jurassic to the present, using a geochronological compilation largely based on K–Ar ages. As previously discussed, K–Ar chronometers may not always record true crystallization ages, especially at local scales. Moreover, the data presented in this study do not fit well within the spatial positions proposed by their model. In contrast, the results of this work indicate that, in each segment, the arc remained within approximately the same longitudinal range between ~40 and 10 Ma, suggesting a more stationary magmatic front during this interval. Similarly, Schütte et al. (2010) proposed both latitudinal and longitudinal arc migrations between the Oligocene and the middle–late Miocene. The latitudinal migration in the central–southern segment was inferred from progressively younger ages northward from the Portachuela batholith to approximately ~2.5°S. Meanwhile the longitudinal migration involved: (1) a Late Oligocene westward frontal-arc migration and broadening in the central–southern segment, (2) a possible Mid-Miocene eastward frontal-arc migration causing arc narrowing, and (3) a Late Miocene eastward shift of both the frontal and rear arcs (Fig. 6.2).

However, the new ages presented here, extending to at least 6 Ma between 3° and 5°S, challenge the proposed latitudinal migration. Likewise, ages of ~39–32 Ma at 79°16′–79°28′W indicate that the arc was already established in its present position (Fig. 6.2), contradicting the idea of a Late Oligocene westward broadening. Additional evidence from the Paleocene–Eocene San Lucas batholith at 79°15′–79°12′W further suggests that the arc was inherently wider than previously inferred (Fig. 6.2).

Overall, the spatial–temporal distribution defined in this study outlines a long-lived, near-continuous magmatic record along the Ecuadorian arc, challenging previously proposed migration models that were established based on the data available at the time. Instead, they highlight the need for denser and more spatially integrated chronological constraints to conclusively test and refine such regional reconstructions. Although, the chronological framework established here represents a significant advance, yet a more definitive reconstruction will require higher-resolution sampling and a more complete temporal dataset.

Within this broader temporal framework, each arc segment (North: Chapter 3; Central: Chapter 4; and South: Chapter 5) preserves distinct magmatic intervals that reflect local tectono-magmatic controls and the evolving dynamics of the Andean margin.

6.2 Petrogenesis: Insights from geochemistry and zircon isotopes

Geochemical and isotopic data provide critical insights into the petrogenetic processes that governed the evolution of the Ecuadorian Cenozoic arc. Combined zircon $\epsilon\text{Hf}(t)$ – $\delta^{18}\text{O}$ systematics, whole-rock geochemistry, and zircon trace-element data reveal a geochemically continuous magmatic system dominated by mantle-derived melts that evolved under variable crustal architectures, yet overall sourced from a homogeneous mantle reservoir.

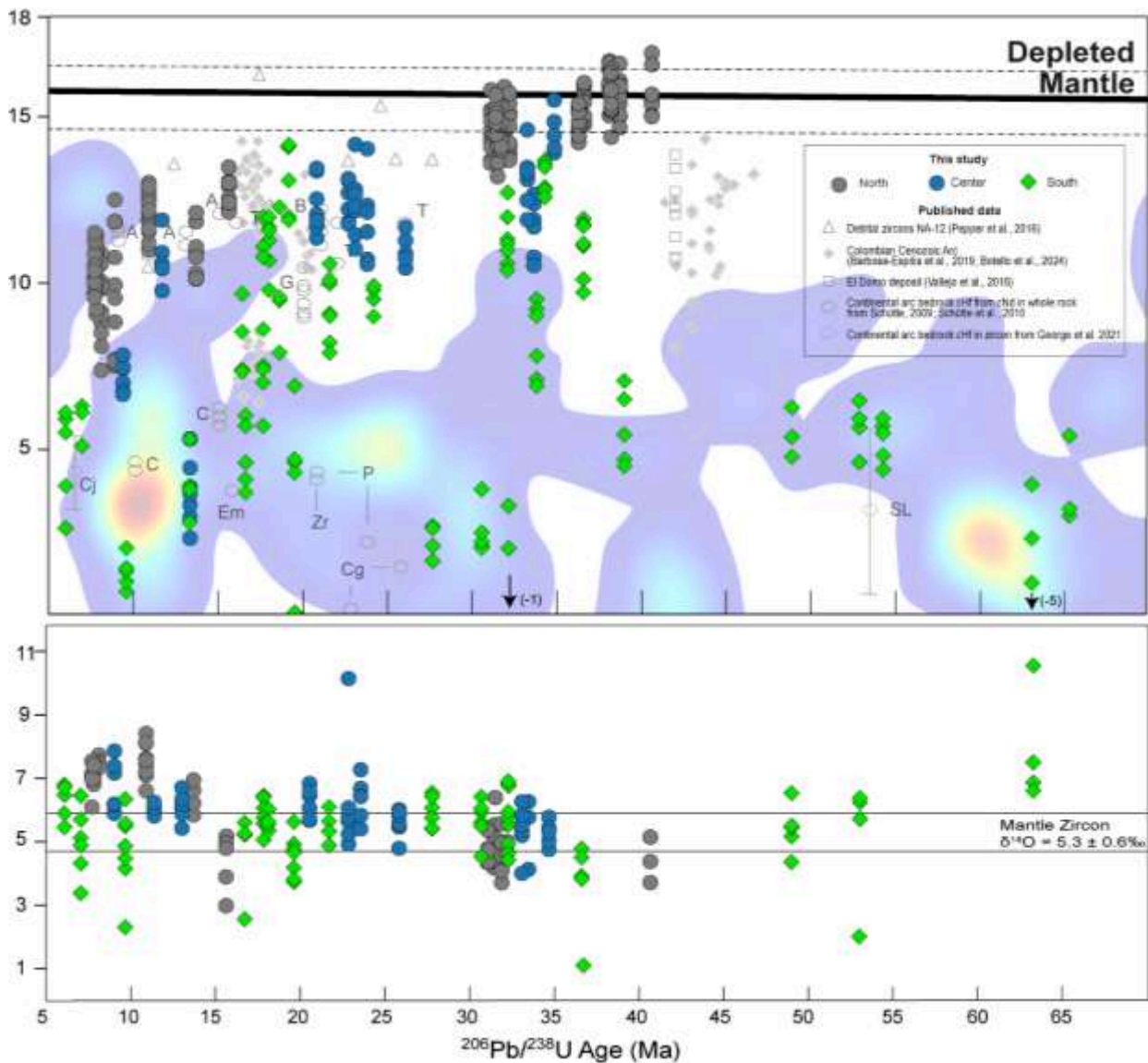


Figure 6.3 Zircon Hf and O isotopic composition versus U–Pb age for Cenozoic Ecuadorian arc granitoids. The heat map and 95% contour (method after Sundell et al., 2019) represent a kernel density estimate (KDE) of detrital zircon analyses from George et al. (2019) and Witt et al. (2023), providing a regional isotopic reference. Granitoid nomenclature as follows: A–Apuela, B–Balzapamba, C–Chaucha, T–Telimbela, G–Gaby, Cj–Cojitambo, Zr–Zaruma, P–Portachuela, Em–El mozo, Cg–Cangrejos, Sl–San Lucas.

6.2.1 Early Cenozoic magmatism: 65–45 Ma

The southern segment records the earliest phase of Cenozoic magmatism, represented by the San Lucas Batholith emplaced between 65 and 49 Ma. The early stage of this intrusion (65 Ma; Fig. 6.3) shows $\epsilon\text{Hf}_{(t)}$ values ranging from -5 to $+3$ and $\delta^{18}\text{O}$ values between 6 and 11 ‰, indicative of a mantle-derived magmatic source enriched by crustal assimilation. These features reflect interaction with a thickened continental crust resulting from the main Late Cretaceous accretion event (George et al., 2021; Witt et al., 2023). In addition, localized increases in magmatic enrichment ratios (U/Yb, LREE/HREE) in this early phase point to enhanced reservoir fertility.

In contrast, the late phase of the San Lucas Batholith records a narrower isotopic range, with $\epsilon\text{Hf}_{(t)} = +4.3$ to $+6.5$ and $\delta^{18}\text{O} = 4\text{--}6$ ‰, suggesting a mantle-derived source still enriched but less than the earlier magmatic stage of San Lucas Batholith, possibly linked to tectonic attenuation following the main accretionary event. No coeval (65–45 Ma) in-situ intrusions have been identified in the Western Cordillera (i.e., northern, and central segments); however, the detrital record from the central Ecuadorian forearc indicates significant, more juvenile magmatic activity around 60 Ma (Witt et al., in prep.), possibly related to a Paleocene arc.

6.2.2 Magmatic configuration of the Western Cordillera and southern segment: 45–15 Ma

Following this early phase, in the western Cordillera (northern and central segments), magmatism records a progressive transition from strongly juvenile to more enriched compositions through time. The northernmost magmas display the most juvenile isotopic signatures of the entire the Cenozoic arc, with depleted mantle-like $\epsilon\text{Hf}_{(t)}$ values between $+17$ and $+12$ and $\delta^{18}\text{O}$ values of $\sim 6\text{--}3$ ‰. Similarly, central Ecuadorian intrusions show predominantly juvenile isotopic signatures ($\epsilon\text{Hf}_{(t)} +15.6$ to $+9.9$; $\delta^{18}\text{O}$ 5.2–6.0 ‰). Whole-rock Sr–Nd–Pb isotopic compositions of granitoids in the north-central part of the arc (e.g. Apuela, Balsapamba and Telimbela) also point to derivation from mantle-derived magmas interacting with an oceanic basement (Schütte, 2009). This interpretation is further supported by calculated $\epsilon\text{Hf}_{(t)}$ values of approximately $+10$ to $+12$ (Fig. 6.3), derived from the quantitative relationship between ϵNd and ϵHf defined by Vervoort et al. (1999) through the so-called “terrestrial array” ($\epsilon\text{Hf}_{(t)} = 1.36 \times \epsilon\text{Nd} + 2.95$), which allows ϵNd values to be expressed in terms of ϵHf .

Prior to ~ 14 Ma, some magmas in both the northern and central segments already display slightly enriched $\epsilon\text{Hf}_{(t)}$ values while retaining mantle-like $\delta^{18}\text{O}$ ratios, suggesting

derivation from a predominantly depleted mantle source that was variably modified, possibly by interaction with a more enriched crustal component.

Toward the southern segment, isotopic compositions become more variable, and exhibits the strongest isotopic contrasts, largely structured by the Las Aradas Fault. East of the fault, intrusions record mantle enriched signatures $\epsilon\text{Hf}_{(t)} = +5$ to $+1$ and $\delta^{18}\text{O}$ up to $11\text{--}12\text{‰}$, indicative of depleted-mantle sources variably modified by sediment input. West of the fault, magmas display juvenile $\epsilon\text{Hf}_{(t)}$ values of $+14$ to $+10$ and mantle-like $\delta^{18}\text{O}$ values $= 5.3\text{--}5.8\text{‰}$, comparable to the depleted-mantle compositions of the north–central segment. These signatures are consistent with magmas emplaced into a thin, juvenile crust of oceanic affinity.

Comparable zircon Hf–O signatures have been reported for Cretaceous magmatism in southern Ecuador and northern Peru (Sandoval-Espinel et al., 2026), interpreted as reflecting an oceanic-type basement, such as that linked to the opening of the Celica–Lancones basin, possibly coeval with slab rollback (Jaillard et al., 1999; Riel et al., 2014, Sandoval-Espinel et al., 2026). Furthermore, a Late Cretaceous intrusion in this region shows Sr–Nd–Pb compositions akin to those of accreted oceanic plateau crust farther north (Schütte, 2009). Additionally, different oceanic-type basements are also recognized within the Ecuadorian arc, including the Triassic Peltetec ophiolites formed in a back-arc extensional setting (Villares et al., 2021), MORB-derived oceanic lithosphere of the Raspas Complex (John et al., 2010; Riel et al., 2013).

6.2.3 Isotopic enrichment and crustal thickening: <15 Ma

From ~ 14 Ma onwards, the northern and central segments record clearly enriched isotopic compositions ($\epsilon\text{Hf}_{(t)} +11$ to $+2$; $\delta^{18}\text{O}$ $6\text{--}8\text{‰}$), indicating the growing influence of an enriched mantle source. Slightly supra-crustal $\delta^{18}\text{O}$ values documented during the Late Miocene in the north–central segment likely reflects limited sediment assimilation associated with the arrival of the young, buoyant Nazca Plate, or melting of an enriched oceanic crustal source. $\delta^{18}\text{O}$ data display only a modest but clearly marked enrichment, with maximum values around 7‰ (Fig. 6.3), consistent with a very limited incorporation of supracrustal material. Isotopic modelling for Andean magmatic systems (e.g., Jones et al., 2015) indicates that sediment inputs exceeding $\sim 5\%$ are typically required to raise $\delta^{18}\text{O}$ values above 8‰ . As this threshold is not reached in the present dataset, the results support minimal sediment input during magma evolution. This interpretation supports the stability and isotopic homogeneity of the underlying mantle wedge, like the Central Andes, where isotopic variations are attributed primarily to crustal interaction rather than other geodynamic elements such as subduction

erosion (Mamani et al., 2010). The homogeneous mantle composition with minor sedimentary enrichment is also consistent with the isotopic signatures in the Eocene Macuchi arc and Quaternary volcanism in Ecuador (Chiaradia, 2009; Chiaradia et al., 2009).

Similarly, 14–7 Ma magmatism in the northern segment yields progressive increases in whole-rock Sr/Y, La/Yb ratios, and zircon LREE/HREE and U/Yb. This evolution reflects magmatic differentiation at progressively greater depths under thickened crust, within the garnet stability field, and minor assimilation of subducted sediments or enriched oceanic lithosphere. These processes triggered the emergence of adakite-like signatures at ~14 Ma, best explained by crustal thickening associated with the arrival of the buoyant Nazca Plate, prior to Carnegie Ridge subduction (5–6 Ma; Hernández et al., 2020), and possibly increase the compressional tectonic regime.

Likewise, in the central segment, Miocene intrusions show increasingly enriched isotopic signatures, reduced amphibole control, and garnet stability in between 20 and 11 Ma, showing adakite-like compositions. These results highlight the primary control exerted by the oceanic-type basement and a secondary, but significant, influence of crustal thickening on magma evolution, as also stated by Schütte (2009a), who proposed that variations in isotopic compositions of Late Tertiary magmas in northern–central Ecuador likely reflect assimilation of specific crustal lithologies, modulated by changes in crustal thickness. Evidence presented here, suggest that the shift toward enriched sources and deeper differentiation under mid- to thick-crust conditions around 14 Ma occurs earlier than in previous regional models, which place this transition closer to 9 Ma (Chiaradia et al., 2004), emphasizing the need for a denser chronological record to fully resolve the time of these transitions along the arc.

In the north–central segment, the mantle-like ϵHf_t – $\delta^{18}\text{O}$ signatures and the absence of inherited zircons or inherited zircon cores in the analysed intrusions (45–7 Ma) argue against crustal reworking or assimilation of continental material. These observations indicate that no major continental terranes underlie the accreted oceanic crust of the Western Cordillera, supporting a dominantly oceanic basement architecture consistent with a subduction jam–type accretion of these terranes, as proposed by Jaillard et al. (2000, 2009). This interpretation contrasts with, although it does not invalidate, obduction-based models (e.g., Vallejo et al., 2009, 2019), which invoke underthrusting of the continental margin beneath oceanic crustal blocks.

Additionally, to the Hf–O isotopic evidence, zircon trace-elements patterns in the northern and central segments, also indicate progressive enrichment of magmatic reservoirs through time, as shown by increasing U/Yb and LREE/HREE ratios. These trends reflect

magmatic evolution at mid crustal levels dominated, toward deeper magmatic evolution in thickened crustal conditions. Proxies sensitive to pressure, such as Eu/Eu^* , Nb/Ta , Dy/Yb , and Yb/Gd (Bell and Kirkpatrick, 2021; Claiborne et al., 2010; Drabon et al., 2024; Tang et al., 2019), suggest a temporal shift from amphibole-dominated fractionation at shallow to mid-crustal levels toward deeper differentiation regimes, occasionally within the garnet stability field. The evolution of these parameters implies a gradual deepening of magma generation and storage zones associated with crustal thickening and the transition to a more compressional tectonic regime.

In the southern segment, Late Miocene intrusions (13–6 Ma) show enriched $\epsilon\text{Hf}_{(t)}$ (+1 to +6) and $\delta^{18}\text{O}$ (4–7‰) values, consistent with more evolved sources and crustal thickening. Furthermore, ratios indicative of magmatic enrichment (U/Yb , LREE/HREE) reveal also increases in reservoir fertility toward the Late Miocene intrusions, suggesting deeper melting conditions with enhanced crustal influence. Meanwhile, pressure-sensitive proxies (e.g., Nb/Ta , Dy/Yb) display broad variability, pointing to differentiation under amphibole-bearing assemblages with limited garnet or rutile stability, yet with transient periods of elevated oxidation or suppressed plagioclase crystallization. Together, these trace-element trends delineate a southward increase in magmatic complexity, where differentiation depth, oxidation state, and complex crustal architecture jointly modulated magma evolution.

Despite zircon trace-elements provide valuable insights into magmatic processes, including melt evolution, source characteristics, and crystallization conditions, they must be interpreted with caution, as their behaviour can be influenced by multiple, interdependent factors. This interpretative ambiguity is particularly evident in Eu/Eu^* , as it is affected by a variety of factors, including redox conditions, plagioclase stability, water content (e.g., Tang et al., 2024; Yakymchuk et al., 2023).

Enriched $\epsilon\text{Hf}_{(t)}$ values (+2.8–+5.3) observed in the southern segment at 13 Ma, interpreted as reflecting interaction with a continental-type basement, overlap with some enriched $\epsilon\text{Hf}_{(t)}$ values (+2.3–+4.5) of the same age from the central segment of the arc located south of the CTSZ fault (Fig. 6.1, 6.2). These complex isotopic signatures reveal the presence of continental crust at depth, delineating a transitional basement composition between the CTSZ and Jubones faults. This transitional domain contrast with the oceanic-type crust characteristic of the northern domain (Fig. 6.1) and consistent with the crustal configuration proposed by Witt et al. (2024). In contrast, Schütte (2009) proposed that the main basement boundary is located farther south, around 3°S, approximately along the Jubones Fault, north of the Cangrejos–Zaruma intrusive belt (Fig. 6.1). This interpretation based on whole-rock Sr–

Nd–Pb isotopic compositions, suggest that intrusions near 3°S (e.g., Gaby) display isotopic signatures comparable to those of the northern arc, whereas the Cangrejos–Zaruma belt exhibits isotopic ratios indicative of interaction between mantle-derived magmas and a more evolved, continental-type basement. However, additional data between 2°–3°S, are required to better constrain the crustal architecture and its influence on isotopic variability.

George et al. (2021) reported a homogenization of $\epsilon\text{Hf}_{(t)}$ values to +6–+12 after ~10 Ma, possibly attributed to the removal of subcontinental lithospheric mantle, this work documents a broader range (+1 to +11) for the whole arc, challenging this interpretation and instead indicating instead that isotopic evolution within each segment was primarily controlled by the nature of the underlying basement and secondarily by crustal thickness variations associated with changes in subduction geometry.

Collectively, these data indicate that petrogenesis in the Ecuadorian Cenozoic arc was governed by the interplay between juvenile mantle inputs, inherited basement composition, and crustal thickening.

6.3 The role of crustal thickness in magmatic differentiation

One of the central contributions of this thesis is to demonstrate that crustal thickness exerted a first-order control on magma differentiation, while isotopic compositions of Cenozoic magmas in Ecuador primarily reflect source characteristics established early in the magmatic system at depth. Crustal thickness estimates derived from both whole-rock (Sr/Y , $\text{La}_\text{N}/\text{Yb}_\text{N}$) and supported by zircon-based pressure-sensitive proxies (e.g., Nb/Ta , Yb/Gd) reveal significant spatial and temporal variations along the arc.

However, caution is required when interpreting whole-rock crustal thickness estimates (Sr/Y , La/Yb) due to their sensitivity to source characteristics (Macpherson et al., 2006; Moyen, 2009; Richards and Kerrich, 2007). These complexities can be mitigated by integrating multiple, independent lines of evidence, including mineral-scale geochemistry (e.g., zircon), whereas isotopic compositions may record variations in the source material that melted, potentially linked to changes in tectonic regime and crustal architecture.

In the Northern and Central segments, these values define a transition from moderately thickened crust of ~30–35 km during the Eocene–Oligocene to ~50–60 km, reflecting progressive crustal thickening at ~14 Ma coeval with the possibly contractional framework triggered by the arrival of the more buoyant Nazca plate, and inferred for the central segment at a similar time or sometime between ~20 and ~11 Ma. This progressive crustal thickening coincided with a transition from magmatic differentiation dominated by amphibole in the

northern segment and plagioclase $\pm$ amphibole in the central segment to conditions favouring the stabilization of amphibole $\pm$ garnet at higher pressures in both.

In contrast, the southern segment exhibits more heterogeneous crustal and magmatic conditions, largely divided by the Las Aradas fault. To the east, in the continental domain, the earliest San Lucas pulse (65–60 Ma), the 39 Ma Catamayo pulse, and several Late Miocene intrusions (10–6 Ma) yield high Sr/Y and $\text{La}_\text{N}/\text{Yb}_\text{N}$ ratios consistent with average crustal thicknesses of ~60 km and zircon signatures consistent with garnet stability and deep magmatic differentiation. Conversely, the late phase of the San Lucas batholith (53–49 Ma), and to the west of the Las Aradas fault, in the oceanic domain, the Gonzanamá batholith, the younger Catamayo pulse (36–32 Ma), and a 13 Ma intrusion generally exhibit low Sr/Y and $\text{La}_\text{N}/\text{Yb}_\text{N}$ ratios, recording crustal thicknesses of approximately ~30 km. Along with zircon Nb/Ta and Yb/Gd ratios and negative Eu anomalies, these data point instead to plagioclase-dominated fractionation at shallower levels. The coexistence of both regimes highlights the strong spatial control of crustal architecture on magma evolution, rather than a purely temporal variation.

In general, at intermediate crustal thickness, magmatism throughout the arc was characterized by typical calc-alkaline compositions dominated by plagioclase $\pm$ amphibole fractionation. However, crustal thickening possibly linked to compression associated with variations in subduction geometry, favoured magmatic differentiation toward deeper regimes where garnet became stable, giving rise to more enriched, adakite-like signatures. Whole-rock ($\text{La}_\text{N}/\text{Yb}_\text{N}$, Sr/Y) and zircon proxies (Dy/Yb, Yb/Gd) consistently record this deepening of differentiation levels through time.

Overall, these estimates are in good agreement with present-day crustal thicknesses constrained by geophysical models (Koch et al., 2021), suggesting that geochemical barometers provide a reliable first-order approximation of crustal architecture. This compatibility highlights their utility as an effective initial proxy for reconstructing the tectono-magmatic evolution of any give arc.

Chiaradia et al. (2004) documented the onset of adakite-like signatures predominantly in the northern and central segments at around 9 Ma, where differentiation under garnet-stable conditions has been well established (e.g., Schütte, 2009). Nevertheless, the results presented here indicate that such transitions did not occur synchronously along the Ecuadorian arc. Instead, adakite-like magmatism developed at different times, appearing earlier than previously proposed, at ~14 Ma in the northern segment and possibly at a similar time in the central segment. In contrast, magmas from the southern segment have generally been characterized by Schütte (2009) by plagioclase-dominated fractionation, suggesting evolution under

comparatively thinner crustal conditions. However, the results of this work reveal that toward the southern segment, adakite-like signatures emerge after ~9 Ma.

The onset of adakite-like magmatism in the southern segment coincides with a long-lived compressional regime linked to nearly constant convergence direction since ~25 Ma (Jaillard, 2025). Consistently, Chen et al. (2022) also reported adakitic signatures in the south, in intrusions hosted by the Portachuela Batholith from ~12 Ma onward. These authors linked the adakite-like signatures to high-pressure fractionation during crustal thickening driven by the flat subduction of the Inca oceanic plateau. Furthermore, Maloney et al. (2013) proposed that uplift and the initiation of thin-skinned fold-and-thrust belts around 11 Ma in the southern Northern Andes were driven by trench-normal convergence rates combined with the subduction of progressively younger Nazca lithosphere. Although the results of this study do not allow to rule out any of the models, confirm both the isotopic enrichment and the shift toward adakitic signatures.

These conditions favoured significant surface uplift, as evidenced by the high exhumation rates documented by Hungerbühler et al. (2002), and Wipf (2006). Notably, from ~10 Ma onward, widespread crustal shortening led to regional Andean uplift of up to ~3000 m and the development of thickened crustal domains (Hungerbühler et al., 2002). This uplift is recorded in the sedimentary successions of southern Ecuador basins, which show a marked transition from marine–tidal–estuarine to fully continental depositional environments, reflecting the progressive isolation of these basins as surface uplift and compression intensified (Hungerbühler et al., 2002; Steinmann et al., 1999).

Although granitoids younger than ~9 Ma in this study are scarce and spatially discontinuous, their isotopic continuity with older intrusions suggests that deep-level differentiation persisted during the waning stages of Miocene compression and uplift. Additional geochronological and geochemical data from younger intrusions will be essential to further constrain the timing and extent of this crustal thickening and uplift episode.

These findings support a dynamic model in which the Ecuadorian Cenozoic arc alternated between periods of moderate crustal thickness and phases of pronounced thickening. In the southern segment, evidence indicates that the crust was already relatively thick (~60 km) by ~60 Ma, possibly reflecting crustal thickening acquired following the main accretionary event (George et al., 2021; Witt et al., 2023). The later Miocene thickening episodes across all three segments promoted magma differentiation at greater depths, resulting in compositional enrichment and the emergence of adakite-like signatures.

6.4 Regional connections: the Northern Andes

When considered at the scale of the Northern Andes, the Ecuadorian Cenozoic arc is part of a continuous magmatic belt extending from southern Colombia to northern Peru.

In southwestern Colombia, magmatic activity dated at ~65 Ma and ~39 Ma reveal the development of a moderately mature continental arc emplaced over accreted oceanic plateau crust (Barbosa-Espitia et al., 2019; Kerr et al., 2002; McCourt et al., 1984). These magmas display mixed isotopic signatures, combining juvenile $\epsilon\text{Hf}_{(t)}$ values with enriched Sr–Nd isotopes, reflecting assimilation of both sedimentary and mafic lower-crustal components (Barbosa-Espitia et al., 2019). Similarly, zircon Hf–O data from northern Ecuador reveal the interplay of more juvenile mantle-derived inputs with either subducted sediments or enriched oceanic lithosphere, underscoring a shared tectono-magmatic evolution across the northern segment of the arc that responded to similar geodynamic triggers, likely involving shifts in subduction geometry (this study, Botello et al., 2024). The occurrence of the most juvenile isotopic signatures, with $\epsilon\text{Hf}_{(t)}$ values approaching and even matching those of depleted mantle (Fig. 6.3), suggests that northern Ecuador possibly may have maintained a more direct connection with the mantle, possibly facilitated by the change in orientation of the Western Cordillera axis from N–S in Ecuador to NNE in Colombia.

Across the northern segment, the magmatic record suggests a quasi-continuous arc activity despite the apparent gap in exposure between ~30 and 20 Ma. The absence of large Oligocene–Miocene plutonic outcrops within the Colombian Andes has been attributed to factors related to uplift and erosional level (Barbosa-Espitia et al., 2019). Nevertheless, latest Oligocene to Early Miocene magmatism is well recorded by plutons in southwestern Colombia dated between ~24–21 Ma (Leal Mejía, 2011; Leal-Mejía et al., 2019), consistent with zircon U–Pb ages of ~23.8 Ma reported farther north (Echeverri et al., 2015), as well as with in situ zircon ages of ~23 Ma and detrital zircon populations ranging from 31 to 16 Ma in northern Ecuador (Margirier et al., 2023; Pepper et al., 2016). Collectively, these datasets point to a temporally and spatially continuous magmatic system connecting southern Colombia and northern Ecuador, suggesting either a quasi-continuous magmatic activity throughout this interval or, alternatively, a temporary reduction in the intensity of arc construction rather than a complete magmatic hiatus during 30 to 20 Ma. Moreover, the absence of pre-Paleogene zircons in southwestern Colombia further supports a shared evolution over an oceanic or transitional crustal substrate, reinforcing the interpretation of a continuous magmatic domain between both regions (Barbosa-Espitia et al., 2019).

Geophysical data from southwestern Colombia also indicate present-day crustal thicknesses exceeding 50 km (Poveda et al., 2015), consistent with current models for the Ecuadorian volcanic arc (Koch et al., 2021) and with the estimates presented here for the northern segment of the Ecuadorian Cenozoic arc. This concordance supports the interpretation of a contiguous, thickened crustal domain extending across the Ecuador–Colombia transition, with similar implications for magma differentiation and depth of emplacement.

Botello et al. (2024) further suggest that plutons in southwestern Colombia record assimilation of continental crustal fragments, likely derived from reworked portions of the South American plate within the lower–middle crust as expressed in the southern segment and south of the central segment. In contrast, the results presented here for northern Ecuador show mantellic to slightly supracontinental $\delta^{18}\text{O}$ zircon values and absence of inherited zircons, ruling out significant assimilation of continental crust. This difference may reflect variations in crustal composition along strike, with the Colombian segment incorporating continental components absent, or at least not recorded, in the northern and central segments of Ecuador, thereby highlighting the spatial and depth extent of the underlying oceanic or at least not recorded, in the northern and central segments of Ecuador, thereby highlighting the spatial and depth extent of the underlying oceanic basement.

In the northern segment of the arc, a reduction in geochemical enrichment and crustal thickness trends around 9 Ma is recorded in both whole-rock and zircon proxies, suggesting changes in magmatic reservoir conditions. Whether this reflects a sustained source depletion or a brief attenuation within a longer enrichment trend remains uncertain, as younger magmatic records are not available in this dataset. Meanwhile, in Colombia, the subsequent steepening of the Nazca slab to its present $\sim 35^\circ$ angle after ~ 6 Ma, following an earlier phase of slab shallowing associated with Nazca plate subduction, as also discussed in this work, marked the onset of alkaline magmatism in the foreland and eastern Central Cordillera (Echeverri et al., 2015; Vásquez et al., 2009). This geodynamic reorganization may likewise have influenced magmatic reservoir conditions in the northern Ecuadorian Cenozoic arc, contributing to the compositional changes observed in the northern segment.

As previously suggested (see section 6.2 and 6.3), toward the southern segment of the Ecuadorian Cenozoic arc, isotopic compositions become more variable and display the strongest contrasts, largely structured by the Las Aradas Fault. East of the fault, magmas exhibit enriched mantle-like isotopic signatures in both ϵHf_t and $\delta^{18}\text{O}$, whereas to the west, magmas show distinctly juvenile isotopic values, consistent with emplacement into a thin (30 km), juvenile crust of oceanic affinity. Similar isotopic characteristics are also recognized farther

south in northern Peru (Sandoval-Espinal et al., 2026). This pattern supports the interpretation that isotopic contrast (juvenile vs. enriched signatures) in the southern segment primarily reflects the interaction of magmas derived from an isotopically homogeneous and stable mantle wedge, as proposed for the Central Andes (Mamani et al., 2010), with both oceanic- and continental-type basement domains.

Additionally, Late Miocene magmatism in northern Peru shares remarkable similarities with that of southern Ecuador. Intrusions emplaced between ~9 and 6 Ma in the southern segment of the Ecuadorian Cenozoic arc display adakite-like geochemical signatures and enriched isotopic compositions consistent with differentiation beneath a thickened crust of ~50–75 km, values also proposed for northern Peru (Baby et al., 2025). Their origin may be related either to the flat subduction of the Inca Plateau that arrived at the trench near 5°S around 13 Ma (Beate et al., 2001; Chiaradia et al., 2004; Rosenbaum et al., 2005) or, alternatively, to enhanced trench-normal convergence and the subduction of progressively younger Nazca lithosphere (Maloney et al., 2013), both scenarios favouring crustal thickening.

In either case, the similarity in age, isotopic enrichment, and adakite-like geochemical features between southern Ecuador and northern Peru, where Chen et al. (2022a, 2022b) reported comparable increases in whole-rock Sr/Y, La_N/Yb_N , and Dy/Yb ratios, along with enriched isotopic compositions from ~12 Ma onward in porphyritic intrusions hosted by the Portachuela Batholith, suggests that both regions responded to a comparable Late Miocene geodynamic reorganization driven by crustal thickening and enhanced compressional stress. This interpretation is consistent with the transition to fully continental conditions recorded in sedimentary basins south of the equator (Hungerbühler et al., 2002; Steinmann et al., 1999).

Overall, these regional comparisons reinforce the interpretation of a geodynamical integrated Andean system, where the northern and southern borders of the Ecuadorian arc, toward Colombia and Peru, share a broadly coherent tectono-magmatic evolution throughout the Cenozoic.

6.5 General Conclusion

This thesis demonstrates that the Ecuadorian Cenozoic arc represents a dynamic, yet coherent magmatic system whose evolution reflects the interplay between mantle inputs, crustal architecture, and subduction dynamics, constituting a key natural laboratory for better understanding the evolution of complex subduction systems. Through the integration of zircon U–Pb geochronology, Hf–O isotopes, trace-element geochemistry, and whole-rock data, this work provides a comprehensive dataset for understanding magmatic and crustal evolution in

the Ecuadorian Andes. The multiproxy approach adopted here enables a clear distinction between juvenile and enriched magmatic sources, while simultaneously constraining the pressure conditions and depths of magma differentiation.

The results reveal a protracted magmatic evolution spanning more than 60 million years, from the Paleocene to the Late Miocene, characterized by punctual episodes of crustal thickening and relaxation that modulated contributions from depleted and enriched mantle sources, with only localized input from continental crustal material. Periods of enhanced compression and crustal thickening promoted a transition from shallow–mid-crustal differentiation to deeper levels within the garnet stability field, leading to the generation of adakite-like signatures during the Miocene, particularly at ~14 Ma in the north, inbetween 20 and 11 Ma in the center, and at ~9 Ma in the south. Conversely, lower crustal thicknesses, such as those inferred west of the Las Aradas Fault in the southern segment between 36 and 16 Ma, are interpreted as reflecting intervals of tectonic attenuation, during which magmas differentiated at shallower levels and produced more juvenile geochemical signatures. These temporal variations underscore the sensitivity of magmatic processes to fluctuations in subduction parameters and lithospheric state, reflecting the dynamic interplay between mantle input, inherited basement heterogeneity, and variations in slab geometry and crustal thickness.

Crucially, this study demonstrates that the tectono-magmatic evolution of the Ecuadorian Cenozoic arc cannot be described through a single, homogeneous model. The pronounced contrasts in isotopic composition, basement character, and crustal thickness between the northern, central, and southern domains indicate that the arc evolved as a segment-partitioned system, each domain reflecting distinct lithospheric architectures and tectonic controls. The northern and central segments, underlain by dominantly oceanic-type crust, record more juvenile isotopic compositions, whereas the southern segment exhibits an internally pronounced contrast between oceanic and continental basement domains, the latter characterized by more evolved isotopic signatures, underscoring the strong lithospheric control exerted on magma generation. This spatial variability highlights the primary control exerted by inherited lithospheric structure on magma generation, differentiation, and isotopic diversity along strike, underscoring the need of segment-specific tectono-magmatic models to adequately capture the complexity of the arc's evolution.

Methodologically, this research also illustrates the potential of zircon petrochronology as a powerful tool for studying long-lived magmatic systems. The capacity to obtain U–Pb ages and Hf isotopic compositions simultaneously from single zircon analyses allows for the rapid acquisition of temporal and isotopic datasets, providing broader spatial coverage and analytical

efficiency compared with traditional whole-rock or single-isotope techniques. This integrated approach opens new opportunities for characterizing volcanic arcs at regional scales, bridging temporal and spatial gaps in magmatic records, and refining models of crustal evolution in convergent margins.

6.6 Perspectives and future research

This thesis represents a first attempt to unravel the tectono-magmatic history of the Ecuadorian Cenozoic arc through the integration of zircon petrochronology and whole-rock geochemistry. While the results provide a robust framework for understanding the temporal, geochemical, and isotopic evolution of the arc, several key regions and questions remain unexplored. Addressing these gaps will be critical for advancing a more comprehensive reconstruction of the arc's geodynamic evolution in future studies.

In the northern segment, future work should focus on systematic sampling aimed at filling the ~20-30 Ma gap of this study. Obtaining *in situ* geochronological data for this interval, such as the 23 Ma reported by Margirier et al. (2023), would be essential to determine whether this apparent gap reflects magmatic quiescence or merely the limited preservation and exposure of rocks from that time. Likewise important is the study of younger intrusions (<7 Ma), which remain underexplored. Zircon and whole-rock analyses of these suites would allow to evaluate whether the relaxation of adakitic trends and isotopic enrichment observed in earlier phases followed systematic patterns into the Pliocene and Quaternary.

For the central segment, future research should emphasize broader spatial coverage and finer-scale mapping of transitional domains, particularly across the Chimbo–Toachi shear zone. This region appears to represent a fundamental boundary between juvenile and enriched magmatic sources yet remains poorly sampled. Further analysis of zircon isotopes and trace-elements in this area could clarify the extent to which it acted as a long-lived lithospheric control on magma genesis. Moreover, targeted work in underrepresented plutonic bodies would help to better constrain the distribution of adakitic versus calc-alkaline signatures through space and time.

In the southern segment, as part of the broader research project in which this thesis was developed, a robust dataset has already been acquired from areas not yet fully integrated into this study, such as the Cangrejos–Zaruma belt and adjacent domains. These datasets will be addressed in the near future and are expected to provide key insights into the transitional basement zones identified here, allowing for a more detailed characterization. Similarly, correlating the identified magmatic Cenozoic pulses of the Eastern Cordillera (Eguez et al.,

2017) with the tectono-magmatic history established in this thesis could reveal whether they represent contemporaneous events, thereby refining the spatial limits of arc magmatism.

To further strengthen this framework, future work should integrate low temperature thermochronology to link magmatism with exhumation and uplift histories, complemented by paleoaltimetry reconstructions that would provide direct constraints on surface elevation changes. Together, these approaches would help denudate the timing and magnitude of crustal thickening and tectonic reorganization across the arc. Comparative studies with the Central Andes, such as that of Sandoval-Espinel et al.(2026) in northern Peru, where Mesozoic crustal and tectonic frameworks have been shown to influence the tectono-magmatic characteristics of the southern Ecuadorian Cenozoic arc, could help test whether the temporal and geochemical trends identified in Ecuador represent local responses to plate reconfiguration or are instead part of a broader Andean pattern.

In summary, while this thesis provides a solid framework for the evolution of the Ecuadorian Cenozoic arc, further research is crucial to gain a more comprehensive understanding of how subduction processes and crustal architecture have influenced the long-term tectono-magmatic evolution of the Northern Andes.

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APPENDICES

APPENDIX 1: Supplementary data for Chapter 3

Methodology

For whole-rock geochemical analyses, samples were dried and crushed to 70% passing a 2 mm sieve, followed by pulverizing a representative split to 85% passing 75 μm . Analyses were performed at MSALABS Laboratories (Langley, Canada) following their standard protocols: lithium metaborate/tetraborate fusion at 1000°C ensured complete dissolution of refractory phases, with fused samples cooled and dissolved in mineral acids. Major element oxides were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES; WRA-310 package), while trace and rare-earth elements were analysed by inductively coupled plasma mass spectrometry (ICP-MS; IMS-300). Detection limits are provided in the following tables:

DETECTION RANGE (%; CODE: WRA-310)					
Al₂O₃	0.01 – 100	K₂O	0.01 – 100	SiO₂	0.01 – 100
BaO	0.01 – 100	MgO	0.01 – 100	SrO	0.01 – 100
CaO	0.01 – 100	MnO	0.01 – 100	TiO₂	0.01 – 100
Cr₂O₃	0.01 – 100	Na₂O	0.01 – 100	LOI	0.01 – 100
Fe₂O₃	0.01 – 100	P₂O₅	0.01 – 100		

DETECTION RANGE (PPM; CODE: IMS-300)					
Ba	0.5 – 10,000	Ho	0.01 – 1,000	Ta	0.1 – 2,500
Ce	0.1 – 10,000	La	0.1 – 10,000	Tb	0.01 – 1,000
Cr	10 – 10,000	Lu	0.01 – 1,000	Th	0.05 – 1,000
Cs	0.01 – 10,000	Nb	0.1 – 2,500	Tm	0.01 – 1,000
Dy	0.05 – 1,000	Nd	0.1 – 10,000	U	0.05 – 1,000
Er	0.03 – 1,000	Pr	0.03 – 1,000	V	10 – 10,000
Eu	0.03 – 1,000	Rb	0.2 – 10,000	W	1 – 10,000
Ga	0.2 – 1,000	Sm	0.03 – 1,000	Y	0.5 – 10,000
Gd	0.05 – 1,000	Sn	5 – 10,000	Yb	0.03 – 1,000
Hf	0.2 – 10,000	Sr	0.1 – 10,000	Zr	2 – 10,000

For U-Pb dating, a zircon separation process was carried out at Lille University. The rocks were crushed and sieved to retain only the fraction <250 μm . This fraction was treated using the Wifley table to concentrate the heavy minerals, which then underwent heavy liquid

separation. The resulting fraction was cleaned of magnetic minerals using a Frantz isodynamic (Malusà & Fitzgerald, 2019; and references therein). The zircon grains were handpicked under a binocular microscope, mounted on an adhesive tape, and placed in resin mounts. These mounts were ground and polished with a lap wheel grinder and diamond polishing suspension of 6, 3 and 1 μm . To examine the internal structures and select the zones to be dated, cathodoluminescence (CL) images were obtained using a Reliotron CI system equipped with a digital colour camera. In situ U-Pb dating was carried out by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) on 253 different zircon grains (Table 3). At the Geosciences Montpellier laboratory (University of Montpellier), laser ablation split-stream analyses (simultaneous U-Pb and Lu-Hf analyses on 20 samples) were conducted using a Teledyne G2 excimer laser (193 nm) coupled to a single collector Element XR (ThermoScientific) ICP-MS equipped with a dual pumping system to enhance sensitivity (Edwards 80 m^3/h) for U-Pb dating and to a Neptune+ (ThermoScientific) MC-ICP-MS for Lu-Hf analyses. The analytical conditions are summarized below.

Laser ablation system	
Make, Model & type	Teledyne G2 193nm, Excimer
Ablation cell & volume	Helex 2, 2 volumes, 16 x 16 cm
Laser wavelength	193 nm
Pulse width	< 4 ns
Fluence	5.0 $\text{J}\cdot\text{cm}^{-2}$
Repetition rate	5 Hz
Spot size	50 μm
Sampling mode / pattern	Single spot
Carrier gas	100% He in the cell, N_2 added after the cell, Ar from the ICP-MS sample gas flow before entering the torch.
Background collection	80 secs
Ablation duration	40 secs
Wash-out delay	variable
Cell carrier gas flow	1.05 l/min (He), 7 mL/min (N_2) after the cell
ICP-MS Instrument	
Make, Model & type	Element XR (ThermoScientific) for U-Pb Neptune+ (ThermoScientific) for Lu-Hf
Sample introduction	Via conventional tubing
RF power	1350W
Make-up gas flow	0.6 l/min Ar for the Element XR; 0.8 l/min for the Neptune+

Detection system	Secondary electron multiplier for the Element XR; Faraday cups equipped with $10^{11} \Omega$ resistors for the Neptune+
Masses measured	^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th , ^{238}U for U-Pb; ^{171}Yb , ^{173}Yb , ^{174}Hf , ^{175}Lu , ^{176}Hf , ^{177}Hf , ^{178}Hf , ^{179}Hf for Lu-Hf
Integration time per peak	Variable for U-Pb (5 ms for ^{208}Pb and ^{232}Th , 10 ms for ^{206}Pb and ^{238}U , 45 ms for ^{207}Pb); 1.04 s for Lu-Hf
Total integration time per reading	90 ms for U-Pb; 1.04 s for Lu-Hf
Sensitivity / Efficiency	≥ 2500 cps/ppm Pb ($20\mu\text{m}$, 4 Hz, 5 J/cm ²); ≥ 5 V Hf total ($50\mu\text{m}$, 5 Hz, 5 J/cm ²)
Dead time	20 ns for SEM
Data Processing	
Gas blank	80 second on-peak
Calibration strategy	91500 used as primary reference material, GJ1 used as secondary reference material (quality control) for U-Pb; 91500, GJ1 and Plesovice used as quality control for Lu-Hf
Reference Material info	91500 (Wiedenbeck et al., 1995), GJ1 (Jackson et al., 2004), Plesovice (Slama et al., 2008) for U-Pb ; 91500 (Blichert-Toft, 2008), GJ1 (Morel et al., 2008), Plesovice (Slama et al., 2008)
Data processing package used / Correction for LIEF	GLITTER ® (van Achterbergh et al., 2001)
Mass discrimination	Standard-sample bracketing with $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ normalized to reference material 91500 for U-Pb; Natural $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ (after Patchett et al., 1981) using an exponential law for Hf isotopes and natural $^{173}\text{Yb}/^{171}\text{Yb} = 1.130172$ (after Segal et al., 2003) using an exponential law for Yb and Lu isotopes.
Correction, composition and uncertainty	No common-Pb correction for U-Pb; ^{176}Hf corrected from ^{176}Yb and ^{176}Lu isobaric interferences assuming $\beta_{\text{Lu}} = \beta_{\text{Yb}}$ using the natural $^{173}\text{Yb}/^{171}\text{Yb} = 1.130172$ (after Segal et al., 2003) and an exponential law.
Uncertainty level & propagation	Ages are quoted at 2sigma absolute, propagation is by quadratic addition according to Horstwood et al. (2003). Reproducibility (and age uncertainty) of reference material are propagated.

At the Magmas and Volcans Laboratory, U-Pb dating (4 samples) was conducted with the following conditions:

Laser ablation system	
Make, Model & type	Resonetics/M-50E 193nm, Excimer
Ablation cell & volume	Laurin Cell ® two volumes cell, Laurin Technic Ltd., volume ca. 1-2 cm ³
Laser wavelength	193 nm
Pulse width	< 4 ns
Fluence	2,8 J.cm ⁻²
Repetition rate	3 Hz
Spot size	27 μm
Sampling mode / pattern	Single spot
Carrier gas	100% He, Ar make-up gas and N ₂ combined using the Squid® device from RESolution Instruments.

Background collection	30 secs
Ablation duration	60 secs
Wash-out delay	30 secs
Cell carrier gas flow	0.75 l/min
ICP-MS Instrument	
Make, Model & type	Element XR
Sample introduction	Via conventional tubing
RF power	1350W
Make-up gas flow	0.87 l/min Ar
Detection system	Single collector secondary electron multiplier
Masses measured	204, 206, 207, 208, 232, 238
Integration time per peak	10 ms
Total integration time per reading	130 ms <i>(should represent the time resolution of the data)</i>
Sensitivity / Efficiency	20000 cps/ppm Pb (44µm, 10Hz)
Dead time	35 ns
Data Processing	
Gas blank	30 second on-peak
Calibration strategy	GJ-1 used as primary reference material, 91500 used as secondary reference material (Quality Control)
Reference Material info	91500 (Wiedenbeck et al., 1995) GJ1 (Jackson et al., 2004)
Data processing package used / Correction for LIEF	GLITTER ® (van Achterbergh et al., 2001)
Mass discrimination	Standard-sample bracketing with $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ normalized to reference material GJ-1
Common-Pb correction, composition and uncertainty	No common-Pb correction. Analyses discarded when discordance >10% (reported in Tera & Wasserburg diagrams)
Uncertainty level & propagation	Ages are quoted at 2sigma absolute, propagation is by quadratic addition according to Horstwood et al. (2003). Reproducibility and age uncertainty of reference material are propagated.

To ensure a direct correlation between age and composition, analyses of ϵHf and $\delta^{18}\text{O}$ were accurately collocated with previously dated U-Pb domains. When analytically feasible, measurements were performed within the same ablation spot as the U-Pb analyses, particularly for domains >50 µm. Otherwise, measurements were positioned in adjacent areas of the same chronological zone. This spatial selection protocol, implemented after CL characterization, maintains the temporal fidelity of isotopic signatures.

In situ Lu-Hf isotope analyses were carried following conditions: Laser ablation spot size of 50 µm, fluence 5 J/cm², repetition rate of 5 Hz, and He combined with slight amounts of N₂ as

the gas mixture to carry the ablated particles before they entered the Ar-plasma torch to increase sensitivity. Standard measurements were performed at low mass resolution in 120 cycles of 1s duration, with blanks acquired on-peak during 80s and analytes from the sample during.

Oxygen isotopic compositions were obtained using Cameca IMS1270 with a Cs^+ primary ion beam, whose intensity was 2.5nA and an acceleration of 10kV with a FC/FC detection mode. The 91500-zircon reference material was used to correct the instrumental mass fractionation. The range of $\delta^{18}\text{O}$ values of 91500-zircon goes from 4.41‰ to 6.418‰.

Table 2. U-Pb data (Montpellier)

Sample	No.Zr	Pb*	Th	U	Th/	²⁰⁷ Pb/	±	²⁰⁶ Pb/	±	Rho	²⁰⁷ Pb/	±	Rho	Apparent ages (Ma)	
		(ppm)	(ppm)	(ppm)	U	²³⁵ U	(1s)	²³⁸ U	(1s)		²⁰⁶ Pb	(1s)		²⁰⁶ Pb/	±
														²³⁸ U	(1s)
NB-04	da_31	0.2	38.5	103.3	0.37	0.0145	0.0037	0.0017	0.0001	0.23	0.0614	0.0161	0.23	11	0.6
	da_32	0.3	61.0	185.6	0.33	0.0137	0.0022	0.0018	0.0001	0.25	0.0559	0.0092	0.25	11.4	0.5
	da_33	0.5	112.8	274.9	0.41	0.0132	0.0016	0.0017	0.0001	0.30	0.0575	0.0072	0.30	10.7	0.4
	da_34	0.6	95.9	331.0	0.29	0.0144	0.0013	0.0018	0.0001	0.31	0.0582	0.0055	0.31	11.5	0.3
	da_35	0.4	76.7	232.1	0.33	0.0125	0.0017	0.0017	0.0001	0.27	0.0543	0.0076	0.27	10.8	0.4
	da_36	0.4	44.7	161.9	0.28	0.0291	0.0028	0.0018	0.0001	0.46	0.1165	0.0122	0.46	11.7	0.5
	da_37	0.5	98.8	261.0	0.38	0.0134	0.0016	0.0017	0.0001	0.30	0.0561	0.0067	0.30	11.1	0.4
	da_38	0.3	25.9	122.4	0.21	0.0233	0.0045	0.0018	0.0001	0.38	0.0939	0.0192	0.38	11.6	0.8
	da_39	0.5	81.9	244.5	0.34	0.0223	0.0020	0.0018	0.0001	0.38	0.0921	0.0089	0.38	11.3	0.4
	da_40	0.7	146.0	347.5	0.42	0.0167	0.0014	0.0018	0.0001	0.35	0.0682	0.0059	0.35	11.4	0.3
NB-05	da_41	0.6	198.5	324.8	0.61	0.0131	0.0013	0.0017	0.0001	0.29	0.0556	0.0058	0.29	11	0.3
	da_42	0.3	34.7	120.2	0.29	0.0244	0.0033	0.0019	0.0001	0.36	0.0952	0.0138	0.36	12	0.6
	da_43	0.4	69.0	218.5	0.32	0.0129	0.0018	0.0017	0.0001	0.25	0.0544	0.0080	0.25	11.1	0.4
	da_44	0.5	154.0	301.4	0.51	0.0129	0.0014	0.0017	0.0001	0.26	0.0549	0.0063	0.26	11	0.3
	da_45	0.9	86.6	552.1	0.16	0.0121	0.0009	0.0017	0.0000	0.32	0.0519	0.0040	0.32	10.9	0.3
	da_46	0.5	151.4	269.1	0.56	0.0122	0.0015	0.0017	0.0001	0.29	0.0510	0.0063	0.29	11.2	0.4
	da_47	0.3	52.0	172.8	0.30	0.0172	0.0027	0.0017	0.0001	0.33	0.0722	0.0120	0.33	11.1	0.6
	da_48	0.3	47.4	193.0	0.25	0.0123	0.0020	0.0017	0.0001	0.26	0.0522	0.0086	0.26	11	0.5
	da_49	0.4	79.1	210.1	0.38	0.0128	0.0019	0.0017	0.0001	0.24	0.0544	0.0081	0.24	11	0.4
	da_50	0.3	36.5	136.0	0.27	0.0180	0.0028	0.0018	0.0001	0.32	0.0732	0.0121	0.32	11.5	0.6
NB-11	wc_11	1.4	65.7	531.5	0.12	0.0522	0.0024	0.0018	0.0001	0.85	0.2110	0.0122	0.85	11.6	0.5
	wc_12	1.1	91.0	740.4	0.12	0.0142	0.0009	0.0014	0.0000	0.43	0.0729	0.0052	0.43	9.1	0.3
	wc_13	1.5	87.4	776.2	0.11	0.0268	0.0011	0.0016	0.0000	0.65	0.1235	0.0059	0.65	10.1	0.3

	wc_14	1.5	78.0	758.0	0.10	0.0140	0.0007	0.0014	0.0000	0.41	0.0717	0.0038	0.41	9.1	0.2
	wc_15*	1.0	93.8	313.1	0.30	0.0505	0.0017	0.0025	0.0001	0.62	0.1484	0.0058	0.62	15.9	0.3
	wc_16	3.6	155.0	823.1	0.19	0.0780	0.0033	0.0020	0.0001	0.59	0.2838	0.0097	0.59	12.8	0.3
	wc_17	1.0	51.3	323.0	0.16	0.0521	0.0020	0.0017	0.0001	0.76	0.2178	0.0093	0.76	11.2	0.3
	wc_18	0.6	70.7	326.0	0.22	0.0192	0.0012	0.0015	0.0000	0.42	0.0944	0.0063	0.42	9.5	0.3
	db_14	0.9	69.0	524.6	0.13	0.0191	0.0011	0.0016	0.0000	0.46	0.0877	0.0054	0.46	10.2	0.3
	db_15	0.8	20.1	343.2	0.06	0.0429	0.0042	0.0017	0.0001	0.72	0.1835	0.0224	0.72	10.9	0.8
	db_16	1.0	50.1	451.3	0.11	0.0322	0.0015	0.0017	0.0001	0.66	0.1406	0.0074	0.66	10.7	0.3
	wc_20	2.9	86.6	1215.7	0.07	0.0396	0.0009	0.0017	0.0000	0.77	0.1740	0.0051	0.77	10.6	0.2
NB-13	wc_21	0.5	58.4	230.0	0.25	0.0160	0.0013	0.0022	0.0001	0.35	0.0532	0.0045	0.35	14.0	0.4
	wc_22	0.5	49.8	201.8	0.25	0.0272	0.0018	0.0023	0.0001	0.41	0.0863	0.0061	0.41	14.7	0.4
	wc_23	0.4	49.8	171.3	0.29	0.0190	0.0018	0.0022	0.0001	0.35	0.0633	0.0062	0.35	14.0	0.5
	wc_24	0.6	56.1	247.6	0.23	0.0230	0.0014	0.0022	0.0001	0.43	0.0748	0.0051	0.43	14.4	0.4
	wc_25	0.5	58.4	244.3	0.24	0.0146	0.0013	0.0021	0.0001	0.33	0.0504	0.0046	0.33	13.5	0.4
	wc_26	0.9	147.8	407.2	0.36	0.0142	0.0009	0.0021	0.0000	0.32	0.0488	0.0031	0.32	13.5	0.3
	wc_27	0.6	77.3	246.8	0.31	0.0176	0.0015	0.0022	0.0001	0.38	0.0592	0.0054	0.38	13.8	0.5
	wc_28	0.8	34.4	192.1	0.18	0.0848	0.0034	0.0027	0.0001	0.84	0.2314	0.0122	0.84	17.1	0.6
NB-16	aa11		111.8	279.3	0.40	0.0104	0.0019	0.0017	0.0001	0.17	0.0449	0.0081	0.17	10.9	0.3
	aa12	0.6	129.7	359.6	0.36	0.0128	0.0015	0.0017	0.0000	0.20	0.0541	0.0063	0.20	11.0	0.3
	aa13	0.6	135.7	331.8	0.41	0.0134	0.0015	0.0017	0.0000	0.20	0.0572	0.0067	0.20	10.9	0.3
	aa14	0.4	73.0	210.7	0.35	0.0112	0.0023	0.0017	0.0001	0.17	0.0482	0.0101	0.17	10.8	0.4
	aa15	0.5	101.9	294.5	0.35	0.0144	0.0018	0.0017	0.0001	0.23	0.0619	0.0081	0.23	10.9	0.3
	aa16	0.4	83.9	254.1	0.33	0.0127	0.0021	0.0017	0.0001	0.22	0.0538	0.0089	0.22	11.0	0.4
	aa17	0.4	70.3	258.3	0.27	0.0125	0.0018	0.0017	0.0001	0.20	0.0530	0.0079	0.20	11.0	0.3
	aa18	0.7	185.5	385.9	0.48	0.0108	0.0013	0.0017	0.0000	0.20	0.0456	0.0054	0.20	11.1	0.3
	aa19	0.4	80.5	220.7	0.36	0.0129	0.0023	0.0017	0.0001	0.19	0.0547	0.0100	0.19	11.1	0.4
	aa20*	0.3	32.8	131.4	0.25	0.0202	0.0041	0.0017	0.0001	0.26	0.0853	0.0179	0.26	11.1	0.6
	aa33*	0.3	38.1	140.7	0.27	0.0314	0.0037	0.0019	0.0001	0.36	0.1201	0.0150	0.36	12.2	0.5
	aa34	0.7	212.0	370.0	0.57	0.0122	0.0015	0.0017	0.0001	0.24	0.0517	0.0063	0.24	11.0	0.3
NB-18	da_51	0.3	24.8	60.6	0.41	0.0445	0.0060	0.0050	0.0002	0.29	0.0641	0.0090	0.29	32.4	1.3

	da_52	0.4	22.1	65.2	0.34	0.0481	0.0061	0.0051	0.0002	0.31	0.0688	0.0092	0.31	32.7	1.3
	da_53	0.2	11.5	37.7	0.31	0.0597	0.0095	0.0053	0.0003	0.32	0.0819	0.0137	0.32	34	1.7
	da_54	0.4	28.5	72.4	0.39	0.0441	0.0053	0.0048	0.0002	0.29	0.0665	0.0084	0.29	30.9	1.1
	da_55	0.3	21.2	55.1	0.38	0.0394	0.0079	0.0048	0.0003	0.27	0.0591	0.0123	0.27	31.1	1.7
	da_56	0.3	17.4	49.5	0.35	0.0412	0.0072	0.0048	0.0002	0.26	0.0621	0.0112	0.26	31	1.4
	da_57	1.9	275.9	323.2	0.85	0.0346	0.0019	0.0050	0.0001	0.33	0.0504	0.0029	0.33	32	0.6
	da_58	0.4	35.3	86.4	0.41	0.0414	0.0043	0.0050	0.0002	0.31	0.0604	0.0066	0.31	32	1
	da_59	0.2	17.2	46.4	0.37	0.0394	0.0082	0.0051	0.0003	0.23	0.0556	0.0119	0.23	33	1.6
	da_60	0.3	29.0	69.1	0.42	0.0348	0.0053	0.0048	0.0002	0.26	0.0522	0.0082	0.26	31.1	1.2
NB-19	db_1	0.4	33.5	83.7	0.40	0.0432	0.0045	0.0050	0.0002	0.34	0.0620	0.0068	0.34	32.4	1.2
	db_2	0.3	22.3	64.2	0.35	0.0403	0.0053	0.0051	0.0002	0.31	0.0576	0.0079	0.31	32.6	1.3
	db_3	0.5	54.0	96.5	0.56	0.0417	0.0039	0.0051	0.0002	0.33	0.0591	0.0059	0.33	32.9	1
	db_4	0.4	24.3	60.0	0.40	0.0606	0.0063	0.0052	0.0002	0.41	0.0852	0.0095	0.41	33.2	1.4
	db_5	0.5	43.5	98.3	0.44	0.0406	0.0037	0.0049	0.0002	0.34	0.0604	0.0058	0.34	31.3	1
	db_6	0.3	24.3	61.9	0.39	0.0407	0.0057	0.0051	0.0002	0.29	0.0580	0.0085	0.29	32.7	1.3
	db_7	0.8	90.3	151.9	0.59	0.0368	0.0046	0.0051	0.0002	0.34	0.0525	0.0070	0.34	32.7	1.4
	db_8	0.5	48.7	89.2	0.55	0.0361	0.0044	0.0049	0.0002	0.30	0.0538	0.0068	0.30	31.3	1.2
NB-20	wc_29	0.2	71.4	172.3	0.41	0.0106	0.0017	0.0013	0.0001	0.30	0.0613	0.0103	0.30	8.1	0.4
	wc_30	0.2	50.6	167.8	0.30	0.0084	0.0013	0.0012	0.0001	0.26	0.0494	0.0078	0.26	7.9	0.3
	wc_31	0.3	76.2	174.4	0.44	0.0117	0.0015	0.0013	0.0001	0.30	0.0640	0.0084	0.30	8.6	0.3
	wc_32	0.2	37.1	135.2	0.27	0.0093	0.0017	0.0013	0.0001	0.26	0.0532	0.0098	0.26	8.2	0.4
	wc_33	0.1	19.3	72.0	0.27	0.0091	0.0028	0.0013	0.0001	0.22	0.0498	0.0157	0.22	8.5	0.6
	wc_34	0.8	106.2	247.5	0.43	0.0631	0.0021	0.0018	0.0001	0.86	0.2610	0.0115	0.86	11.3	0.3
	wc_35	0.6	87.9	209.5	0.42	0.0609	0.0023	0.0017	0.0001	0.92	0.2581	0.0130	0.92	11.0	0.4
	wc_36	0.2	31.5	108.3	0.29	0.0147	0.0024	0.0013	0.0001	0.33	0.0827	0.0144	0.33	8.3	0.5
	wc_37	0.5	52.5	151.9	0.35	0.0633	0.0030	0.0018	0.0001	0.85	0.2626	0.0162	0.85	11.3	0.5
	wc_38	0.3	83.4	209.9	0.40	0.0172	0.0020	0.0013	0.0001	0.46	0.0964	0.0126	0.46	8.3	0.5
	wc_39	0.2	44.5	162.1	0.27	0.0116	0.0017	0.0013	0.0001	0.31	0.0637	0.0096	0.31	8.5	0.4
	wc_40	0.2	38.5	124.3	0.31	0.0081	0.0020	0.0013	0.0001	0.23	0.0464	0.0114	0.23	8.2	0.5
NB-21	wc_1	0.1	7.4	27.8	0.27	0.0841	0.0169	0.0017	0.0003	0.89	0.3510	0.0942	0.89	11.2	2.0

	wc_2	0.2	70.0	169.1	0.41	0.0107	0.0015	0.0012	0.0001	0.29	0.0648	0.0095	0.29	7.7	0.3
	wc_3	0.4	35.3	120.1	0.29	0.0808	0.0042	0.0019	0.0001	0.91	0.3065	0.0214	0.91	12.3	0.6
	wc_4	0.2	25.4	133.4	0.19	0.0083	0.0020	0.0013	0.0001	0.20	0.0479	0.0116	0.20	8.1	0.4
	wc_5	0.2	19.7	83.6	0.23	0.0404	0.0050	0.0015	0.0001	0.64	0.1945	0.0287	0.64	9.7	0.8
	wc_6	8.3	6379.1	5552.9	1.15	0.0099	0.0005	0.0012	0.0001	0.81	0.0608	0.0019	0.81	7.6	0.3
	wc_7	0.7	177.0	359.8	0.49	0.0301	0.0020	0.0014	0.0001	0.66	0.1595	0.0127	0.66	8.8	0.4
	wc_8	0.7	13.6	73.5	0.19	0.2576	0.0156	0.0035	0.0001	0.62	0.5384	0.0255	0.62	22.3	0.8
	wc_9	0.3	61.1	194.5	0.31	0.0106	0.0015	0.0012	0.0001	0.29	0.0621	0.0090	0.29	8.0	0.3
	wc_10	0.6	65.1	218.0	0.30	0.0517	0.0026	0.0016	0.0001	0.85	0.2313	0.0150	0.85	10.4	0.5
NB-22	wd_1	0.2	40.5	143.8	0.28	0.0105	0.0016	0.0012	0.0001	0.27	0.0612	0.0094	0.27	8.0	0.3
	wd_2	0.2	63.2	191.0	0.33	0.0107	0.0012	0.0012	0.0000	0.28	0.0623	0.0074	0.28	8.0	0.3
	wd_3	0.2	44.2	180.0	0.25	0.0085	0.0013	0.0012	0.0000	0.23	0.0534	0.0082	0.23	7.4	0.3
	wd_4	0.2	57.8	193.4	0.30	0.0095	0.0012	0.0012	0.0000	0.26	0.0569	0.0074	0.26	7.8	0.3
	wd_5	0.2	45.7	168.6	0.27	0.0091	0.0013	0.0012	0.0001	0.30	0.0556	0.0082	0.30	7.7	0.3
	wd_6	0.2	44.7	164.3	0.27	0.0091	0.0015	0.0012	0.0001	0.25	0.0544	0.0091	0.25	7.8	0.3
	wd_7	0.2	65.8	181.3	0.36	0.0090	0.0013	0.0012	0.0001	0.28	0.0529	0.0078	0.28	7.9	0.3
	wd_8	0.2	29.3	130.6	0.22	0.0097	0.0020	0.0012	0.0001	0.27	0.0566	0.0122	0.27	8.0	0.5
	wd_9	0.2	62.1	189.4	0.33	0.0084	0.0012	0.0013	0.0001	0.27	0.0483	0.0074	0.27	8.1	0.3
	wd_10	0.2	46.2	174.1	0.27	0.0082	0.0013	0.0013	0.0001	0.25	0.0472	0.0078	0.25	8.1	0.3
	wd_11	0.1	19.5	93.6	0.21	0.0094	0.0029	0.0012	0.0001	0.25	0.0574	0.0181	0.25	7.7	0.6
	wd_12	0.2	35.5	133.0	0.27	0.0069	0.0016	0.0013	0.0001	0.17	0.0397	0.0095	0.17	8.1	0.3
NB-24	wc_41	0.2	29.1	114.9	0.25	0.0091	0.0021	0.0013	0.0001	0.24	0.0527	0.0126	0.24	8.1	0.5
	wc_42	0.1	24.7	95.9	0.26	0.0102	0.0025	0.0012	0.0001	0.24	0.0607	0.0152	0.24	7.9	0.5
	wc_43	0.2	48.4	137.4	0.35	0.0153	0.0023	0.0013	0.0001	0.41	0.0867	0.0142	0.41	8.2	0.5
	wc_44	0.2	46.5	172.9	0.27	0.0100	0.0015	0.0012	0.0001	0.28	0.0603	0.0092	0.28	7.7	0.3
	wc_45	0.4	46.1	133.2	0.35	0.0568	0.0030	0.0016	0.0001	0.81	0.2506	0.0172	0.81	10.6	0.5
	wc_46	1.4	262.6	1213.3	0.22	0.0083	0.0004	0.0012	0.0000	0.36	0.0503	0.0024	0.36	7.7	0.1
	wc_47	0.2	52.3	147.3	0.36	0.0099	0.0017	0.0013	0.0001	0.27	0.0550	0.0097	0.27	8.4	0.4
	wc_48	0.2	57.9	122.4	0.47	0.0082	0.0028	0.0014	0.0001	0.23	0.0496	0.0154	0.23	8.8	0.7
	wc_49	0.3	71.6	156.0	0.46	0.0178	0.0024	0.0013	0.0001	0.45	0.0972	0.0141	0.45	8.6	0.5

	wc_50	0.1	18.5	69.0	0.27	0.0079	0.0031	0.0012	0.0001	0.20	0.0489	0.0193	0.20	7.5	0.6
	wc_51	0.2	33.1	150.8	0.22	0.0120	0.0019	0.0013	0.0001	0.34	0.0656	0.0107	0.34	8.6	0.5
	wc_52	0.5	219.7	432.0	0.51	0.0079	0.0007	0.0012	0.0000	0.29	0.0493	0.0046	0.29	7.5	0.2
NB-27	da_21	0.3	23.1	63.6	0.36	0.0324	0.0062	0.0048	0.0002	0.21	0.0487	0.0096	0.21	31	1.2
	da_22	0.4	36.2	79.4	0.46	0.0322	0.0055	0.0048	0.0002	0.23	0.0489	0.0086	0.23	30.7	1.2
	da_23	1.0	99.0	181.1	0.55	0.0316	0.0026	0.0050	0.0001	0.27	0.0463	0.0039	0.27	31.8	0.7
	da_24*	0.6	45.8	86.5	0.53	0.1258	0.0069	0.0050	0.0002	0.65	0.1822	0.0118	0.65	32.2	1.2
	da_25	0.7	73.7	135.5	0.54	0.0321	0.0034	0.0049	0.0001	0.25	0.0473	0.0051	0.25	31.7	0.8
	da_26	0.9	107.7	170.2	0.63	0.0340	0.0026	0.0048	0.0001	0.28	0.0519	0.0041	0.28	30.5	0.6
	da_27	0.5	38.8	92.8	0.42	0.0329	0.0045	0.0049	0.0002	0.24	0.0491	0.0069	0.24	31.3	1
	da_28	0.6	73.1	118.6	0.62	0.0332	0.0036	0.0049	0.0001	0.24	0.0494	0.0056	0.24	31.3	0.8
	da_29*	0.4	30.1	66.4	0.45	0.0460	0.0062	0.0050	0.0002	0.28	0.0671	0.0094	0.28	32	1.2
	da_30*	0.4	34.3	74.7	0.46	0.0443	0.0058	0.0050	0.0002	0.29	0.0643	0.0088	0.29	32.1	1.2
NB-28	da_1	0.3	16.6	51.4	0.32	0.0400	0.0081	0.0050	0.0002	0.23	0.0576	0.0119	0.23	32.3	1.5
	da_2	0.3	17.0	51.6	0.33	0.0378	0.0075	0.0051	0.0002	0.21	0.0534	0.0108	0.21	33	1.3
	da_3*	0.3	19.4	49.4	0.39	0.0896	0.0114	0.0055	0.0003	0.36	0.1191	0.0161	0.36	35.1	1.6
	da_4	0.4	29.5	70.7	0.42	0.0416	0.0060	0.0051	0.0002	0.24	0.0590	0.0087	0.24	32.9	1.2
	da_5	1.0	84.4	196.7	0.43	0.0314	0.0026	0.0050	0.0001	0.26	0.0452	0.0039	0.26	32.4	0.7
	da_6	0.3	23.7	60.9	0.39	0.0386	0.0066	0.0051	0.0002	0.23	0.0553	0.0096	0.23	32.5	1.3
	da_7*	0.6	46.0	93.0	0.49	0.0758	0.0070	0.0052	0.0002	0.44	0.1065	0.0107	0.44	33.2	1.3
	da_8	0.5	38.1	102.9	0.37	0.0348	0.0044	0.0050	0.0002	0.24	0.0508	0.0065	0.24	32	1
	da_9	0.3	21.1	60.9	0.35	0.0371	0.0071	0.0048	0.0002	0.23	0.0558	0.0109	0.23	31.1	1.3
	da_10	0.4	33.5	86.4	0.39	0.0319	0.0050	0.0049	0.0002	0.22	0.0470	0.0076	0.22	31.6	1.1
NB-29	da_11	0.5	33.7	92.1	0.37	0.0344	0.0047	0.0050	0.0002	0.25	0.0500	0.0071	0.25	32.1	1.1
	da_12	0.7	67.9	125.1	0.54	0.0343	0.0034	0.0052	0.0001	0.25	0.0476	0.0049	0.25	33.6	0.8
	da_13	0.5	37.4	90.2	0.41	0.0353	0.0049	0.0049	0.0002	0.25	0.0528	0.0075	0.25	31.2	1.1
	da_14	0.3	24.3	63.1	0.39	0.0391	0.0066	0.0050	0.0002	0.24	0.0568	0.0098	0.24	32.1	1.3
	da_15	0.4	26.1	68.9	0.38	0.0362	0.0059	0.0051	0.0002	0.23	0.0513	0.0086	0.23	32.9	1.2
	da_16	0.3	28.2	60.9	0.46	0.0372	0.0069	0.0049	0.0002	0.22	0.0556	0.0105	0.22	31.3	1.3
	da_17	0.5	39.0	82.7	0.47	0.0385	0.0056	0.0052	0.0002	0.24	0.0539	0.0081	0.24	33.3	1.2

	da_18	0.7	57.9	120.4	0.48	0.0333	0.0036	0.0051	0.0001	0.25	0.0471	0.0053	0.25	33	0.9
	da_19	0.4	26.5	61.7	0.43	0.0391	0.0068	0.0051	0.0002	0.24	0.0558	0.0099	0.24	32.7	1.3
	da_20	0.4	32.1	78.2	0.41	0.0426	0.0060	0.0048	0.0002	0.29	0.0638	0.0094	0.29	31.1	1.3
NB-30	aa21	0.8	57.8	127.5	0.45	0.0405	0.0045	0.0058	0.0001	0.22	0.0511	0.0058	0.22	37.0	0.9
	aa22	0.6	52.2	96.5	0.54	0.0388	0.0067	0.0057	0.0002	0.20	0.0496	0.0088	0.20	36.5	1.3
	aa23	1.0	101.1	174.1	0.58	0.0413	0.0035	0.0056	0.0001	0.25	0.0539	0.0047	0.25	35.7	0.8
	aa24	0.7	45.4	101.8	0.45	0.0386	0.0047	0.0057	0.0001	0.20	0.0489	0.0061	0.20	36.8	0.9
	aa25	0.6	59.3	107.2	0.55	0.0365	0.0045	0.0056	0.0001	0.20	0.0469	0.0059	0.20	36.3	0.9
	aa26	1.2	130.2	193.4	0.67	0.0390	0.0030	0.0057	0.0001	0.25	0.0498	0.0039	0.25	36.6	0.7
	aa27	0.7	77.4	114.0	0.68	0.0357	0.0046	0.0057	0.0002	0.20	0.0453	0.0060	0.20	36.8	1.0
	aa28	2.2	183.0	360.2	0.51	0.0390	0.0017	0.0057	0.0001	0.28	0.0496	0.0023	0.28	36.6	0.4
	aa29	1.2	131.9	198.1	0.67	0.0392	0.0028	0.0057	0.0001	0.25	0.0499	0.0037	0.25	36.6	0.6
	aa30	2.4	207.6	395.8	0.52	0.0383	0.0018	0.0057	0.0001	0.29	0.0485	0.0024	0.29	36.8	0.5
	aa31	2.3	291.5	359.6	0.81	0.0392	0.0018	0.0057	0.0001	0.30	0.0499	0.0024	0.30	36.6	0.5
	aa32	1.0	80.5	162.2	0.50	0.0384	0.0034	0.0057	0.0001	0.24	0.0490	0.0045	0.24	36.5	0.8
NB-37	aa1	1.4	75.4	284.4	0.27	0.0324	0.0019	0.0049	0.0001	0.25	0.0479	0.0029	0.25	31.6	0.5
	aa2*	15.1	68.0	146.5	0.46	0.8316	0.0105	0.0982	0.0005	0.43	0.0614	0.0008	0.43	604.1	3.1
	aa3	1.0	58.1	200.5	0.29	0.0467	0.0030	0.0049	0.0001	0.29	0.0695	0.0047	0.29	31.3	0.6
	aa4	2.0	89.4	210.3	0.43	0.1636	0.0035	0.0056	0.0001	0.72	0.1938	0.0049	0.72	35.8	0.6
	aa5	2.7	95.9	471.9	0.20	0.1111	0.0020	0.0053	0.0001	0.62	0.1517	0.0034	0.62	34.2	0.4
	aa6	1.4	57.4	174.8	0.33	0.1247	0.0045	0.0053	0.0001	0.57	0.1707	0.0070	0.57	34.1	0.7
	aa7	0.8	97.5	131.4	0.74	0.0477	0.0045	0.0050	0.0001	0.26	0.0694	0.0068	0.26	32.1	0.8
NB-57	oa_1					0.0247	0.0237	0.0059	0.0005	0.09	0.0302	0.0289	0.09	38.1	3.4
	oa_2					0.0470	0.0136	0.0061	0.0003	0.19	0.0562	0.0160	0.19	38.9	2.2
	oa_3					0.0423	0.0235	0.0059	0.0005	0.16	0.0519	0.0284	0.16	38.0	3.3
	oa_4					0.0484	0.0207	0.0057	0.0005	0.20	0.0618	0.0259	0.20	36.5	3.1
	oa_5					0.0254	0.0274	0.0059	0.0006	0.10	0.0310	0.0334	0.10	38.1	3.9
	oa_6*					0.2678	0.0342	0.0077	0.0005	0.52	0.2525	0.0276	0.52	49.4	3.3
	oa_7					0.0431	0.0192	0.0059	0.0005	0.19	0.0529	0.0231	0.19	38.1	3.3
	oa_8					0.0290	0.0205	0.0060	0.0005	0.12	0.0353	0.0248	0.12	38.2	3.1

	oa_9	0.0689	0.0447	0.0060	0.0009	0.24	0.0827	0.0521	0.24	38.8	6.0
	oa_10	0.0346	0.0234	0.0060	0.0006	0.15	0.0422	0.0282	0.15	38.3	3.8
NB-60	oa_21	0.0423	0.0204	0.0060	0.0005	0.18	0.0514	0.0244	0.18	38.3	3.3
	oa_22	0.0367	0.0154	0.0059	0.0004	0.17	0.0449	0.0186	0.17	38.1	2.7
	oa_23	0.0339	0.0127	0.0059	0.0004	0.17	0.0417	0.0155	0.17	37.9	2.4
	oa_24	0.0394	0.0206	0.0061	0.0005	0.15	0.0471	0.0243	0.15	39.0	3.1
	oa_25	0.0449	0.0142	0.0059	0.0004	0.23	0.0551	0.0169	0.23	38.1	2.7
	oa_26	0.0291	0.0408	0.0058	0.0010	0.12	0.0361	0.0503	0.12	37.5	6.5
	oa_27	0.0460	0.0435	0.0060	0.0010	0.18	0.0559	0.0520	0.18	38.3	6.7
	oa_28	0.0256	0.0256	0.0059	0.0006	0.10	0.0314	0.0313	0.10	38.0	3.8
	oa_29	0.0526	0.0349	0.0062	0.0007	0.17	0.0619	0.0404	0.17	39.7	4.5
	oa_30	0.0382	0.0204	0.0059	0.0005	0.17	0.0468	0.0246	0.17	38.1	3.5
NB-63	oa_41	0.0336	0.0102	0.0056	0.0003	0.19	0.0432	0.0129	0.19	36.3	2.1
	oa_42	0.0427	0.0082	0.0058	0.0003	0.25	0.0537	0.0100	0.25	37.1	1.8
	oa_43	0.0314	0.0111	0.0056	0.0004	0.19	0.0404	0.0140	0.19	36.2	2.4
	oa_44	0.0361	0.0196	0.0056	0.0005	0.18	0.0464	0.0248	0.18	36.3	3.5
	oa_45*	0.0668	0.0110	0.0063	0.0003	0.31	0.0775	0.0122	0.31	40.2	2.0
	oa_46	0.0343	0.0171	0.0056	0.0005	0.17	0.0445	0.0218	0.17	36.0	3.0
	oa_47	0.0354	0.0085	0.0056	0.0003	0.20	0.0457	0.0107	0.20	36.1	1.7
	oa_48	0.0394	0.0170	0.0056	0.0005	0.20	0.0514	0.0217	0.20	35.7	3.1
	oa_49	0.0385	0.0129	0.0056	0.0004	0.19	0.0498	0.0163	0.19	36.1	2.3
	oa_50	0.0439	0.0198	0.0056	0.0005	0.19	0.0568	0.0251	0.19	36.1	3.0
NB-64	oa_31	0.0296	0.0311	0.0025	0.0006	0.22	0.0845	0.0866	0.22	16.4	3.9
	oa_32	0.0175	0.0055	0.0024	0.0002	0.22	0.0525	0.0161	0.22	15.6	1.1
	oa_33	0.0245	0.0059	0.0025	0.0002	0.27	0.0705	0.0163	0.27	16.2	1.0
	oa_34	0.0140	0.0037	0.0024	0.0002	0.25	0.0424	0.0109	0.25	15.4	1.0
	oa_35	0.0142	0.0068	0.0024	0.0002	0.21	0.0425	0.0198	0.21	15.6	1.5
	oa_36	0.0203	0.0063	0.0025	0.0002	0.22	0.0590	0.0178	0.22	16.0	1.1
	oa_37	0.0568	0.0129	0.0028	0.0003	0.42	0.1462	0.0300	0.42	18.2	1.7
	oa_38	0.0312	0.0069	0.0026	0.0002	0.32	0.0875	0.0183	0.32	16.7	1.2

oa_39	0.0365	0.0086	0.0025	0.0002	0.32	0.1062	0.0236	0.32	16.0	1.2
oa_40	0.0217	0.0072	0.0026	0.0002	0.22	0.0619	0.0201	0.22	16.4	1.2

Bold type indicates analyses that were excluded from the age calculation for each sample.

Table 2.1 U-Pb data (LMV-Clermont Ferrand)

Sample	No.Zr	Pb*	Th	U	Th/	²⁰⁷ Pb/	±	²⁰⁶ Pb/	±	Rho	²⁰⁷ Pb/	±	Apparent ages (Ma)	
		(ppm)	(ppm)	(ppm)	U	²³⁵ U	(2s)	²³⁸ U	(2s)		²⁰⁶ Pb	(2s)	²⁰⁶ Pb/	±
														²³⁸ U
NB-3	zr56	0.6	21.0	88.7	0.24	0.0584	0.0051	0.0061	0.0002	0.32	0.0695	0.0063	39.2	1.28
	zr57	0.3	15.6	59.8	0.26	0.0327	0.0040	0.0057	0.0002	0.24	0.0416	0.0052	36.6	1.28
	zr58	0.7	33.4	121.9	0.27	0.0348	0.0030	0.0056	0.0001	0.27	0.0450	0.0039	36.0	0.64
	zr59	0.9	52.4	153.8	0.34	0.0365	0.0028	0.0059	0.0001	0.29	0.0445	0.0035	37.9	0.64
	zr60	0.4	18.9	66.5	0.28	0.0411	0.0041	0.0058	0.0002	0.29	0.0514	0.0052	37.3	1.28
	zr61	0.8	76.2	122.8	0.62	0.0375	0.0029	0.0057	0.0001	0.29	0.0476	0.0038	36.6	0.64
	zr62	0.5	32.1	91.8	0.35	0.0394	0.0036	0.0058	0.0002	0.29	0.0490	0.0045	37.3	1.28
	zr64	0.7	36.4	116.4	0.31	0.0392	0.0031	0.0058	0.0002	0.33	0.0488	0.0040	37.3	1.28
	zr7	0.9	41.7	134.5	0.31	0.0510	0.0034	0.0063	0.0002	0.36	0.0591	0.0040	40.5	1.28
	zr9	0.2	8.7	29.6	0.29	0.0325	0.0054	0.0066	0.0002	0.22	0.0357	0.0061	42.4	1.28
	zr10	1.9	217.4	272.6	0.80	0.0394	0.0024	0.0060	0.0001	0.36	0.0473	0.0028	38.6	0.64
	zr11	0.3	19.8	58.1	0.34	0.0354	0.0043	0.0060	0.0002	0.26	0.0428	0.0053	38.6	1.28
	zr12	0.3	14.3	51.7	0.28	0.0451	0.0052	0.0060	0.0002	0.27	0.0541	0.0064	38.6	1.28
	zr13	0.7	41.6	114.5	0.36	0.0345	0.0030	0.0060	0.0002	0.29	0.0421	0.0037	38.6	1.28
	zr14	1.4	96.0	218.6	0.44	0.0386	0.0024	0.0060	0.0001	0.35	0.0466	0.0029	38.6	0.64
	zr15	0.5	34.8	76.4	0.46	0.0400	0.0041	0.0059	0.0002	0.28	0.0491	0.0051	37.9	1.28

NB-41	Zr7	0.2	9.2	28.1	0.33	0.0379	0.0046	0.0064	0.0002	0.24	0.0432	0.0054	41.45	0.7
	Zr8	0.7	32.5	76.4	0.43	0.0543	0.0038	0.0084	0.0002	0.33	0.0468	0.0034	53.97	0.6
	Zr9	0.4	24.7	63.4	0.39	0.0413	0.0032	0.0064	0.0002	0.30	0.0465	0.0037	41.16	0.6
	Zr10	0.3	22.3	46.1	0.48	0.0371	0.0037	0.0064	0.0002	0.27	0.0419	0.0042	41.57	0.7
	Zr11	0.9	71.7	145.5	0.49	0.0393	0.0022	0.0062	0.0001	0.38	0.0464	0.0027	39.88	0.6
	Zr13	0.5	24.9	63.3	0.39	0.0836	0.0049	0.0068	0.0002	0.43	0.0889	0.0054	39.83	0.5
	Zr18	0.3	18.2	41.6	0.44	0.0413	0.0040	0.0062	0.0002	0.28	0.0481	0.0048	39.74	0.6
	Zr19	0.3	15.6	50.7	0.31	0.0423	0.0038	0.0063	0.0002	0.30	0.0485	0.0045	40.34	0.6
	Zr20	0.4	24.2	52.1	0.46	0.0646	0.0047	0.0067	0.0002	0.36	0.0703	0.0053	40.88	0.6
	Zr21	0.2	12.0	35.2	0.34	0.0495	0.0048	0.0065	0.0002	0.30	0.0555	0.0056	40.99	0.6
	Zr22	0.4	20.2	56.3	0.36	0.0405	0.0038	0.0065	0.0002	0.28	0.0455	0.0043	41.89	0.6
	Zr23	0.4	25.9	57.7	0.45	0.0532	0.0040	0.0064	0.0002	0.32	0.0608	0.0047	39.92	0.6
	Zr24	0.4	20.6	54.3	0.38	0.0418	0.0035	0.0062	0.0002	0.29	0.0486	0.0042	39.7	0.6
	Zr25	0.5	25.4	70.2	0.36	0.0555	0.0038	0.0067	0.0002	0.34	0.0605	0.0042	41.76	0.6
NB-65	zr7	0.5	25.6	75.5	0.34	0.0391	0.0035	0.0061	0.0002	0.28	0.0467	0.0043	39.2	1.3
	zr8	4.3	525.0	571.8	0.92	0.0412	0.0019	0.0061	0.0001	0.40	0.0491	0.0024	39.2	1.3
	zr9	0.5	21.4	77.7	0.28	0.0383	0.0038	0.0061	0.0002	0.28	0.0457	0.0047	39.2	1.3
	zr10	6.9	1051.8	1013.1	1.04	0.0431	0.0016	0.0054	0.0001	0.46	0.0581	0.0023	34.7	1.3
	zr11	11.1	3134.0	1015.8	3.09	0.0452	0.0018	0.0058	0.0001	0.49	0.0561	0.0023	37.3	1.3
	zr12	0.7	29.3	98.9	0.30	0.0761	0.0056	0.0059	0.0002	0.39	0.0940	0.0072	37.9	1.3
NB-66	zr36	0.4	14.8	58.6	0.25	0.0385	0.0043	0.0062	0.0002	0.27	0.0453	0.0052	39.84	1.26
	zr38	0.5	22.1	86.4	0.26	0.0342	0.0035	0.0063	0.0002	0.26	0.0394	0.0041	40.49	1.26
	zr39	0.3	12.2	48.3	0.25	0.0399	0.0050	0.0060	0.0002	0.25	0.0484	0.0062	38.56	1.26
	zr40	0.5	27.3	74.3	0.37	0.0355	0.0037	0.0061	0.0002	0.26	0.0420	0.0045	39.20	1.26
	zr41	0.2	8.6	35.3	0.24	0.0415	0.0057	0.0062	0.0002	0.24	0.0483	0.0068	39.84	1.26
	zr42	0.6	36.0	95.6	0.38	0.0388	0.0035	0.0058	0.0002	0.29	0.0488	0.0045	37.28	1.26
	zr47	0.6	30.1	97.7	0.31	0.0416	0.0039	0.0059	0.0002	0.31	0.0508	0.0049	37.92	1.26
	zr48	0.7	42.9	118.9	0.36	0.0381	0.0031	0.0059	0.0002	0.31	0.0466	0.0039	37.92	1.26
	zr49	0.8	47.5	126.4	0.38	0.0376	0.0031	0.0062	0.0002	0.30	0.0441	0.0037	39.84	1.26
	zr50	0.5	19.9	75.4	0.26	0.0385	0.0038	0.0060	0.0002	0.28	0.0465	0.0048	38.56	1.26

zr51	0.3	12.9	50.8	0.25	0.0400	0.0057	0.0063	0.0002	0.23	0.0462	0.0067	40.49	1.26
zr52	0.4	18.9	68.7	0.27	0.0333	0.0044	0.0063	0.0002	0.23	0.0385	0.0051	40.49	1.26

Table 3. Whole-rock Geochemistry

Sample	NB-03	NB-04	NB-05	NB-11	NB-13	NB-16	NB-18	NB-19	NB-20	NB-21	NB-22	NB-24
SiO ₂ (%)	65.30	74.44	68.22	70.14	66.96	70.77	72.84	64.86	69.31	68.77	65.87	72.02
Al ₂ O ₃ (%)	16.19	13.78	17.05	16.77	17.33	15.36	12.52	15.97	15.67	15.60	16.91	12.80
CaO (%)	6.07	2.09	3.02	2.53	4.59	3.10	1.42	4.14	2.91	3.01	3.92	2.18
Fe ₂ O ₃ (%)	5.22	3.00	3.84	2.30	3.24	3.50	7.99	7.51	3.59	4.38	4.46	5.17
K ₂ O (%)	1.36	1.80	1.09	2.21	1.80	1.66	1.27	1.42	2.11	1.99	1.61	1.89
MgO (%)	1.90	0.83	1.33	0.79	1.16	0.79	1.49	3.60	1.82	1.73	2.08	1.75
MnO (%)	0.17	0.02	0.02	0.03	0.04	0.04	0.04	0.10	0.02	0.04	0.04	0.03
Na ₂ O (%)	3.28	3.61	4.87	4.85	4.33	4.23	2.03	1.86	3.99	3.94	4.52	3.75
P ₂ O ₅ (%)	0.13	0.10	0.14	0.13	0.15	0.12	0.07	0.06	0.16	0.10	0.11	0.08
TiO ₂ (%)	0.38	0.32	0.42	0.26	0.40	0.41	0.32	0.49	0.41	0.44	0.47	0.33
Total (%)	100.00	100	100	100	100	100	100	100	100	100	100	100
Ba (ppm)	290.8	838.7	838.2	1021.9	771.9	984.3	285.7	130.5	612.7	580.9	632	429.9
Ce (ppm)	14.2	13.4	17.2	9.7	14.8	16.6	10.6	7.6	13.5	13.3	14.5	12.3
Cr (ppm)	13	<10	15	11	11	22	<10	13	60	65	33	33
Cs (ppm)	0.51	1.21	1.15	2.2	1.87	2.04	0.37	0.43	3.28	2.53	1.95	0.89
Dy (ppm)	2.42	0.8	1.16	0.69	0.86	0.99	1.28	2.87	1.04	1.27	1.27	1.2
Er (ppm)	1.75	0.39	0.57	0.28	0.34	0.51	0.8	1.8	0.55	0.64	0.61	0.58
Eu (ppm)	0.73	0.52	0.76	0.54	0.59	0.66	0.44	0.64	0.59	0.58	0.71	0.48
Ga (ppm)	15	15.5	19.1	20.1	18.3	21.1	12.8	12.9	17.6	17.1	18.9	16.6
Gd (ppm)	2.06	1.25	1.8	1.2	1.42	1.72	1.14	1.96	1.35	1.56	1.79	1.42
Hf (ppm)	1.7	2.1	2.5	2.4	2.3	2.2	1.6	1	2	2	2.3	1.8
Ho (ppm)	0.57	0.14	0.2	0.12	0.14	0.17	0.27	0.62	0.2	0.24	0.23	0.23

La (ppm)	6.8	7.2	9.2	4.7	7.3	9.1	5	2.9	6.7	6.2	6.8	5.8
Lu (ppm)	0.3	0.06	0.08	0.05	0.03	0.05	0.14	0.31	0.07	0.09	0.08	0.08
Nb (ppm)	0.9	2.2	2.6	2.4	2	2.3	1.4	0.5	1.9	1.8	2.3	1.7
Nd (ppm)	9.8	7.9	10.7	6.4	8.8	10.3	5.8	5.8	7.8	8.7	9.5	7.1
Pr (ppm)	2.11	1.86	2.51	1.4	2.03	2.42	1.37	1.15	1.8	1.86	2.12	1.71
Rb (ppm)	21	33.2	29.3	34.7	37	29.1	19	24.7	37.1	34.1	31.2	28.5
Sm (ppm)	2.29	1.83	2.49	1.6	2	2.08	1.23	1.78	1.68	1.87	2.12	1.68
Sn (ppm)	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Sr (ppm)	482	441.4	647.1	494.1	323.5	520.2	167	133.2	399.6	394	516	320.9
Ta (ppm)	<0.1	0.7	1	0.6	0.9	<0.1	0.8	0.5	0.7	0.7	1.2	2.4
Tb (ppm)	0.38	0.17	0.25	0.17	0.2	0.2	0.21	0.39	0.2	0.22	0.27	0.23
Th (ppm)	1.48	1.36	1.61	1.01	1.29	1.45	1.26	0.34	1.41	1.24	1.15	1.08
U (ppm)	0.64	0.71	1.02	1.04	0.72	0.44	0.21	0.13	0.49	0.73	0.66	0.6
V (ppm)	92	64	82	29	61	86	132	216	95	102	108	113
W (ppm)	<1	3	3	<1	<1	5	1	<1	4	4	<1	3
Y (ppm)	14.9	3.9	5.5	3.7	4.3	5.1	7.8	16.1	5.4	6.5	6.6	6.5
Yb (ppm)	2	0.34	0.43	0.24	0.26	0.39	0.89	2.06	0.47	0.58	0.52	0.56
Zr (ppm)	52	67	79	80	78	79	48	27	71	63	70	57

Continuation Table 3. Whole-rock Geochemistry

Sample	NB-27	NB-28	NB-29	NB-30	NB-37	NB-57	NB-60	NB-63	NB-64	NB-65	NB-66
SiO2 (%)	73.32	68.61	69.29	62.27	63.38	69.34	63.72	60.42	67.20		
Al2O3 (%)	13.55	16.34	16.66	17.16	17.24	17.18	17.49	17.43	15.59		
CaO (%)	1.55	3.01	2.37	5.92	3.24	2.93	5.46	7.23	4.53		
Fe2O3 (%)	5.33	4.12	3.70	7.06	7.23	3.47	5.86	7.35	4.40		
K2O (%)	0.98	0.97	1.38	1.12	2.13	1.93	1.68	1.21	2.11		
MgO (%)	1.58	1.98	1.36	2.89	2.90	2.08	2.12	2.77	1.85		

MnO (%)	0.03	0.06	0.05	0.17	0.22	0.03	0.05	0.18	0.08		
Na ₂ O (%)	3.23	4.41	4.64	2.76	3.03	2.48	3.04	2.79	3.73		
P ₂ O ₅ (%)	0.05	0.07	0.13	0.13	0.17	0.17	0.17	0.12	0.10		
TiO ₂ (%)	0.38	0.42	0.41	0.53	0.46	0.37	0.41	0.50	0.42		
Total (%)	100	100	100	100	100	100	100	100	100		
Ba (ppm)	216.1	265.9	323.6	277.8	680.5	431.8	335.7	244.7	476.3	191	100
Ce (ppm)	8.8	11.1	11.5	15	15.4	20.4	15.5	11.9	15.1	12.88	11.12
Cr (ppm)	<10	<10	<10	13	54	<10	<10	<10	24	2	4
Cs (ppm)	0.26	0.37	0.5	0.71	1.72	0.37	0.35	0.59	2.86	2.42	0.79
Dy (ppm)	1.53	1.69	1.76	3.1	1.63	2.55	1.9	2.36	1.91		
Er (ppm)	0.98	1.02	1.04	2.13	1.13	1.8	1.48	1.89	1.38		
Eu (ppm)	0.56	0.65	0.68	0.88	0.62	0.98	0.71	0.65	0.55		
Ga (ppm)	9.9	11.3	13.2	17.3	17.8	13.7	14.4	14.1	15	14.62	14.83
Gd (ppm)	1.41	1.42	1.52	2.82	1.75	2.65	2.44	2.66	2.26		
Hf (ppm)	2.1	2.1	2.4	1.4	1.8	1.6	1.5	2	2.8	-0.1	0.3
Ho (ppm)	0.35	0.34	0.37	0.74	0.38	0.52	0.41	0.59	0.39		
La (ppm)	3.5	4.9	5	7	8.4	10.6	8.6	6.1	7.7	6.1	5.1
Lu (ppm)	0.17	0.21	0.2	0.34	0.19	0.32	0.24	0.29	0.17		
Nb (ppm)	1.3	1.6	1.6	1	1.7	1	1	0.7	2.3	0.7	0.6
Nd (ppm)	6.2	6.4	7.5	10.8	8.6	11.6	9.5	8.7	8.9		
Pr (ppm)	1.31	1.52	1.71	2.26	2.09	2.77	2.11	1.86	2.1		
Rb (ppm)	16.2	17.1	27.2	23.1	25.4	24.9	28.9	18.5	43.1	39.6	8
Sm (ppm)	1.37	1.49	1.68	2.88	1.88	2.69	2.26	2.22	2.2		
Sn (ppm)	<5	<5	<5	<5	<5	<5	<5	<5	<5	0.6	0.4
Sr (ppm)	187	327	329.4	431.8	444.7	369.80	557.80	396.20	357.20	185	389.9
Ta (ppm)	1.2	0.5	0.5	<0.1	<0.1	1.1	0.3	0.7	0.3	0.13	0.07
Tb (ppm)	0.26	0.26	0.28	0.51	0.27	0.43	0.38	0.42	0.35		
Th (ppm)	1.43	1.23	1.38	1.32	1.36	1.35	1.34	0.77	2.49	1	0.9
U (ppm)	0.25	0.28	0.32	0.72	0.66	0.53	0.34	0.54	1.09	0.2	0.2
V (ppm)	104	90	59	151	148	112	129	138	86	140	152
W (ppm)	1	<1	1	<1	2	<1	<1	<1	<1	0.1	0.2

Y (ppm)	8.5	8.9	10.1	19	10.2	14.9	12.5	16	11.5	13.5	10.9
Yb (ppm)	1	1.29	1.25	2.28	1.33	1.96	1.52	1.89	1.21		
Zr (ppm)	67	65	81	39	65	56	55	67	107	3.1	2.4

Table 4. Hf Data

Sample	No.Zr	Measured				Rock age (Ma)	Corrected		
		$^{176}\text{Yb}/^{177}\text{Hf}$	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$	$\pm 2s$		$^{176}\text{Hf}/^{177}\text{Hf}$	eHf _{CHUR}	T _{DM} (Ma)
NB-03	ga_1	0.03114	0.00132	0.283178	0.000033	37.9	0.2832	14.56	151.89
	ga_2	0.04681	0.00186	0.283192	0.000032	37.9	0.2832	15.06	119.75
	ga_3	0.13097	0.00510	0.283248	0.000038	37.9	0.2832	16.94	-1.9747
	ga_4	0.04571	0.00195	0.283204	0.000031	37.9	0.2832	15.48	92.239
	ga_5	0.11406	0.00445	0.283236	0.000053	37.9	0.2832	16.54	23.663
	gb_6	0.05742	0.00228	0.283186	0.000025	37.9	0.2832	14.84	134.11
	gb_7	0.06994	0.00288	0.283219	0.000037	37.9	0.2832	15.96	61.341
	gb_8	0.05247	0.00217	0.283180	0.000021	37.9	0.2832	14.63	147.65
NB-04	da_31	0.01486	0.00062	0.283133	0.000022	11.07	0.2831	12.60	260.00
	da_32	0.01284	0.00048	0.283136	0.000019	11.07	0.2831	12.60	255.00
	da_33	0.0142	0.00052	0.283113	0.00002	11.07	0.2831	11.80	307.00
	da_34	0.01265	0.00047	0.283114	0.000023	11.07	0.2831	11.90	303.00
	da_35	0.01485	0.00055	0.283089	0.000022	11.07	0.2831	11.00	360.00
	da_36	0.01414	0.00054	0.28312	0.000026	11.07	0.2831	12.10	291.00
	da_37	0.01368	0.0005	0.28312	0.000019	11.07	0.2831	12.10	290.00
	da_38	0.00649	0.00024	0.283096	0.000021	11.07	0.2831	11.20	345.00
	da_39	0.01683	0.00063	0.283129	0.000024	11.07	0.2831	12.40	270.00

NB-05	da_40	0.01747	0.00065	0.283113	0.000019	11.07	0.2831	11.80	306.00
	da_41	0.01301	0.00046	0.283138	0.000021	10.9	0.2831	12.70	248.00
	da_42	0.0132	0.00052	0.283119	0.000025	10.9	0.2831	12.10	292.00
	da_43	0.01611	0.0006	0.283136	0.000029	10.9	0.2831	12.60	255.00
	da_44	0.01487	0.00053	0.283115	0.000018	10.9	0.2831	11.90	302.00
	da_45	0.01501	0.00057	0.283132	0.000022	10.9	0.2831	12.50	263.00
	da_46	0.01348	0.00048	0.283141	0.000021	10.9	0.2831	12.80	242.00
	da_47	0.01389	0.00053	0.283112	0.000025	10.9	0.2831	11.80	308.00
	da_48	0.01042	0.0004	0.283136	0.000022	10.9	0.2831	12.60	254.00
	da_49	0.01307	0.00048	0.283129	0.000027	10.9	0.2831	12.40	270.00
NB-11	da_50	0.01261	0.00048	0.283143	0.000025	10.9	0.2831	12.90	237.00
	wc_11	0.0279	0.00115	0.282992	0.000049	9.1	0.2830	7.51	582.34
	wc_12	0.0237	0.00095	0.282994	0.000028	9.1	0.2830	7.59	577.38
	wc_13	0.0207	0.00082	0.283061	0.000043	9.1	0.2831	9.95	425.90
	wc_14	0.0201	0.00075	0.283050	0.000022	9.1	0.2830	9.55	451.50
	wc_15*	0.0087	0.00032	0.283114	0.000030	9.1	0.2831	11.84	304.09
	wc_16	0.0281	0.00112	0.282998	0.000041	9.1	0.2830	7.71	569.36
	wc_17	0.0132	0.00054	0.283084	0.000023	9.1	0.2831	10.77	373.06
	wc_18	0.0288	0.00111	0.282996	0.000044	9.1	0.2830	7.65	573.56
	db_14	0.02277	0.0008	0.283134	0.000029	9.1	0.2831	12.50	259.00
	db_15	0.01612	0.0006	0.283132	0.000343	9.1	0.2831	12.50	263.00
	db_16	0.02968	0.0011	0.283133	0.000026	9.1	0.2831	12.50	262.00
NB-13	wc_20	0.0212	0.00079	0.283029	0.000043	9.1	0.2830	8.83	497.57
	wc_21	0.0131	0.00058	0.283085	0.000040	13.7	0.2831	10.91	367.16
	wc_22	0.0107	0.00046	0.283090	0.000035	13.7	0.2831	11.09	354.76
	wc_23	0.0102	0.00045	0.283112	0.000025	13.7	0.2831	11.85	307.04
	wc_24	0.0120	0.00050	0.283081	0.000038	13.7	0.2831	10.78	375.34
	wc_25	0.0086	0.00037	0.283119	0.000035	13.7	0.2831	12.12	290.54
	wc_26	0.0142	0.00062	0.283063	0.000031	13.7	0.2831	10.13	418.41
	wc_27	0.0181	0.00080	0.283068	0.000024	13.7	0.2831	10.29	407.48

	wc_28	0.0175	0.00073	0.283063	0.000040	13.7	0.2831	10.14	411.65
NB-16	aa11	0.01752	0.00063	0.283137	0.000021	10.9	0.2831	12.69	251.39
	aa12	0.01707	0.00062	0.283133	0.000019	10.9	0.2831	12.55	260.54
	aa13	0.01439	0.00053	0.283146	0.000018	10.9	0.2831	13.02	229.94
	aa14	0.01456	0.00053	0.283105	0.000021	10.9	0.2831	11.54	324.85
	aa15	0.02165	0.00081	0.283139	0.000025	10.9	0.2831	12.76	246.61
	aa16	0.01593	0.00058	0.283138	0.000022	10.9	0.2831	12.71	250.02
	aa17	0.02297	0.00083	0.283129	0.000027	10.9	0.2831	12.41	269.27
	aa18	0.02469	0.00090	0.283121	0.000018	10.9	0.2831	12.11	288.58
	aa19	0.01592	0.00060	0.283132	0.000021	10.9	0.2831	12.50	263.49
	aa20*	0.01244	0.00047	0.283128	0.000025	10.9	0.2831	12.39	270.62
	aa33*	0.01024	0.00038	0.283106	0.000019	10.9	0.2831	11.63	320.62
	aa34	0.02001	0.00071	0.283123	0.000023	10.9	0.2831	12.19	283.42
NB-18	da_51	0.02112	0.00092	0.283152	0.000025	31.5	0.2832	13.60	206.00
	da_52	0.01274	0.00054	0.283189	0.000026	31.5	0.2832	15.00	120.00
	da_53	0.01539	0.00068	0.283167	0.000023	31.5	0.2832	14.20	170.00
	da_54	0.01799	0.00079	0.283138	0.000028	31.5	0.2831	13.20	237.00
	da_55	0.01903	0.00082	0.283165	0.000033	31.5	0.2832	14.10	176.00
	da_56	0.0156	0.00068	0.283178	0.000024	31.5	0.2832	14.60	145.00
	da_57	0.05368	0.00218	0.28318	0.00003	31.5	0.2832	14.60	143.00
	da_58	0.02248	0.00099	0.283172	0.000028	31.5	0.2832	14.40	159.00
	da_59	0.01466	0.00065	0.283174	0.000022	31.5	0.2832	14.50	154.00
	da_60	0.0223	0.00097	0.283163	0.000026	31.5	0.2832	14.10	179.00
NB-19	db_1	0.02812	0.00128	0.28317	0.000021	31.7	0.2832	14.30	165.00
	db_2	0.02517	0.00113	0.283164	0.00003	31.7	0.2832	14.10	177.00
	db_3	0.03738	0.00163	0.283163	0.000027	31.7	0.2832	14.00	181.00
	db_4	0.02419	0.00109	0.283162	0.00003	31.7	0.2832	14.00	182.00
	db_5	0.03453	0.00153	0.283185	0.000023	31.7	0.2832	14.80	129.00
	db_6	0.0234	0.00105	0.283161	0.00003	31.7	0.2832	14.00	185.00
	db_7	0.03995	0.00173	0.283199	0.000033	31.7	0.2832	15.30	99.00

	db_8	0.03062	0.00136	0.283166	0.000028	31.7	0.2832	14.10	174.00
NB-20	wc_29	0.0179	0.00085	0.282989	0.000033	8.1	0.2830	7.38	589.87
	wc_30	0.0135	0.00066	0.283064	0.000036	8.1	0.2831	10.04	419.42
	wc_31	0.0195	0.00092	0.283058	0.000033	8.1	0.2831	9.81	433.91
	wc_32	0.0069	0.00035	0.283088	0.000028	8.1	0.2831	10.89	364.41
	wc_33	0.0124	0.00062	0.283029	0.000036	8.1	0.2830	8.79	499.67
	wc_34	0.0170	0.00079	0.283036	0.000032	8.1	0.2830	9.06	481.96
	wc_35	0.0213	0.00104	0.283039	0.000035	8.1	0.2830	9.14	476.86
	wc_36	0.0109	0.00052	0.283060	0.000033	8.1	0.2831	9.89	428.96
	wc_37	0.0177	0.00084	0.283079	0.000035	8.1	0.2831	10.58	384.57
	wc_38	0.0227	0.00105	0.283009	0.000031	8.1	0.2830	8.10	543.72
	wc_39	0.0194	0.00094	0.283036	0.000028	8.1	0.2830	9.04	483.49
	wc_40	0.0187	0.00090	0.283021	0.000034	8.1	0.2830	8.51	517.75
NB-21	wc_1	0.0133	0.00066	0.283074	0.000021	7.7	0.2831	10.40	396.07
	wc_2	0.0138	0.00066	0.283053	0.000041	7.7	0.2831	9.65	443.92
	wc_3	0.0136	0.00066	0.283054	0.000042	7.7	0.2831	9.68	442.35
	wc_4	0.0099	0.00049	0.283078	0.000036	7.7	0.2831	10.54	386.66
	wc_5	0.0115	0.00056	0.283068	0.000026	7.7	0.2831	10.17	410.78
	wc_6	0.0827	0.00319	0.283067	0.000035	7.7	0.2831	10.12	414.07
	wc_7	0.0170	0.00079	0.283062	0.000049	7.7	0.2831	9.95	425.10
	wc_8	0.0087	0.00044	0.283053	0.000025	7.7	0.2831	9.66	443.69
	wc_9	0.0154	0.00073	0.283060	0.000033	7.7	0.2831	9.91	427.55
	wc_10	0.0157	0.00078	0.283055	0.000041	7.7	0.2831	9.73	438.89
NB-22	wd_1	0.0059	0.00028	0.283087	0.000024	7.8	0.2831	10.85	367.08
	wd_2	0.0061	0.00029	0.283092	0.000029	7.8	0.2831	11.02	355.90
	wd_3	0.0143	0.00070	0.283060	0.000036	7.8	0.2831	9.88	429.54
	wd_4	0.0105	0.00051	0.283086	0.000033	7.8	0.2831	10.82	369.05
	wd_5	0.0113	0.00055	0.283085	0.000023	7.8	0.2831	10.77	372.33
	wd_6	0.0059	0.00028	0.283074	0.000029	7.8	0.2831	10.38	397.55
	wd_7	0.0123	0.00061	0.283036	0.000038	7.8	0.2830	9.06	481.89

	wd_8	0.0047	0.00023	0.283104	0.000035	7.8	0.2831	11.45	328.62
	wd_9	0.0143	0.00070	0.283065	0.000032	7.8	0.2831	10.07	417.02
	wd_10	0.0109	0.00052	0.283101	0.000027	7.8	0.2831	11.36	334.43
	wd_11	0.0102	0.00052	0.283041	0.000044	7.8	0.2830	9.22	471.61
	wd_12	0.0062	0.00030	0.283096	0.000022	7.8	0.2831	11.16	347.10
NB-24	wc_41	0.0123	0.00062	0.283073	0.000036	7.7	0.2831	10.36	398.71
	wc_42	0.0134	0.00067	0.283088	0.000023	7.7	0.2831	10.88	365.09
	wc_43	0.0131	0.00063	0.283052	0.000028	7.7	0.2831	9.61	446.39
	wc_44	0.0180	0.00088	0.283060	0.000041	7.7	0.2831	9.89	428.40
	wc_45	0.0136	0.00067	0.283099	0.000034	7.7	0.2831	11.26	340.88
	wc_46	0.0245	0.00117	0.283065	0.000033	7.7	0.2831	10.07	417.08
	wc_47	0.0134	0.00064	0.283060	0.000033	7.7	0.2831	9.89	428.86
	wc_48	0.0223	0.00103	0.283064	0.000035	7.7	0.2831	10.03	419.45
	wc_49	0.0117	0.00053	0.283078	0.000042	7.7	0.2831	10.52	388.37
	wc_50	0.0111	0.00056	0.283106	0.000041	7.7	0.2831	11.51	324.38
	wc_51	0.0159	0.00078	0.283073	0.000036	7.7	0.2831	10.37	398.05
	wc_52	0.0172	0.00080	0.283051	0.000036	7.7	0.2831	9.57	449.26
NB-27	da_21	0.01835	0.00082	0.283171	0.000027	31.1	0.2832	14.30	162.00
	da_22	0.03168	0.00134	0.283154	0.000028	31.1	0.2832	13.70	201.00
	da_23	0.05791	0.00238	0.283197	0.000029	31.1	0.2832	15.20	106.00
	da_24*	0.03462	0.00148	0.28315	0.000023	31.1	0.2832	13.60	210.00
	da_25	0.0744	0.00303	0.283177	0.000037	31.1	0.2832	14.50	150.00
	da_26	0.08249	0.00326	0.283213	0.000037	31.1	0.2832	15.80	69.00
	da_27	0.04542	0.00196	0.283194	0.000038	31.1	0.2832	15.10	112.00
	da_28	0.06658	0.00265	0.283181	0.000038	31.1	0.2832	14.60	141.00
	da_29*	0.0223	0.00095	0.283163	0.000028	31.1	0.2832	14.10	179.00
	da_30*	0.03796	0.00161	0.283188	0.000033	31.1	0.2832	14.90	124.00
NB-28	da_1	0.01158	0.00052	0.28319	0.000022	31.9	0.2832	15.00	117.00
	da_2	0.01456	0.00066	0.283166	0.000026	31.9	0.2832	14.20	173.00
	da_3*	0.00889	0.00039	0.283159	0.000026	31.9	0.2832	13.90	189.00

	da_4	0.03131	0.00136	0.283164	0.000027	31.9	0.2832	14.10	179.00
	da_5	0.08018	0.00333	0.283211	0.000039	31.9	0.2832	15.70	74.00
	da_6	0.02534	0.0011	0.283167	0.000024	31.9	0.2832	14.20	170.00
	da_7*	0.01806	0.00078	0.283214	0.000037	31.9	0.2832	15.90	63.00
	da_8	0.0339	0.0015	0.283156	0.00003	31.9	0.2832	13.80	197.00
	da_9	0.02147	0.00096	0.283176	0.00002	31.9	0.2832	14.50	150.00
	da_10	0.01446	0.00065	0.283152	0.000024	31.9	0.2832	13.70	205.00
NB-29	da_11	0.03523	0.00144	0.28316	0.000024	32.2	0.2832	13.90	187.00
	da_12	0.03805	0.00156	0.283193	0.000027	32.2	0.2832	15.10	112.00
	da_13	0.04305	0.00173	0.283164	0.000024	32.2	0.2832	14.10	177.00
	da_14	0.03459	0.00141	0.283209	0.000022	32.2	0.2832	15.70	74.00
	da_15	0.0322	0.00133	0.283193	0.00003	32.2	0.2832	15.10	111.00
	da_16	0.02851	0.00116	0.283166	0.000029	32.2	0.2832	14.20	173.00
	da_17	0.04806	0.00192	0.28319	0.000028	32.2	0.2832	15.00	118.00
	da_18	0.03705	0.00146	0.283181	0.000027	32.2	0.2832	14.70	139.00
	da_19	0.02302	0.00094	0.283153	0.000032	32.2	0.2832	13.70	202.00
	da_20	0.03187	0.00127	0.283202	0.000033	32.2	0.2832	15.40	92.00
NB-30	aa21	0.03800	0.00179	0.283206	0.000033	36.6	0.2832	15.65	80.75
	aa22	0.04057	0.00176	0.283180	0.000028	36.6	0.2832	14.74	139.54
	aa23	0.05048	0.00225	0.283217	0.000033	36.6	0.2832	16.02	56.06
	aa24	0.03076	0.00144	0.283204	0.000020	36.6	0.2832	15.58	84.99
	aa25	0.03469	0.00152	0.283208	0.000024	36.6	0.2832	15.74	74.12
	aa26	0.05344	0.00238	0.283209	0.000030	36.6	0.2832	15.75	74.20
	aa27	0.05853	0.00242	0.283214	0.000028	36.6	0.2832	15.92	63.23
	aa28	0.05083	0.00232	0.283184	0.000025	36.6	0.2832	14.88	130.29
	aa29	0.04824	0.00215	0.283216	0.000024	36.6	0.2832	16.00	57.66
	aa30	0.03841	0.00174	0.283200	0.000023	36.6	0.2832	15.44	94.46
	aa31	0.10378	0.00451	0.283190	0.000027	36.6	0.2832	15.02	120.91
	aa32	0.03503	0.00160	0.283188	0.000025	36.6	0.2832	15.04	120.06
NB-37	aa1	0.04307	0.00179	0.283175	0.000018	31.4	0.2832	14.46	153.17

	aa2*	0.01537	0.00051	0.282117	0.000021	31.4	0.2821		2189.33
	aa3	0.03756	0.00160	0.283198	0.000024	31.4	0.2832	15.28	100.17
	aa4	0.03568	0.00151	0.283183	0.000023	31.4	0.2832	14.82	133.76
	aa5	0.07100	0.00289	0.283193	0.000023	31.4	0.2832	15.11	113.25
	aa6	0.04337	0.00184	0.283207	0.000034	31.4	0.2832	15.65	78.39
	aa7	0.06364	0.00256	0.283190	0.000027	31.4	0.2832	14.98	120.09
NB-41	gd_50	0.04311	0.00134	0.283227	0.000046	40.59	0.2832	16.55	27.22
	gd_51	0.07110	0.00241	0.283198	0.000062	40.59	0.2832	15.48	96.28
	gd_52	0.07697	0.00240	0.283194	0.000043	40.59	0.2832	15.34	105.17
	gd_53	0.05550	0.00211	0.283184	0.000058	40.59	0.2832	15.00	127.29
	gd_54	0.04912	0.00144	0.283202	0.000042	40.59	0.2832	15.66	84.50
	gd_55	0.04015	0.00124	0.283237	0.000055	40.59	0.2832	16.89	4.68
	gd_56	0.06312	0.00215	0.283185	0.000054	40.59	0.2832	15.02	126.02
NB-45	oa_61	0.09922	0.00353	0.283193	0.000053	40.9	0.2832	14.42	130.88
	oa_62	0.09254	0.00332	0.283166	0.000053	40.9	0.2832	13.49	190.99
	oa_63	0.10741	0.00372	0.283252	0.000055	40.9	0.2833	16.53	-5.45
	oa_64	0.07151	0.00276	0.283145	0.000076	40.9	0.2831	12.72	240.76
	oa_65	0.07881	0.00253	0.283188	0.000024	40.9	0.2832	14.24	142.27
	oa_66*	0.06244	0.00182	0.282859	0.000069	40.9	0.2829		835.10
	oa_67	0.04585	0.00168	0.283232	0.000030	40.9	0.2832	15.80	41.94
NB-57	oa_1	0.03830	0.00129	0.283233	0.000027	38.1	0.2832	16.67	15.68
	oa_2	0.08555	0.00273	0.283227	0.000040	38.1	0.2832	16.41	32.23
	oa_3	0.05076	0.00165	0.283226	0.000032	38.1	0.2832	16.40	33.34
	oa_4	0.04593	0.00156	0.283231	0.000031	38.1	0.2832	16.59	20.95
	oa_5	0.03891	0.00131	0.283214	0.000027	38.1	0.2832	15.97	60.98
	oa_6*	0.04612	0.00150	0.283211	0.000029	38.1	0.2832	15.87	67.54
	oa_7	0.08521	0.00270	0.283212	0.000028	38.1	0.2832	15.89	66.00
	oa_8	0.05492	0.00184	0.283187	0.000029	38.1	0.2832	15.03	121.73
	oa_9	0.04652	0.00146	0.283216	0.000036	38.1	0.2832	16.04	56.78
	oa_10	0.05273	0.00168	0.283207	0.000025	38.1	0.2832	15.72	77.19

NB-60	oa_21	0.03111	0.00105	0.283190	0.000027	38.2	0.2832	15.16	113.66
	oa_22	0.03843	0.00130	0.283192	0.000019	38.2	0.2832	15.21	110.41
	oa_23	0.05297	0.00179	0.283209	0.000031	38.2	0.2832	15.81	71.62
	oa_24	0.03746	0.00131	0.283203	0.000029	38.2	0.2832	15.59	85.52
	oa_25	0.07555	0.00249	0.283194	0.000035	38.2	0.2832	15.25	107.47
	oa_26	0.02142	0.00075	0.283226	0.000028	38.2	0.2832	16.43	31.65
	oa_27	0.03617	0.00125	0.283221	0.000026	38.2	0.2832	16.23	44.02
	oa_28	0.02460	0.00086	0.283196	0.000032	38.2	0.2832	15.38	99.56
	oa_29	0.01570	0.00055	0.283168	0.000032	38.2	0.2832	14.38	163.89
	oa_30	0.03643	0.00126	0.283223	0.000036	38.2	0.2832	16.31	38.85
NB-63	oa_41	0.09220	0.00267	0.283194	0.000030	36.3	0.2832	15.20	109.23
	oa_42	0.05279	0.00159	0.283170	0.000027	36.3	0.2832	14.40	161.08
	oa_43	0.02389	0.00085	0.283191	0.000024	36.3	0.2832	15.14	113.15
	oa_44	0.08938	0.00256	0.283178	0.000029	36.3	0.2832	14.65	144.75
	oa_45*	0.03358	0.00102	0.283183	0.000026	36.3	0.2832	14.84	132.71
	oa_46	0.06526	0.00192	0.283197	0.000026	36.3	0.2832	15.34	100.09
	oa_47	0.11570	0.00332	0.283167	0.000035	36.3	0.2832	14.22	172.82
	oa_48	0.08039	0.00234	0.283191	0.000032	36.3	0.2832	15.12	114.26
	oa_49	0.08981	0.00262	0.283199	0.000024	36.3	0.2832	15.38	97.72
	oa_50	0.05314	0.00157	0.283171	0.000028	36.3	0.2832	14.43	159.06
NB-64	oa_31	0.01836	0.00050	0.283141	0.000022	15.6	0.2831	12.92	239.99
	oa_32	0.03363	0.00103	0.283145	0.000023	15.6	0.2831	13.06	231.34
	oa_33	0.06205	0.00176	0.283157	0.000034	15.6	0.2832	13.48	203.63
	oa_34	0.06024	0.00175	0.283121	0.000027	15.6	0.2831	12.20	286.35
	oa_35	0.03499	0.00111	0.283143	0.000028	15.6	0.2831	13.01	234.22
	oa_36	0.02592	0.00077	0.283125	0.000027	15.6	0.2831	12.38	275.00
	oa_37	0.02516	0.00085	0.283130	0.000035	15.6	0.2831	12.55	264.04
	oa_38	0.04069	0.00123	0.283126	0.000025	15.6	0.2831	12.41	272.99
	oa_39	0.02971	0.00090	0.283119	0.000027	15.6	0.2831	12.14	290.29
	oa_40	0.02953	0.00083	0.283127	0.000024	15.6	0.2831	12.42	272.33

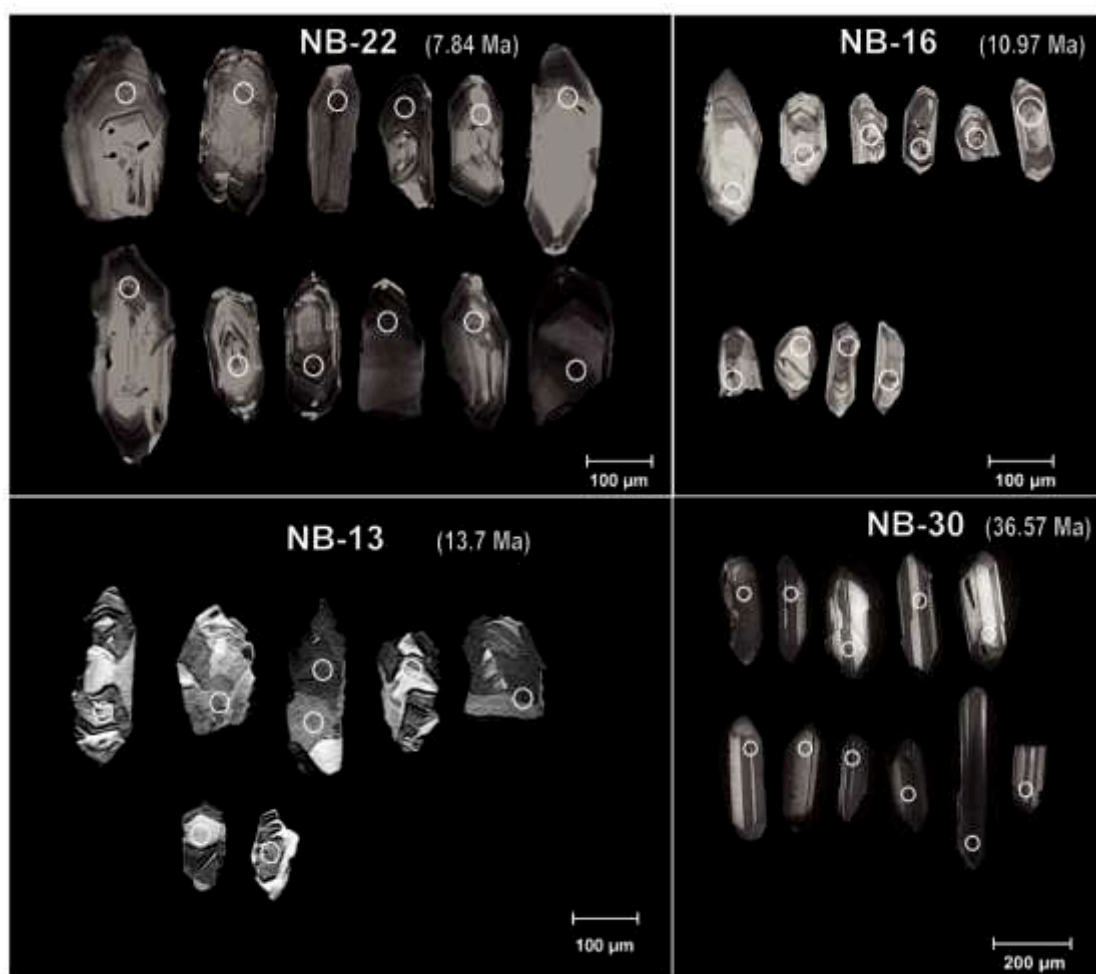
NB-65	gb_23	0.04137	0.00163	0.283203	0.000021	39.3	0.283198	15.43	95.25
	gb_24	0.04096	0.00176	0.283170	0.000037	39.3	0.283165	14.27	170.02
	gb_25	0.12609	0.00481	0.283239	0.000107	39.3	0.283232	16.62	18.32
NB-66	gb_16	0.04552	0.00188	0.283213	0.000038	38.8	0.283208	15.82	71.57
	gb_17	0.03027	0.00130	0.283187	0.000037	38.8	0.283182	14.91	130.23
	gb_18	0.02194	0.00095	0.283230	0.000030	38.8	0.283225	16.43	32.08
	gb_19	0.03867	0.00159	0.283185	0.000033	38.8	0.283179	14.82	136.35
	gb_20	0.03383	0.00142	0.283258	0.000033	38.8	0.283253	17.43	-32.89
	gb_21	0.03637	0.00149	0.283213	0.000037	38.8	0.283208	15.82	71.30
	gb_22	0.03424	0.00138	0.283204	0.000033	38.8	0.283199	15.50	92.50

Table 5. O Data

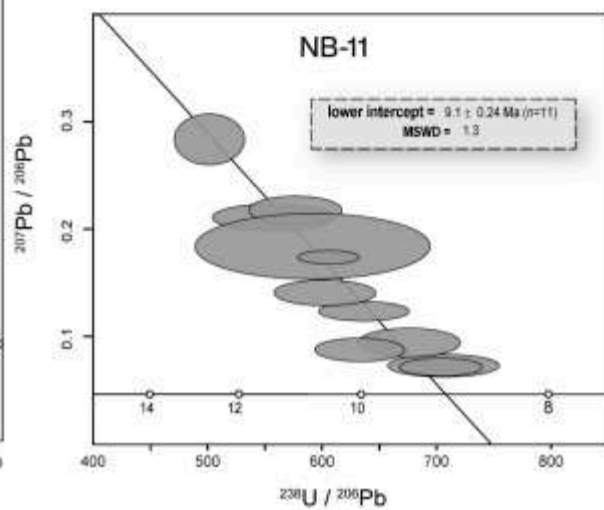
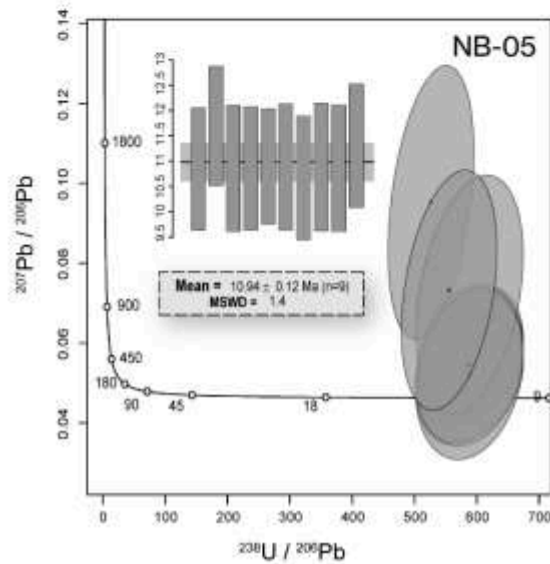
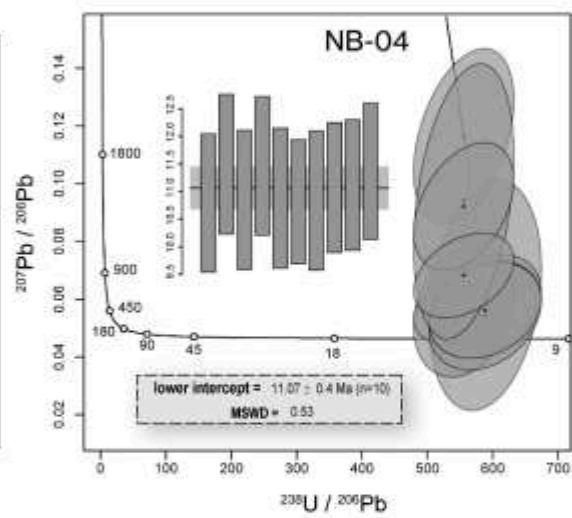
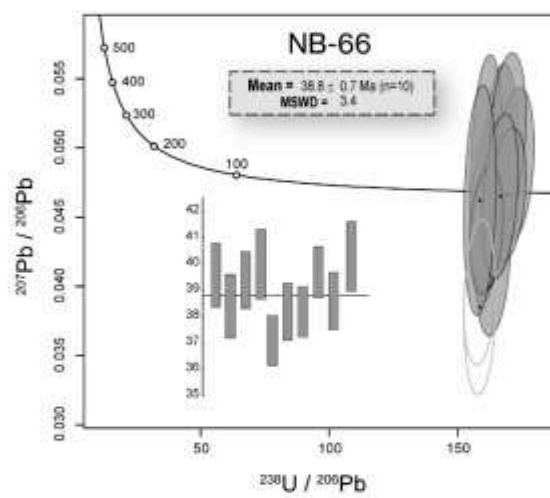
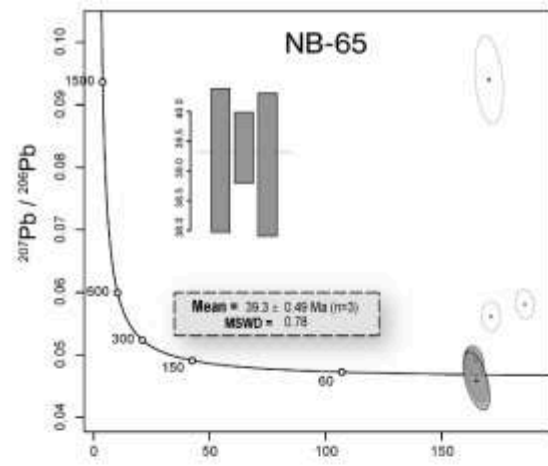
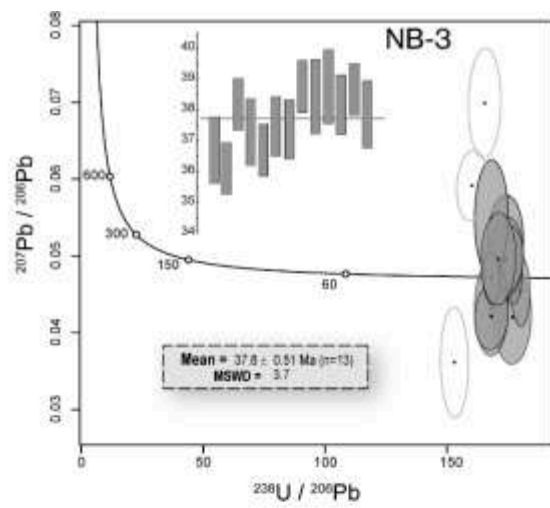
	Rock Age (Ma)	Analysis Name	X	Y	Chamber Pressure	Primary Intensity	¹⁶ O	¹⁸ O	Raw δ ¹⁸ O (‰, SMOW)	Internal Error (‰)	Corrected δ ¹⁸ O (‰)	Total Error (‰)
NB-04	11.07	CS@21	898	-3083	1.0E-08	2.1E-09	1745598722	3607432	7.50	0.09	8.12	0.18
	11.07	CS@22	780	-3231	9.8E-09	2.1E-09	1682670467	3476140	6.81	0.07	7.43	0.15
	11.07	CS@23	488	-3048	9.6E-09	2.1E-09	1653130751	3414151	6.48	0.09	7.10	0.18
	11.07	CS@24	76	-3233	9.5E-09	2.1E-09	1635172286	3374895	5.99	0.08	6.61	0.17
	11.07	CS@25	112	-2896	9.4E-09	2.1E-09	1701771086	3518299	7.79	0.08	8.41	0.17
NB-05	10.9	CS@26	626	2340	9.3E-09	2.1E-09	1706732945	3526331	7.03	0.08	7.65	0.17
	10.9	CS@27	740	2189	9.3E-09	2.1E-09	1719354257	3551023	6.58	0.08	7.20	0.17
	10.9	CS@28	398	1598	9.0E-09	2.2E-09	1715000517	3544207	7.54	0.07	8.16	0.14
	10.9	CS@29	234	1618	8.9E-09	2.2E-09	1757139063	3630507	7.01	0.08	7.63	0.18
	10.9	CS@30	-139	1959	8.8E-09	2.2E-09	1737507215	3589488	6.97	0.08	7.59	0.16
NB-13	13.7	CS@36	3125	-2620	1.8E-08	2.2E-09	1651896424	3409621	6.29	0.08	6.95	0.16
	13.7	CS@37	2999	-2846	1.8E-08	2.1E-09	1444675864	2980360	5.18	0.10	5.84	0.20
	13.7	CS@38	3334	-3132	1.8E-08	2.1E-09	1513012065	3121977	5.56	0.08	6.22	0.16

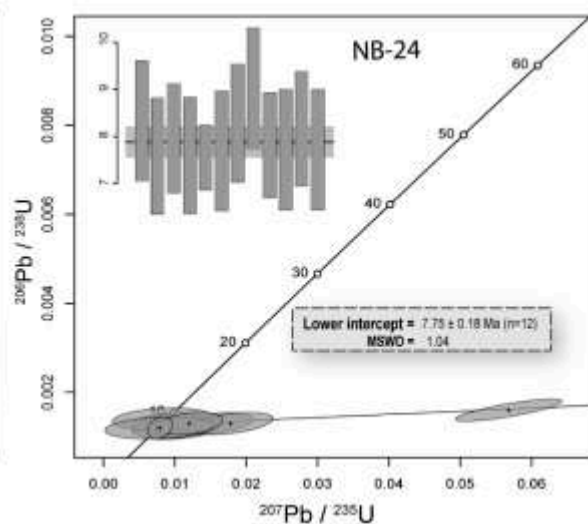
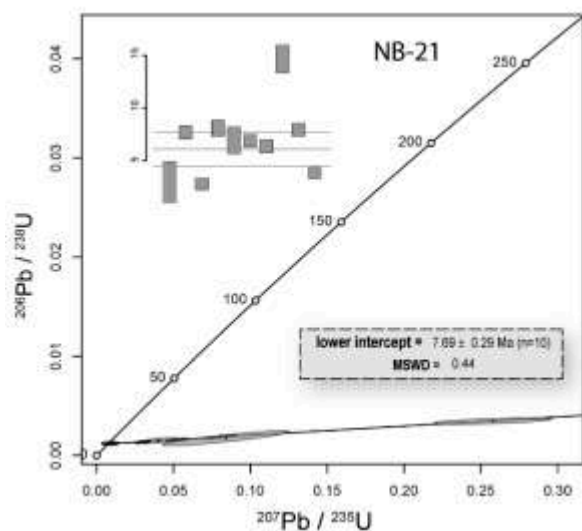
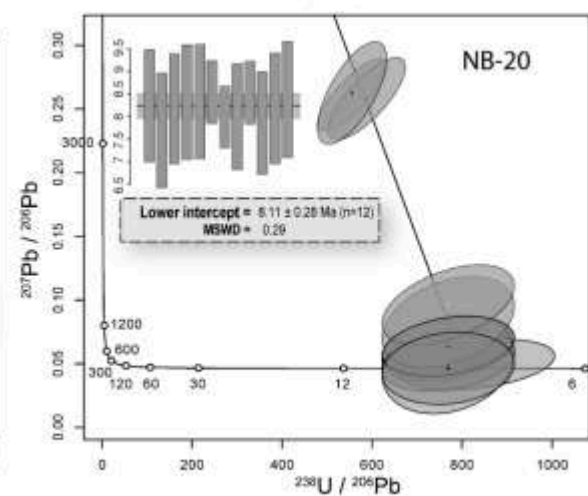
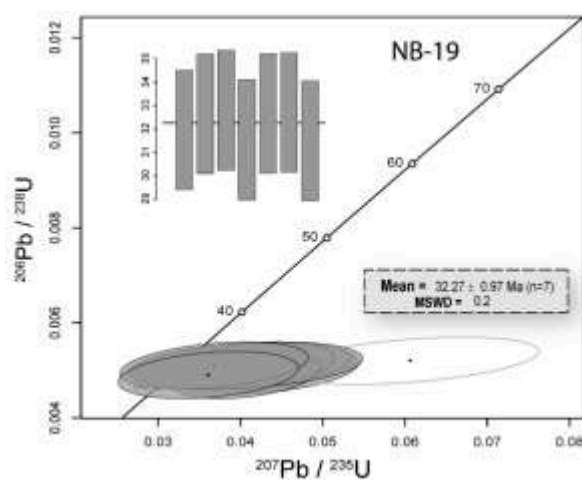
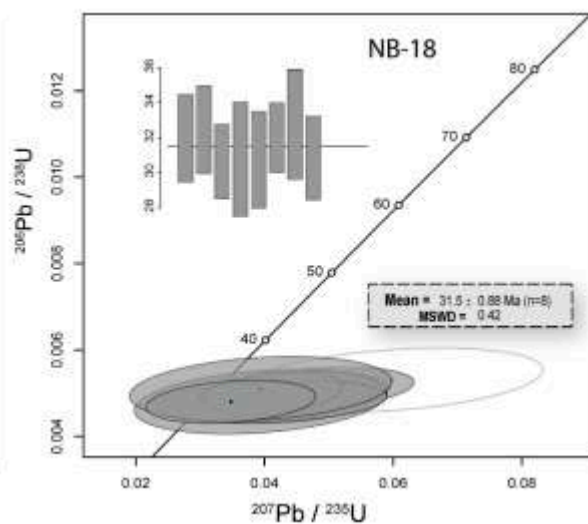
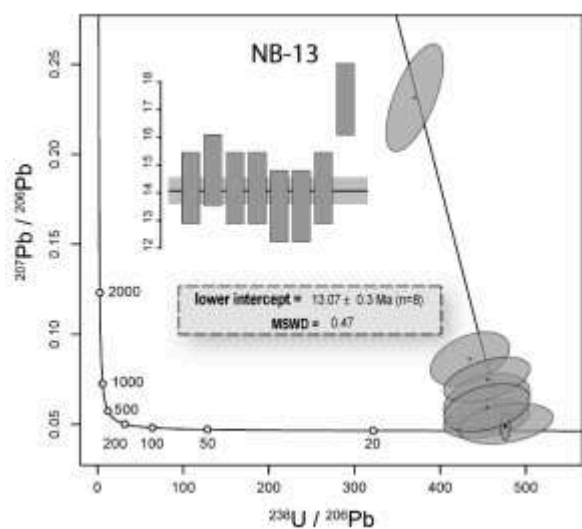
	13.7	CS@39	3538	-2852	1.7E-08	2.1E-09	1600508850	3303310	5.96	0.07	6.62	0.15
NB-18	31.5	CS@16	3086	-3094	1.3E-08	2.1E-09	1659622589	3417157	3.56	0.08	4.18	0.17
	31.5	CS@17	2555	-3138	1.2E-08	2.1E-09	1667897675	3433555	3.58	0.07	4.20	0.15
	31.5	CS@18	2408	-3118	1.2E-08	2.1E-09	1655493424	3410440	4.50	0.07	5.12	0.15
	31.5	CS@19	2323	-3560	1.1E-08	2.1E-09	1661995101	3426028	4.91	0.07	5.53	0.15
	31.5	CS@20	3070	-3735	1.1E-08	2.1E-09	1656153626	3416995	5.77	0.09	6.39	0.18
NB-20	8.1	CS@79	-428	-1643	1.8E-08	2.4E-09	1972687641	4073698	7.16	0.06	7.73	0.13
	8.1	CS@80	-387	-1215	1.8E-08	2.4E-09	1954059449	4035987	6.99	0.07	7.55	0.15
	8.1	CS@81	-545	-966	1.7E-08	2.4E-09	1951747214	4030648	6.98	0.08	7.54	0.16
	8.1	CS@82	-934	-1273	1.7E-08	2.4E-09	1942238085	4010955	6.91	0.09	7.47	0.18
	8.1	CS@83	-1120	-1603	1.7E-08	2.4E-09	1958945609	4044461	6.76	0.07	7.32	0.16
NB-21	7.7	CS@84	4792	-429	5.2E-08	2.3E-09	1807431971	3727547	5.53	0.08	6.09	0.16
NB-22	7.8	CS@31	2139	1730	1.9E-08	2.2E-09	1648054691	3402320	6.33	0.09	6.99	0.18
	7.8	CS@32	2306	1654	1.9E-08	2.2E-09	1633704737	3374138	6.81	0.09	7.46	0.18
	7.8	CS@33	2344	1362	1.9E-08	2.2E-09	1631564484	3369951	6.75	0.07	7.41	0.14
	7.8	CS@34	2223	1312	1.9E-08	2.2E-09	1621039027	3347771	6.15	0.07	6.81	0.15
	7.8	CS@35	2606	1362	1.9E-08	2.2E-09	1628554424	3364011	6.86	0.09	7.52	0.19
NB-24	7.7	CS@74	4284	-2066	1.9E-08	2.4E-09	1951231777	4027552	6.49	0.10	7.06	0.20
	7.7	CS@75	4192	-1809	1.9E-08	2.4E-09	1942617263	4011332	6.97	0.08	7.54	0.16
	7.7	CS@76	4415	-1319	1.9E-08	2.4E-09	1942349310	4009285	6.41	0.07	6.97	0.14
	7.7	CS@77	4750	-1434	1.9E-08	2.4E-09	1948144656	4021377	6.57	0.06	7.13	0.13
	7.7	CS@78	4823	-1495	1.9E-08	2.4E-09	1956059475	4037308	6.48	0.08	7.04	0.16
NB-27	31.1	CS@11	664	-4333	3.0E-08	2.2E-09	1692115549	3483900	3.70	0.08	4.32	0.17
	31.1	CS@12	70	-4557	2.9E-08	2.2E-09	1657382424	3415734	4.74	0.08	5.36	0.16
	31.1	CS@13	515	-4705	2.8E-08	2.2E-09	1685397888	3472534	4.18	0.08	4.80	0.16
	31.1	CS@14	785	-4786	2.7E-08	2.2E-09	1655815020	3410627	3.76	0.07	4.38	0.15
	31.1	CS@15	1166	-4972	2.6E-08	2.1E-09	1661089911	3421770	4.10	0.08	4.72	0.17
NB-28	31.9	CS@1	3972	1339	3.2E-08	2.2E-09	1673674819	3447096	3.93	0.09	4.55	0.19
	31.9	CS@2	3986	869	3.3E-08	2.2E-09	1691469864	3485170	4.32	0.09	4.94	0.18
	31.9	CS@3	3752	711	3.3E-08	2.2E-09	1749946848	3602385	3.09	0.10	3.71	0.20

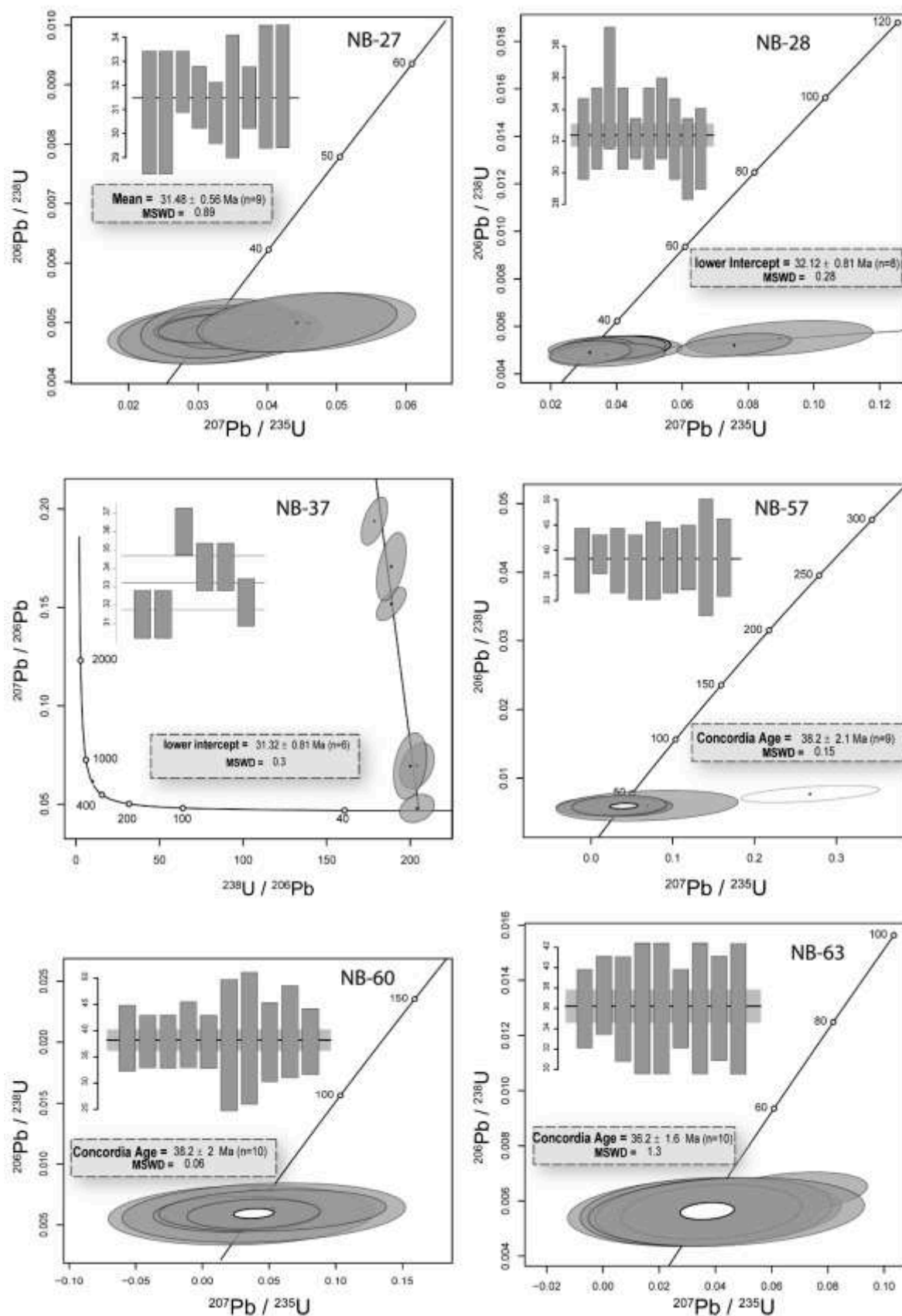
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	31.9	CS@5	3961	388	3.3E-08	2.2E-09	1733994930	3574847	4.94	0.09	5.56	0.18
NB-29	32.2	CS@6	-1886	-255	3.3E-08	2.2E-09	1715876533	3535435	4.25	0.10	4.87	0.21
	32.2	CS@7	-1315	4	3.2E-08	2.2E-09	1742816582	3589539	4.02	0.09	4.64	0.19
	32.2	CS@8	-1231	-117	3.2E-08	2.2E-09	1713924394	3531571	4.39	0.07	5.01	0.15
	32.2	CS@9	-818	-106	3.1E-08	2.2E-09	1722375714	3546810	3.83	0.07	4.45	0.16
	32.2	CS@10	-761	731	3.1E-08	2.2E-09	1750552926	3607440	4.53	0.09	5.15	0.19
NB-41	40.59	N22-B1@1	84	-3731	4.5E-08	1.8E-09	1322602465	2723179	2.16	0.10	5.15	0.21
	40.59	N22-B1@2	671	-3888	4.4E-08	1.8E-09	1272487606	2618133	1.39	0.13	4.37	0.27
	40.59	N22-B1@3	666	-3670	4.5E-08	1.8E-09	1077923391	2220648	2.15	0.21	5.14	0.43
	40.59	N22-B1@4	787	-3949	4.4E-08	1.7E-09	1214981984	2499006	0.74	0.13	3.73	0.26
	40.59	N22-B1@5	550	-4143	4.4E-08	1.7E-09	1029816372	2122327	2.17	0.17	5.15	0.34
NB-64	15.63	NB-64@1	3017	640	8.9E-08	1.8E-09	1417327839	2916047	1.81	0.16	4.79	0.33
	15.63	NB-64@2	3410	675	8.7E-08	1.9E-09	1364154495	2807807	1.98	0.09	4.97	0.20
	15.63	NB-64@3	3633	999	8.6E-08	1.9E-09	1357334286	2789314	0.01	0.14	2.99	0.30
	15.63	NB-64@4	3044	1643	8.3E-08	1.9E-09	810415665	1671079	0.93	0.23	3.91	0.47
	15.63	NB-64@6	4219	110	8.0E-08	1.8E-09	1389981716	2861101	2.20	0.09	5.18	0.20



Supplementary Fig. 1. Cathodoluminescence (CL) images of zircon from representative samples.

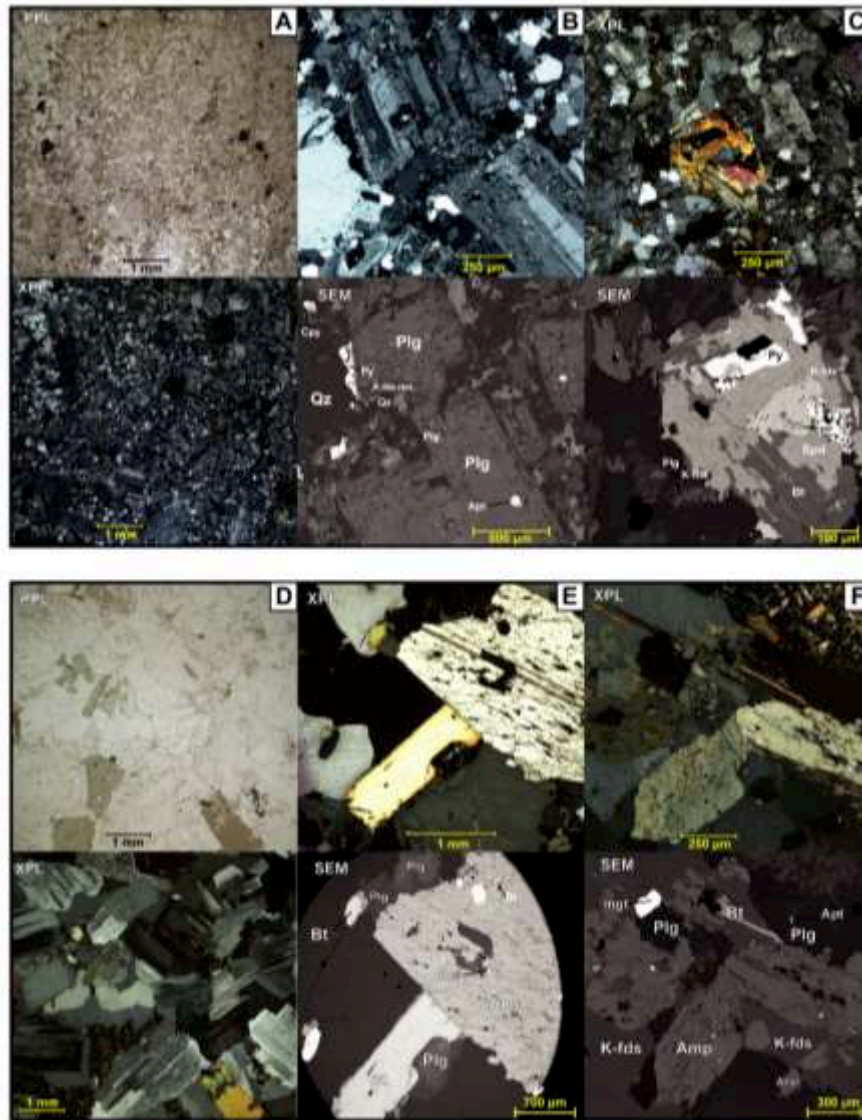




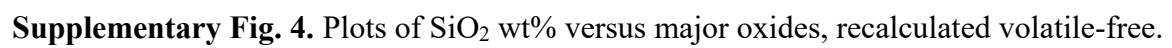


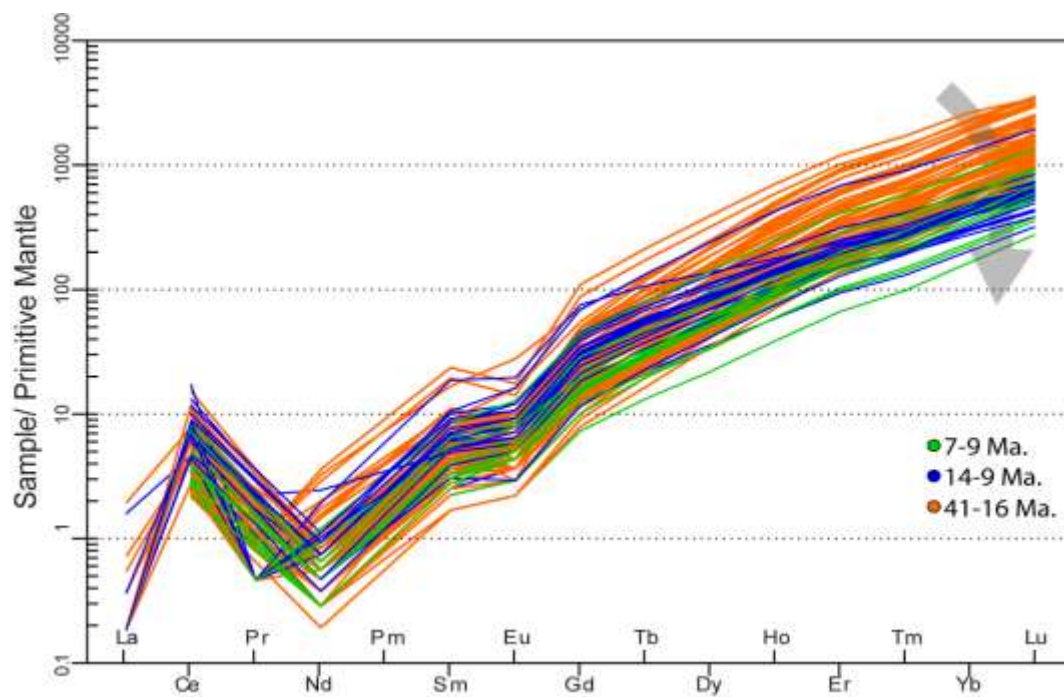
Supplementary Fig. 2. U-Pb Concordia and inverse Concordia diagrams. Open symbols represent analyses that were excluded from the final age determination (details provided in the

supplementary Table 2). MSWD – mean square weighted deviation, n– number of grains dated. Errors are given in 2σ . The Mean Square of Weighted Deviates (MSWD) is reported, reflecting the combined assessment of equivalence and concordance.

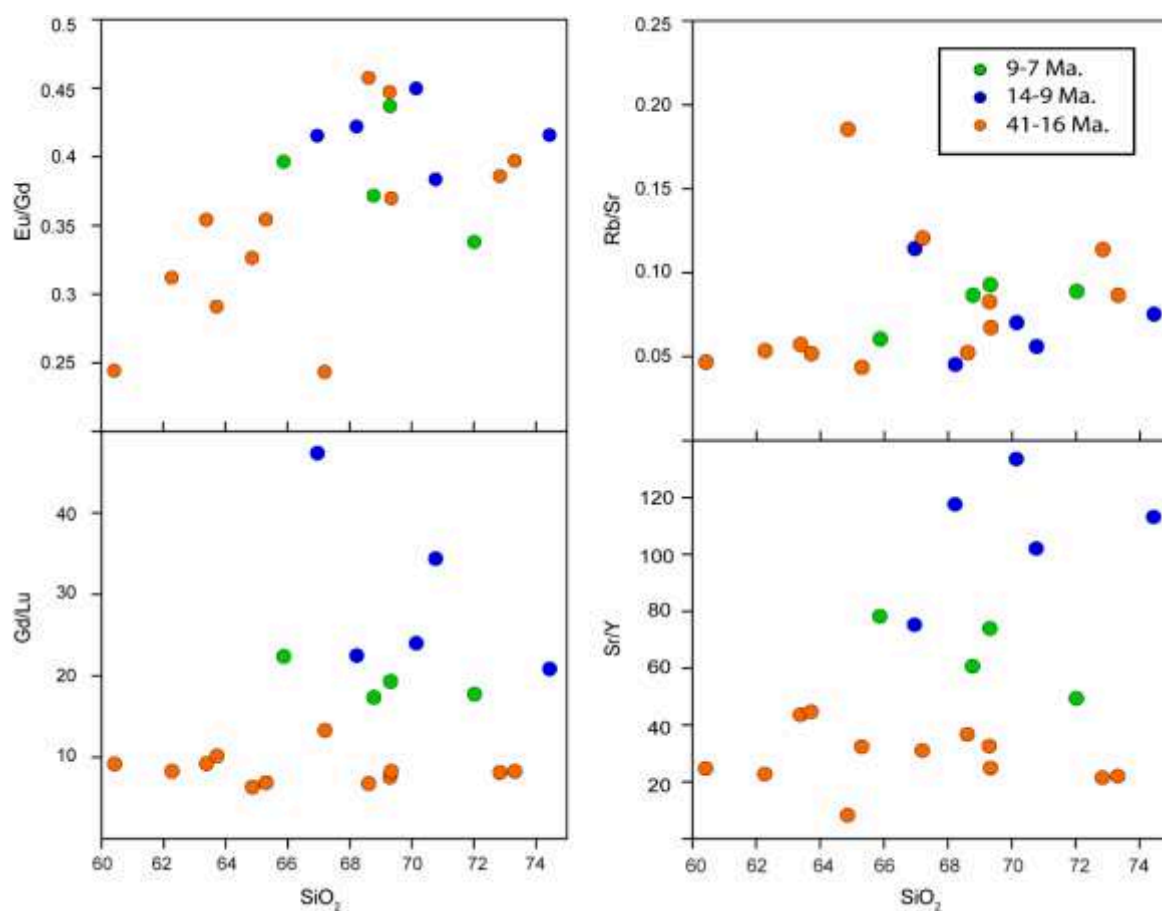


Supplementary Fig. 3. Petrographic light microscope images (PPL-XPL) and scanning electron microscope (SEM) images showing the textural and compositional features of tonalite NB-60 (A, B, C) and granodiorite NB-64 (D, E, F).



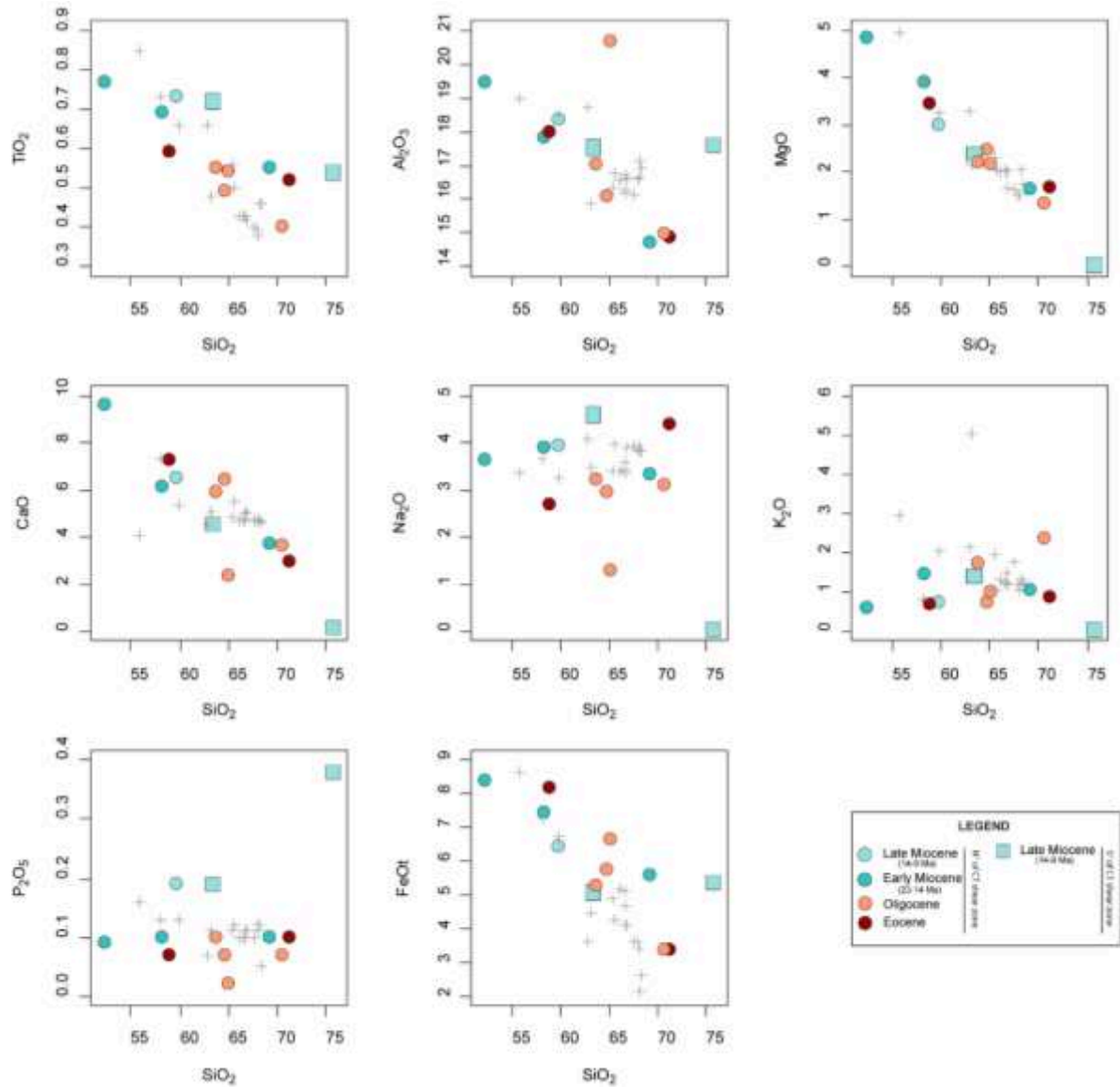


Supplementary Fig. 5. Zircon REE patterns primitive mantle normalized.

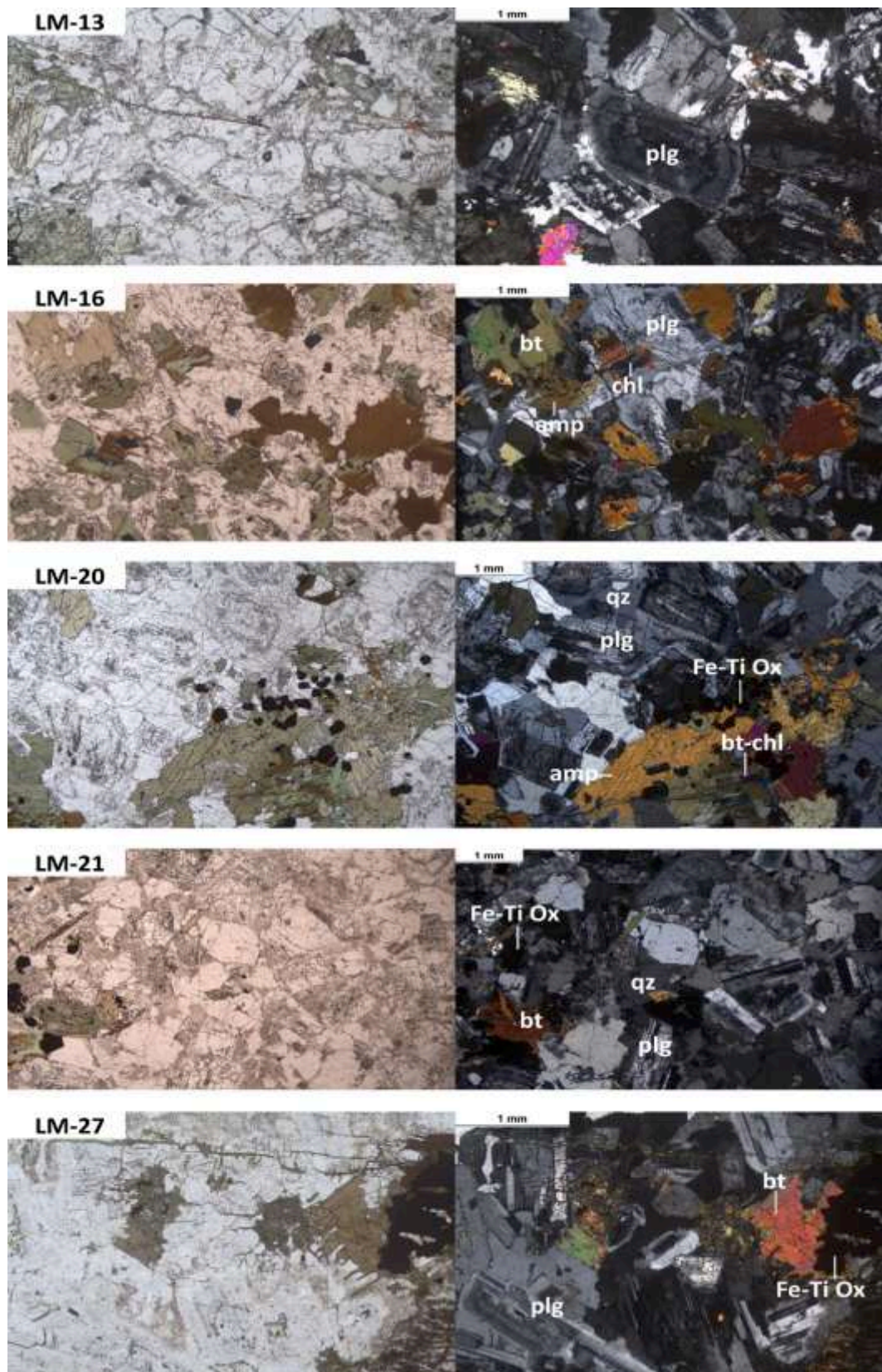


Supplementary Fig. 6. Features of adakite-type magmas

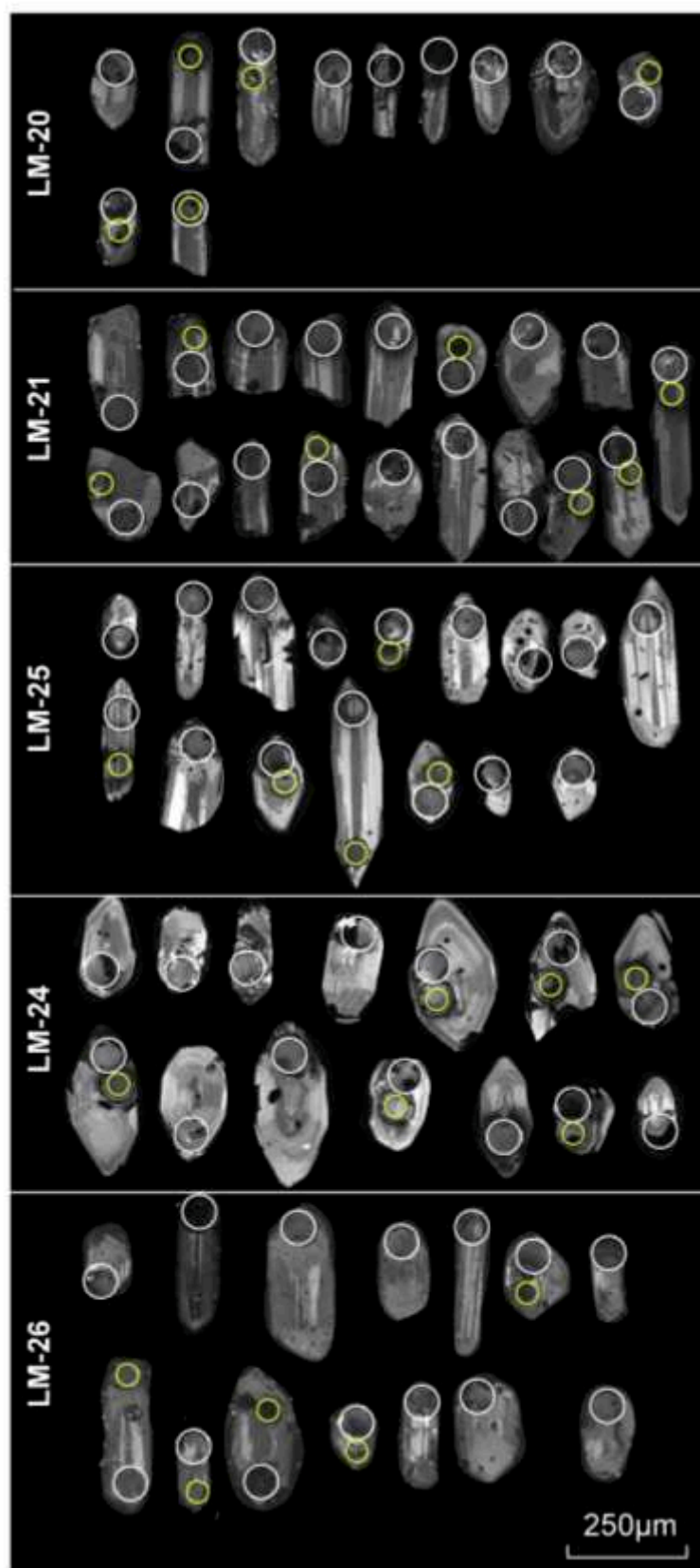
APPENDIX 2: Supplementary data for Chapter 4



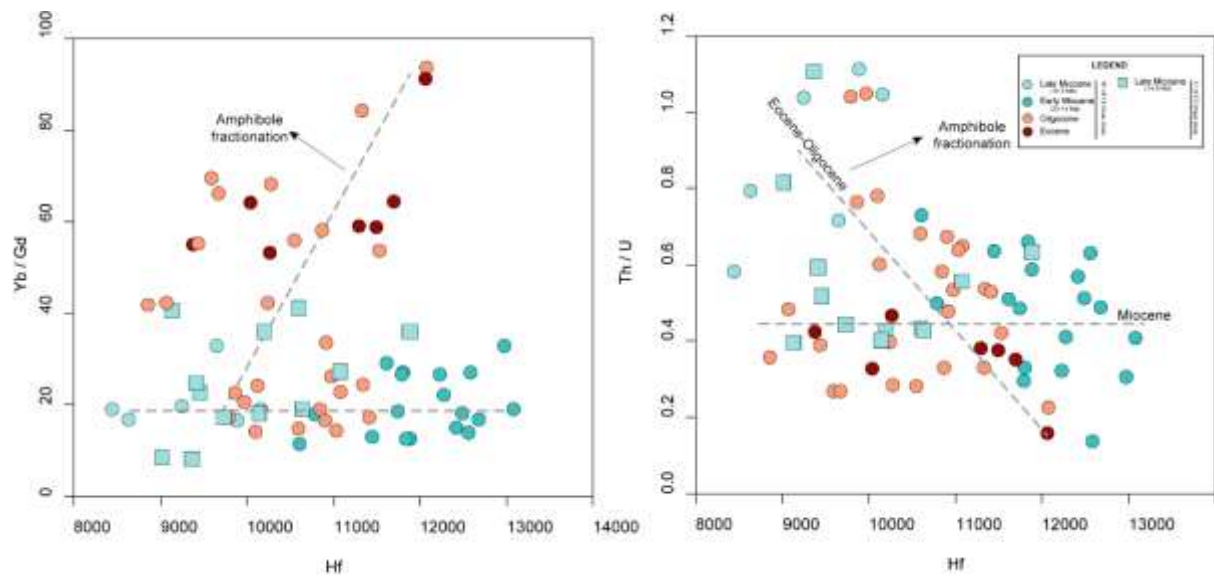
Supplementary Figure 1. Harker diagrams for the analyzed plutons, showing variations in major element compositions. SiO₂ vs. (TiO₂, Al₂O₃, MgO, CaO, Na₂O, K₂O, P₂O₅, FeOt).



Supplementary Figure 2. Pictures of representative thin sections in plane-polarized light (PPL; left) and cross-polarized light (XPL; right) from the analyzed plutons. Minerals coded as follow quartz (Qz), plagioclase (Plg), biotite (Bt), amphibole (Amp), chlorite (chl), Fe-Ti oxides (Fe-Ti Ox).

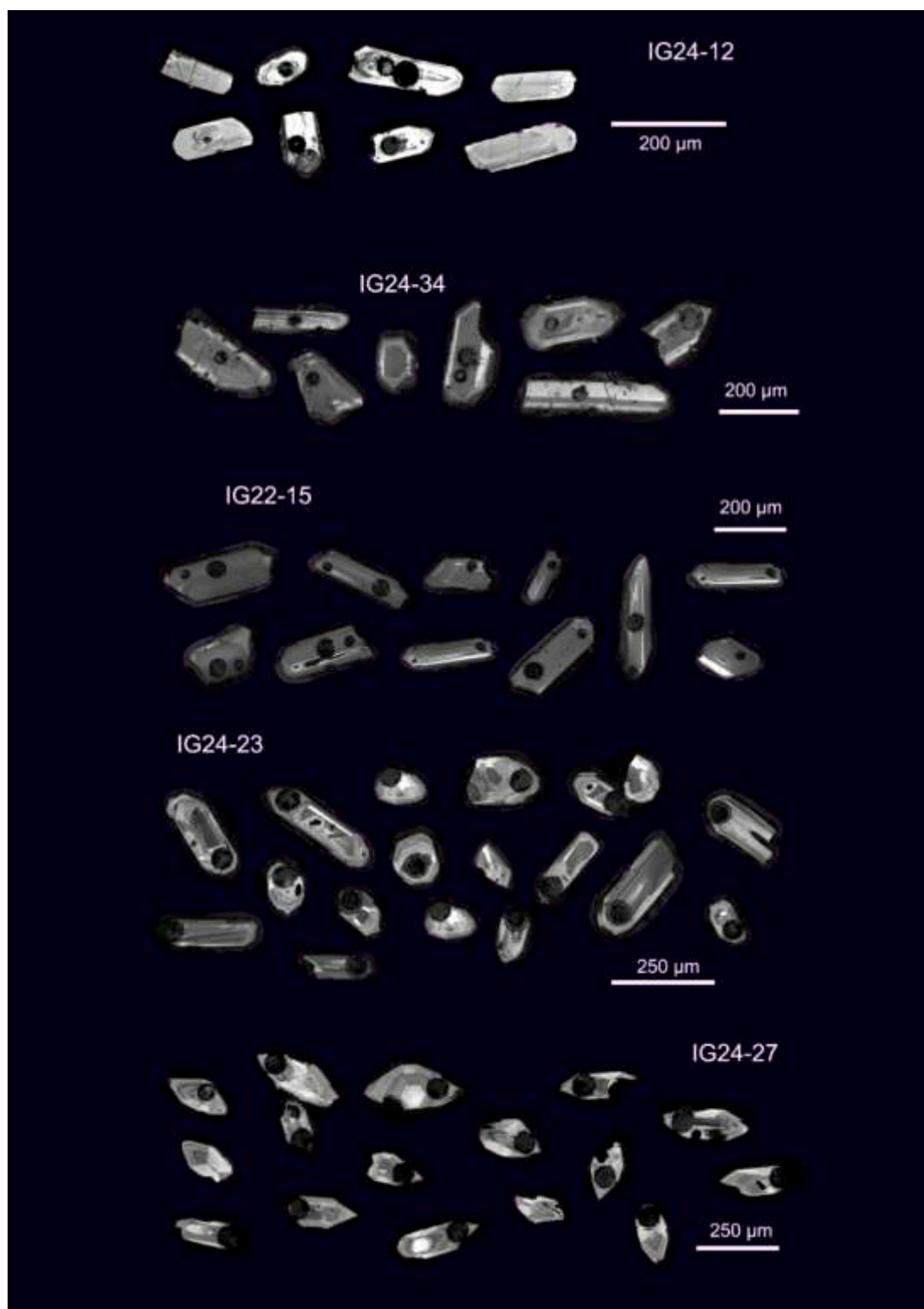


Supplementary Figure 3. CL images of zircon grains from the studied plutons. White circles: U-Pb dating spots; yellow circles: Hf isotope analysis.

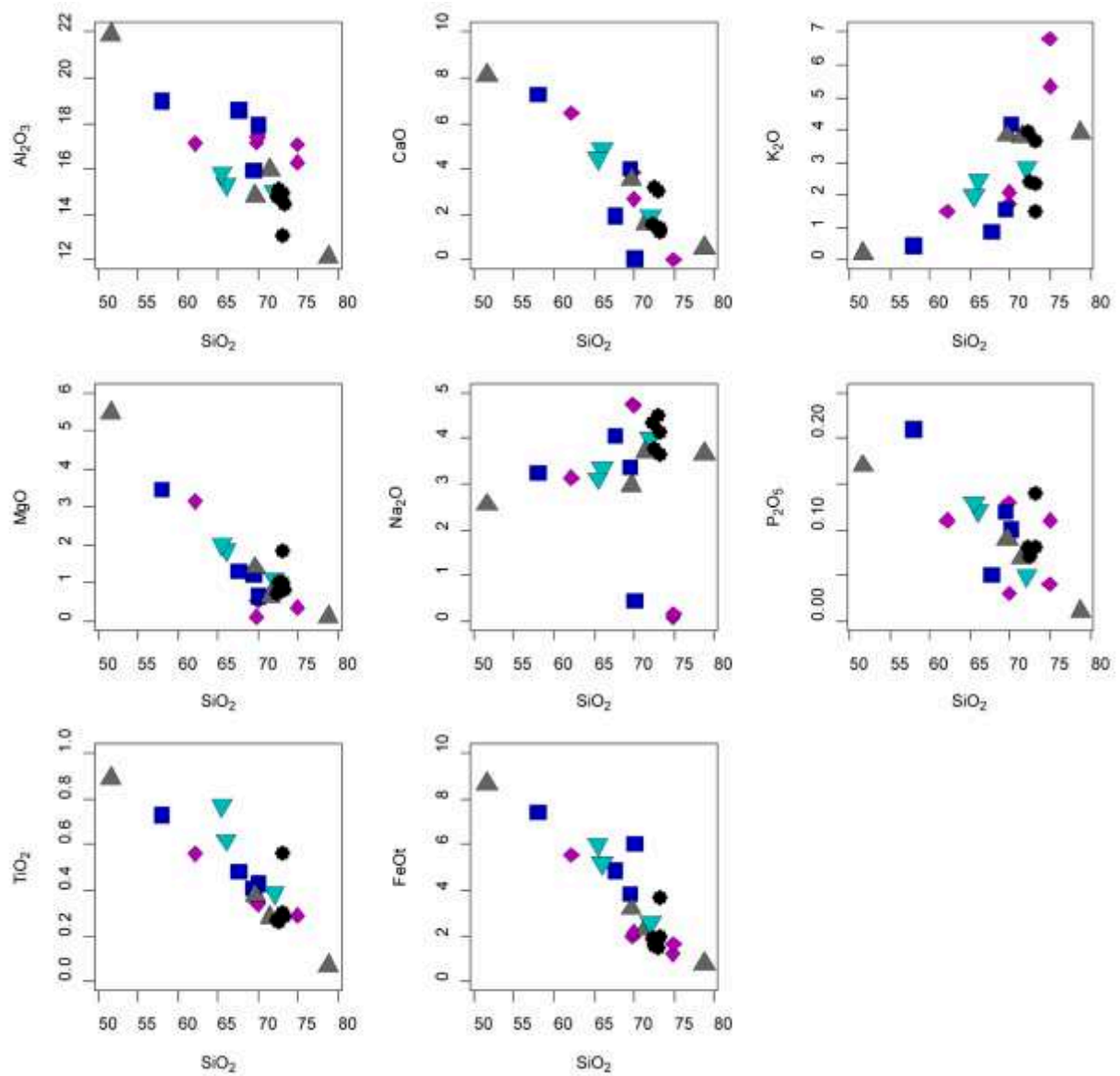


Supplementary Figure 4. Zircon trace-element ratios versus Hf content. (A) Yb/Gd vs. Hf and (B) Th/U vs. Hf. Dashed lines highlight trends associated with amphibole fractionation and shifts from Eocene–Oligocene to Miocene magmatism.

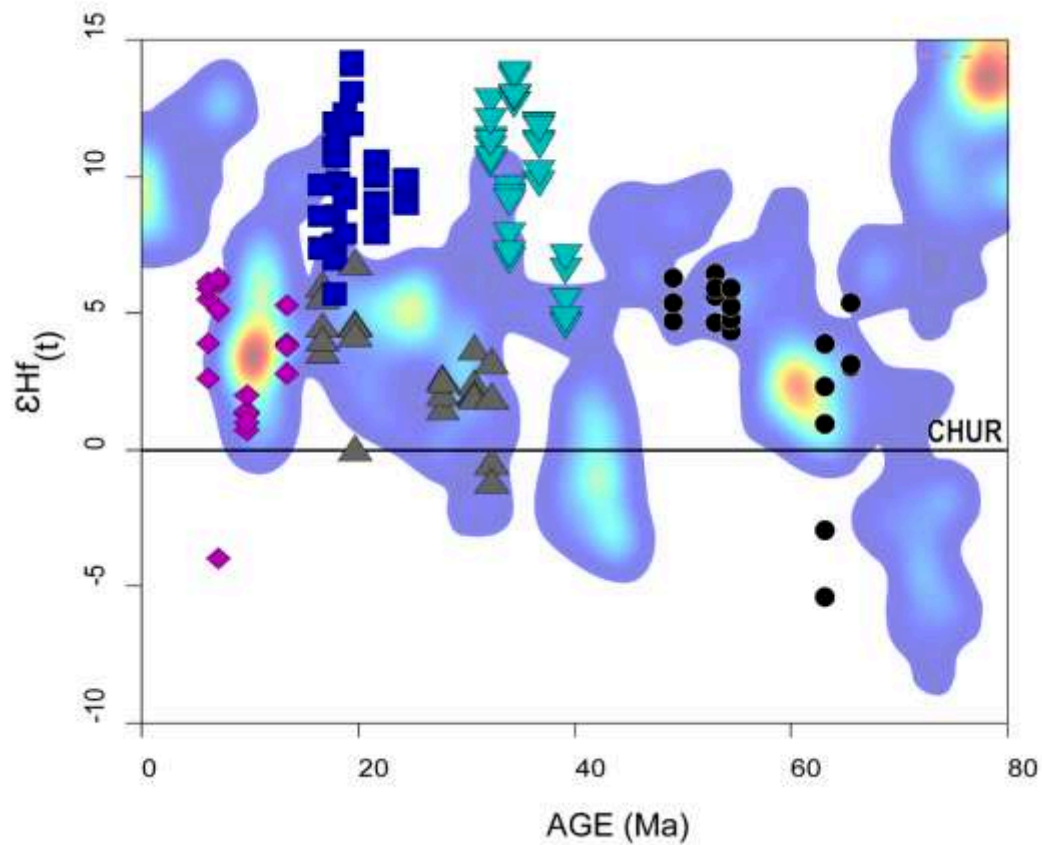
APPENDIX 3: Supplementary data for Chapter 5



Supplementary Figure 1. Cathodoluminescence images of zircon crystals from representative samples (IG24-12, IG24-34, IG22-15, IG24-23, IG24-27) showing a variety of zoning patterns and internal morphologies. Dark circular dots indicate laser ablation spots from U-Pb-Hf isotopic analysis.



Supplementary Figure 3. Harker diagrams.



Supplementary Figure 4. Zircon $\epsilon_{\text{Hf}}(t)$ data vs crystallization age. Base heat map corresponds to detrital data plotted as a two-dimensional bivariate kernel density estimate (KDE) with 95% contour from peak intensity (method after Sundell et al., 2019). Detrital data compiled from George et al. (2019), Witt et al. (2023), and references therein. CHUR—chondritic uniform reservoir.

APPENDIX 4: Mesozoic (240 to 90 Ma) magmatism in the Andes of southern Ecuador – northern Peru: constraints geodynamic insights from whole-rock chemistry and zircon petrochronology



Mesozoic magmatism in the Andes of southern Ecuador and northern Peru: Tectonic insights from whole-rock chemistry and zircon petrochronology

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Leidy Carolina Sandoval Espinel, Cesar Witt, Jorge Iglesias, Massimiliano Zattin, Olivier Bruguier, et al.. Mesozoic magmatism in the Andes of southern Ecuador and northern Peru: Tectonic insights from whole-rock chemistry and zircon petrochronology. *Lithos*, 2026, 522-523, pp.108389. 10.1016/j.lithos.2025.108389 . insu-05440656

HAL Id: insu-05440656

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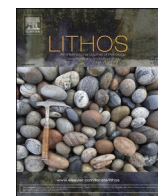
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Mesozoic magmatism in the Andes of southern Ecuador and northern Peru: Tectonic insights from whole-rock chemistry and zircon petrochronology

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ARTICLE INFO

Keywords:

Northern Andes
Zircon petrochronology
Hf–O isotopes
Subduction magmatism

ABSTRACT

The southern Ecuador–northern Peru region marks the transition between the northern and central Andes. This study reconstructs the Mesozoic magmatic history of this key region by integrating petrography, U–Pb geochronology, whole-rock and zircon geochemistry, and $\epsilon\text{Hf}(t)$ and $\delta^{18}\text{O}$ zircon isotopic data from plutonic rocks. Our results indicate that much of the Mesozoic magmatism occurred in an extensional arc setting, with magmatic reservoirs progressively incorporating more depleted, mantle material, while crustal contributions diminished through time. Magmatic reservoirs evolved both spatially and temporally, beginning with an extensive Triassic arc dominated by granitoids exhibiting strong crustal signatures at least until 220 Ma. This was followed by mildly enriched signatures associated with a stationary Jurassic to Early Cretaceous arc active between ~190 and ~126 Ma. Somewhere in between 126 and 104 Ma, the arc underwent a significant westward migration, potentially driven by slab rollback, which coincided with the opening of the Celica–Lancones Basin and the subsequent emplacement of the Late Cretaceous Celica–Lancones arc onto oceanic basement. This migration is consistent with westward shifts observed in central Ecuador and Colombia but contrasts with coeval eastward migration documented in central and southern Peru. In addition, new U–Pb ages challenge current interpretations of a missing Jurassic arc in northern Peru by providing clear evidence that Jurassic magmatism extended at least as far south as 6°S.

1. Introduction

The evolution of arc magmatism at convergent margins is governed by complex interactions between subduction dynamics, mantle flow, and tectonic processes. Variations in slab geometry, including changes in dip, rollback, and flat-slab development, strongly influence mantle wedge circulation, melt generation, and the thermal structure of the overriding lithosphere (Ducea et al., 2015). These processes exert control over the spatial and temporal distribution of magmatic arcs. For instance, observed trenchward or landward arc migration, as well as intervals of magmatic quiescence, are commonly interpreted as the

surface expression of such changes in subduction geometry. Documenting these shifts through time is therefore fundamental for reconstructing the tectonomagmatic evolution of long-lived subduction systems.

The Andean belt developed above the subduction margin of the oceanic Nazca Plate (formerly part of the Farallon Plate) beneath the South American continent (DeCelles et al., 2009). Its northern segment records a particularly intricate evolution, shaped by the accretion of oceanic terranes, changes in subduction direction, episodic magmatism, and multiple exhumation events (Iglesias et al., 2025; Jaillard, 2025; Spikings et al., 2010; Spikings et al., 2015; Vallejo et al., 2009; Witt

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<https://doi.org/10.1016/j.lithos.2025.108389>

Received 19 August 2025; Received in revised form 20 December 2025; Accepted 20 December 2025

Available online 26 December 2025

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et al., 2023). Despite recent advances in reconstructing the long-term magmatic and tectonic evolution of the Northern Andes (Boekhout et al., 2012; Carrasco et al., 2023; Chavarría et al., 2022; Cochrane et al., 2014; Duan et al., 2022; Jaillard, 2022; Pratt et al., 2005; Riel et al., 2014; Sandoval-Espinel et al., 2025; Vallejo et al., 2009; Winter et al., 2010; Witt et al., 2017), the southernmost part, encompassing southern Ecuador and northern Peru, remains poorly understood and is still subject to contrasting interpretations (see Bustamante et al., 2016; Cochrane et al., 2014; Spikings et al., 2015).

These uncertainties primarily reflect the limited availability of high-precision geochronological datasets. Most of the existing age constraints

in this region are derived from the ^{40}Ar – ^{39}Ar and K–Ar analyses of minerals such as muscovite, hornblende, and biotite (e.g., Baldock, 1977; Cochrane et al., 2014; Feininger & Silberman, 1982; Hama, 1990; Litherland, 1994; Spikings et al., 2010; Winter, 2008; Table S1; Fig. S1). While these datasets have provided valuable temporal references, they are often affected by thermal resetting and may not accurately reflect magmatic crystallization ages. In contrast, zircon U–Pb dating offers a more robust chronometer, as zircon is a refractory and chemically resistant mineral that usually retains the composition of its parent magma during subsequent metamorphic or hydrothermal processes. Furthermore, when zircon U–Pb ages are combined with zircon

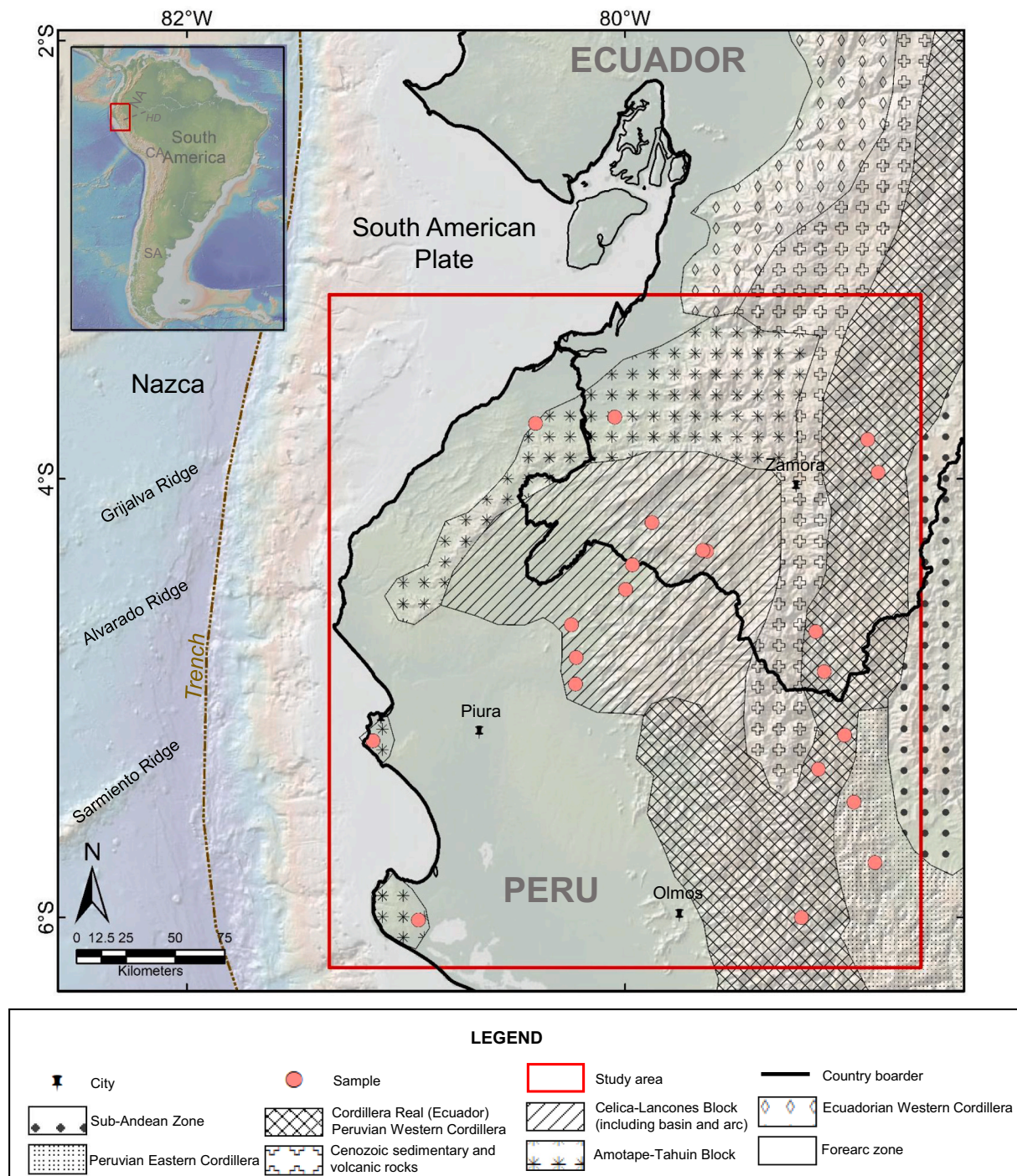


Fig. 1. Geological sketch of northern Peru and Ecuador, showing major units, the study area, and sample locations. CA: Central Andes. HD: Huancabamba Deflection. NA: Northern Andes. SA: Southern Andes.

geochemistry and Hf—O isotopic data, both the timing of magmatism and the nature of magma sources can be constrained simultaneously. However, such high-precision and integrated datasets remain extremely scarce in southern Ecuador and northern Peru, limiting our ability to test competing Mesozoic evolutionary models for this region (e.g., Duan et al., 2022; Spikings et al., 2015), and to accurately constrain the spatiotemporal evolution of magmatism and its sources in this segment of the Andes.

This study integrates U—Pb zircon geochronology, petrographic analysis, and whole-rock and zircon geochemistry for plutonic rocks from the southernmost Northern Andes (~4–6°S). Our new data refine the temporal and geochemical evolution of Mesozoic magmatism in southern Ecuador and northern Peru between 240 and 90 Ma. These results allow us to reassess the timing of arc migration and to propose an updated tectonomagmatic model linked to changes in magmatic reservoirs.

2. Geotectonic framework

2.1. Tectonic background

The Northern Andes spans from Venezuela to northern Peru (Jaillard et al., 1990). The region is separated from the Central Andes by the Huancabamba Deflection, located at approximately 6°S. This zone marks a change in the orientation of the Andean chain from N20°E in the north to N20°W in the south (Fig. 1). Magmatic activity along the Northern Andes is driven by the interaction between the South American Plate with a series of oceanic plate systems, producing a long-lived subduction system characterized by episodic magmatism from the Carboniferous to the Holocene (Horton, 2018; Jaillard et al., 2000).

During the early Mesozoic, the western South American margin was subjected to an extensional regime contemporaneous with voluminous

magmatic activity between ~265 and ~215 Ma (Leal-Mejía et al., 2019; and references therein). This magmatism was driven by prolonged high mantle heat flow and crustal anatexis (e.g., Cochran et al., 2014; Riel et al., 2018). Models proposed for this Triassic magmatic event during the breakup of Pangea can be broadly classified into: (i) those that interpret magmatism as arising from non-subduction processes (Fig. 2; Carrillo et al., 2021; Cochran et al., 2014; Spikings et al., 2015) and (ii) those invoking active subduction (e.g., Riel et al., 2018; Villares et al., 2020). Regardless of the model, studies have shown that crustal reworking during this period resulted in the formation of S-type Triassic granitoids emplaced along the Real Cordillera (including the Sub-Andean zone) and the Amotape–Tahuin block (ATB) in Ecuador (Fig. 1; Aspen et al., 1992; Litherland, 1994; Riel et al., 2014; Sandoval-Espinel et al., 2025; Spikings et al., 2015) as well as in the southern and central segments of the Peruvian Eastern Cordillera (Mišковиć et al., 2009).

Subsequently, two competing hypotheses have been proposed for the Jurassic evolution of the margin. In the first scenario, subduction was re-established between ~209 and ~190 Ma (Cochran et al., 2014), marking the onset of a new continental arc along the South American margin. Alternatively, in the second scenario, oceanic subduction may have continued uninterrupted since the Triassic (Villares et al., 2020).

From both hypotheses, it is agreed that during the Jurassic, the Northern Andes experienced an extensional regime. This setting has been attributed to either (i) highly oblique convergence (Bustamante et al., 2016; Jaillard et al., 1990), or (ii) slab rollback, which drove the westward migration of the arc between 189 and 141 Ma from the present-day Cordillera Real to the Western Cordillera (Fig. 1; Cochran et al., 2014; Spikings et al., 2015). The Jurassic arc extends across much of the Northern Andes, with older crystallization ages (209–196 Ma) recorded in northern Colombia (e.g., Santander and Santa Marta massifs; Van der Lelij, 2013; Villagómez et al., 2011), while younger ages

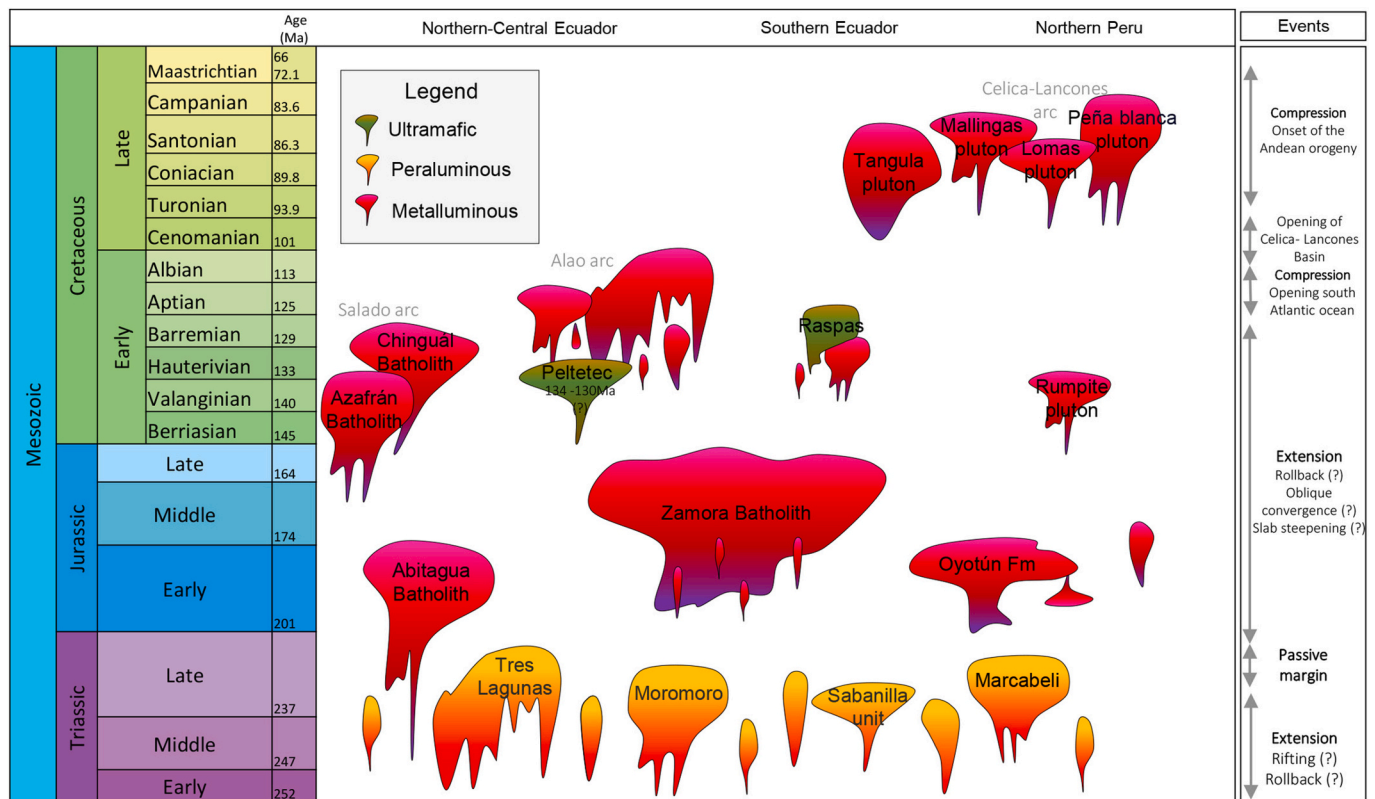


Fig. 2. (A) Overview of the Spatiotemporal distribution of Mesozoic magmatism in Ecuador and northern Peru, along with key tectonic and geodynamic events. The figure is based on data from CGS-INGEMMET (2017), Cochran et al. (2014), Feininger and Silberman (1982), Hama (1990), Litherland et al. (1994), Noble et al. (1997), Schutte et al. (2010), Spikings et al. (2010), Ulrich (2005), Winter (2008), Sandoval-Espinel et al. (2025), and this study.

(180–132 Ma) are reported in Ecuador (e.g., Ambitagua and Zamora batholiths; Chiaradia, 2009; Cochran et al., 2014). This distribution has been interpreted as a general southward-younging magmatic trend from northern Colombia to southern Ecuador (e.g., Spikings et al., 2015). In addition, Jurassic magmatism appears to be absent between 5°S and 12°S, either because an arc never formed in this region or because it was removed by subduction or erosion (Boekhout et al., 2012; Spikings et al., 2015).

The extensional regime persisted until the Early Cretaceous, contemporaneous with emplacement of the Peruvian Coastal Batholith within the Western Cordillera of Peru (Boekhout et al., 2012; Cochran et al., 2014; Miškovčić et al., 2009) as well as the formation of the Salado and Alao arcs in Ecuador (Fig. 3; Carrasco et al., 2023). The Salado Arc is located in northern and central Ecuador and consists of scattered metaluminous granitoids, such as the Azafrán Batholith (~145–140 Ma; Cochran et al., 2014) and the Chingual Pluton (~125 Ma; Spikings et al., 2015). The Alao Arc, located west of the Salado Arc, is composed of two distinct rock assemblages: (i) metaluminous volcanic rocks, formed between ~140 and 110 Ma (Carrasco et al., 2023), and (ii) the E-MORB-like basalts of the Peltetec Complex (130–134 Ma; Gabriele, 2002; Spikings et al., 2015). Notably, rocks with lithological similarities to these E-MORB-like basalts have been identified in the ophiolitic succession of the Rascas Complex in southern Ecuador (130–120 Ma), which has undergone metamorphism under blueschist to eclogite facies conditions (Gabriele, 2002; Riel et al., 2014). It should be noted, however, that recent U–Pb dating suggests that some units previously identified as Early Cretaceous in central Ecuador (west of the older arcs), such as the Peltetec Complex, may instead be Triassic in age (~228 Ma; Villares et al., 2020).

It is likely that the continuation of the extensional setting promoted the opening of the NE–SW Celica–Lancones Basin, situated between the Early Cretaceous volcanic arc and the ATB, as evidenced by rift-related volcanism within the basin (Jaillard et al., 1999; Mourier, 1988; Winter et al., 2010). Basalt-dominated volcanism dated at 104.8 ± 1.3 to 100.2 ± 0.5 Ma (Winter et al., 2010) marked the deep rifting stage of the basin and suggests that its onset is at least middle Albian in age.

Around ~100 Ma, active seafloor spreading in the South Atlantic and the resulting westward drift of the South American Plate triggered a tectonic shift from extension to compression (Jaillard, 2025; and references therein). This transition led to the development of the Early to Late Cretaceous Celica–Lancones Arc (~110–78 Ma; Schütte et al., 2010; Soler, 1991; Winter, 2008), which extends across southern Ecuador and northern Peru (Figs. 1 and 3). This arc is mainly composed of andesitic lavas, pyroclastic deposits, and intrusive bodies, including the Tangula pluton in southern Ecuador and the Peña Blanca, Lomas, and Mallingas plutons in northern Peru (Fig. 2; Schütte et al., 2010; Winter, 2008). Due to the limited geochemical and geochronological constraints in this region, the Celica–Lancones Arc has been tentatively genetically linked to the subduction system that formed the Alao Arc (Jaillard et al., 1999; Spikings et al., 2015). Further south, in central and southern Peru, evidence of this compressional regime is recorded by localized folding and faulting, the cessation of marine sedimentation, and the widespread emplacement of large intrusive bodies that contributed to the final stages of the formation of the Peruvian Coastal Batholith (Martínez-Ardila et al., 2023; and references therein).

3. Analytical methods

Nineteen samples were obtained from igneous outcrops located between 3.5 and 6°S in southern Ecuador and northern Peru. Sample locations and their corresponding nomenclature are provided in Table S2 and illustrated in Fig. 3.

3.1. Petrographic analyses

Twelve samples were selected for petrographic analyses. Hence,

rocks were cut using a diamond saw and then ground and polished until they reached a thickness of about 30 μm , employing progressively finer abrasives. Posteriorly, thin sections were examined at 50–500 $\times$ magnification using a Leica petrographic microscope and photographed under plane and cross-polarized transmitted light at Padova University. Results are shown in Table S3 and Fig. 4.

3.2. LA-ICP-MS zircon U–Pb dating

Zircons were separated by crushing, sieving, magnetic and heavy liquid concentration at the laboratory of thermochronology in the Universidad Pedagógica y Tecnológica de Colombia, UPTC. Subsequently, hand-picked and mounted in epoxy blocks and polished on a lap wheel with a 9 μm , 6 μm and 3 μm diamond suspension successively, until reveal crystal surfaces.

Cathodoluminescence (CL) imaging was performed in order to recognize different micro-area compositional heterogeneities within a crystal before analysis (Fig. S2). Imaging acquisition was performed using a cold cathodoluminescence model 8200 MkII equipment mounted in an Olympus BX41 microscope at Lille university.

Zircon U–Pb dating was conducted using a LA-ICP-MS at the Geo-HeLiS analytical platform (OSUR, Univ. Rennes) using an ESI NWR193UC Excimer laser coupled to a quadrupole Agilent 7700 $\times$ ICP-MS equipped with a dual pumping system to enhance sensitivity. The instrumental setup is presented in Table S4. Additional information can be found in Witt et al. (2017).

Data was analyzed using the ISOPLLOT package program; $^{206}\text{Pb}/^{238}\text{U}$ dates were used since zircons are younger than 1Ga. We only report concordant ages (90 % to 110 % concordance), while, errors are reported at 2 sigma level. U–Pb data and calculated ages can be found in table S5, while quality control reference materials data (Plešovice and GJ1) are on Tables S6 and S7, respectively. Representative concordia and weighted diagrams are presented in Fig. 5.

3.3. ICP-AES whole rock geochemistry

Samples were washed with distilled water to remove impurities. Fresh, unaltered portions were then selected and crushed at Lille university using an agate mortar pulverizer to obtain a < 50 mesh size fraction. This portion was further pulverized using an agate ball mill to achieve a particle size of <10 μm .

Whole-rock major and trace elements were determined for fifteen samples at the Institut Universitaire Européen de la Mer, Université de Bretagne Occidentale (Brest, France) using a Jobin Yvon Ultima 2 inductively coupled plasma atomic emission spectrometer (ICP-AES). Sample preparation followed the procedure outlined by Cotten et al. (1995), which included digestion with HF and HNO₃, neutralization with boric acid, and subsequent dilution in nitric acid. Calibration was performed using international standards (AC-E, BEN, JB-2, PM-S, and WS-E) along with internal standards (MORB-E, CB2, CB15, and CB18), ensuring reliable external reproducibility. Relative standard deviations are <2 %, except for low values (< 0.50 wt%), for which the absolute standard deviation is ± 0.01 wt%.

The geochemical data were processed using the IgRoCS computer program (Verma and Rivera-Gómez, 2013). This software accurately partitions total iron into its two oxidation states (FeO and Fe₂O₃) and normalizes the sum of major oxides to 100 % on an anhydrous basis. Major and trace element concentrations are listed in Table S8.

3.4. Hafnium analysis

Hafnium isotopic compositions of zircon are largely controlled by the time elapsed since a melt is removed from the mantle, whereby recently removed melts display more juvenile isotopic signatures than rocks with longer crustal residence time.

Lu–Hf isotopes analysis were performed at Géosciences Montpellier

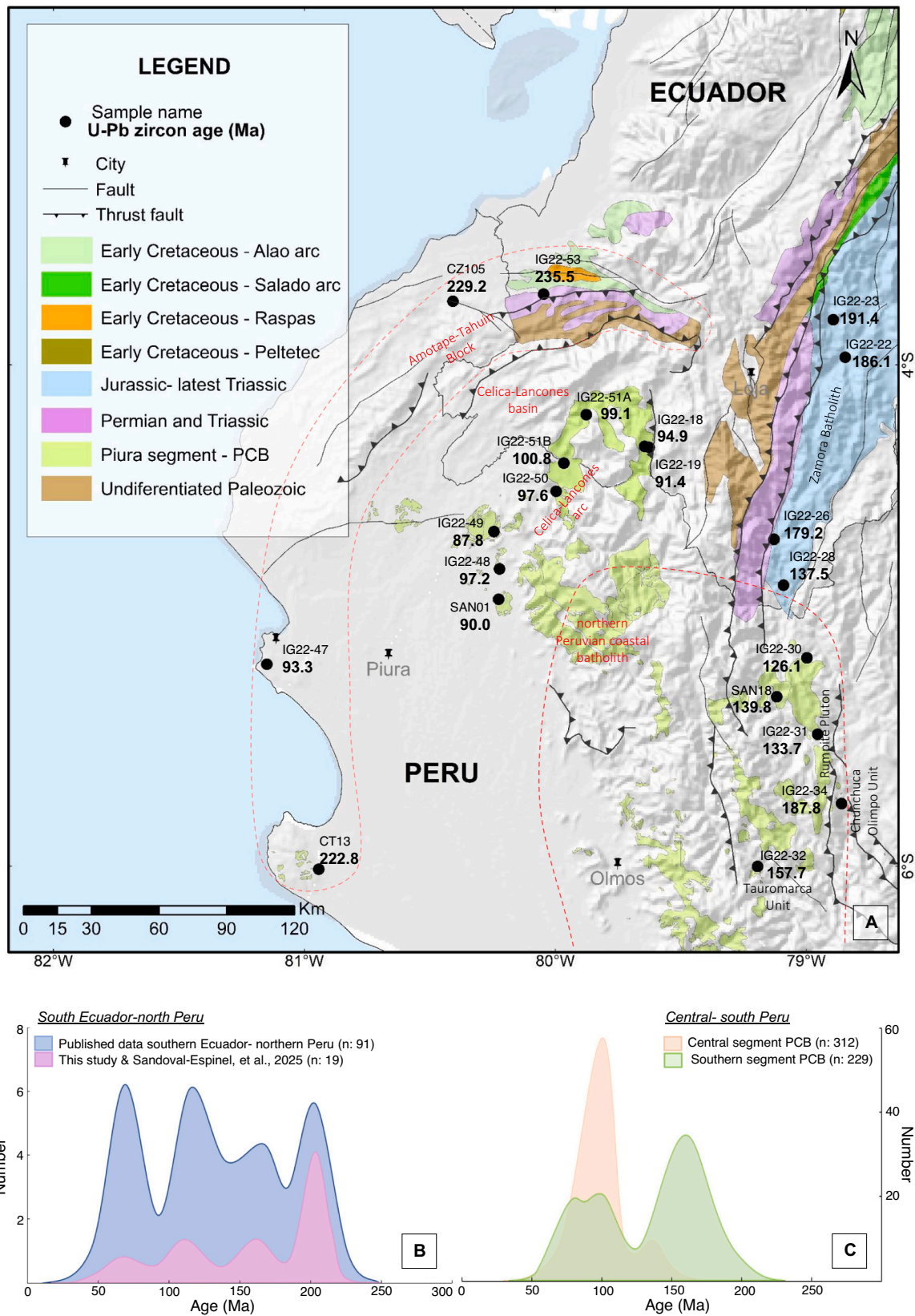


Fig. 3. (A) Map of the study area showing sample locations with their corresponding U–Pb zircon ages. The geological background includes Ordovician to Cretaceous units, while all Cenozoic units are shown in gray. (B) Age distribution functions for the geochronological data from the study area. (C) Age distribution functions for geochronological data from the central and southern segments of Peru, as reported by [Martínez-Ardila et al. \(2023\)](#). Only in situ rock data with ages between 66 and 250 Ma were included. Age spectra were generated using IsoplotR with a kernel bandwidth of 10 Ma for all graphs.

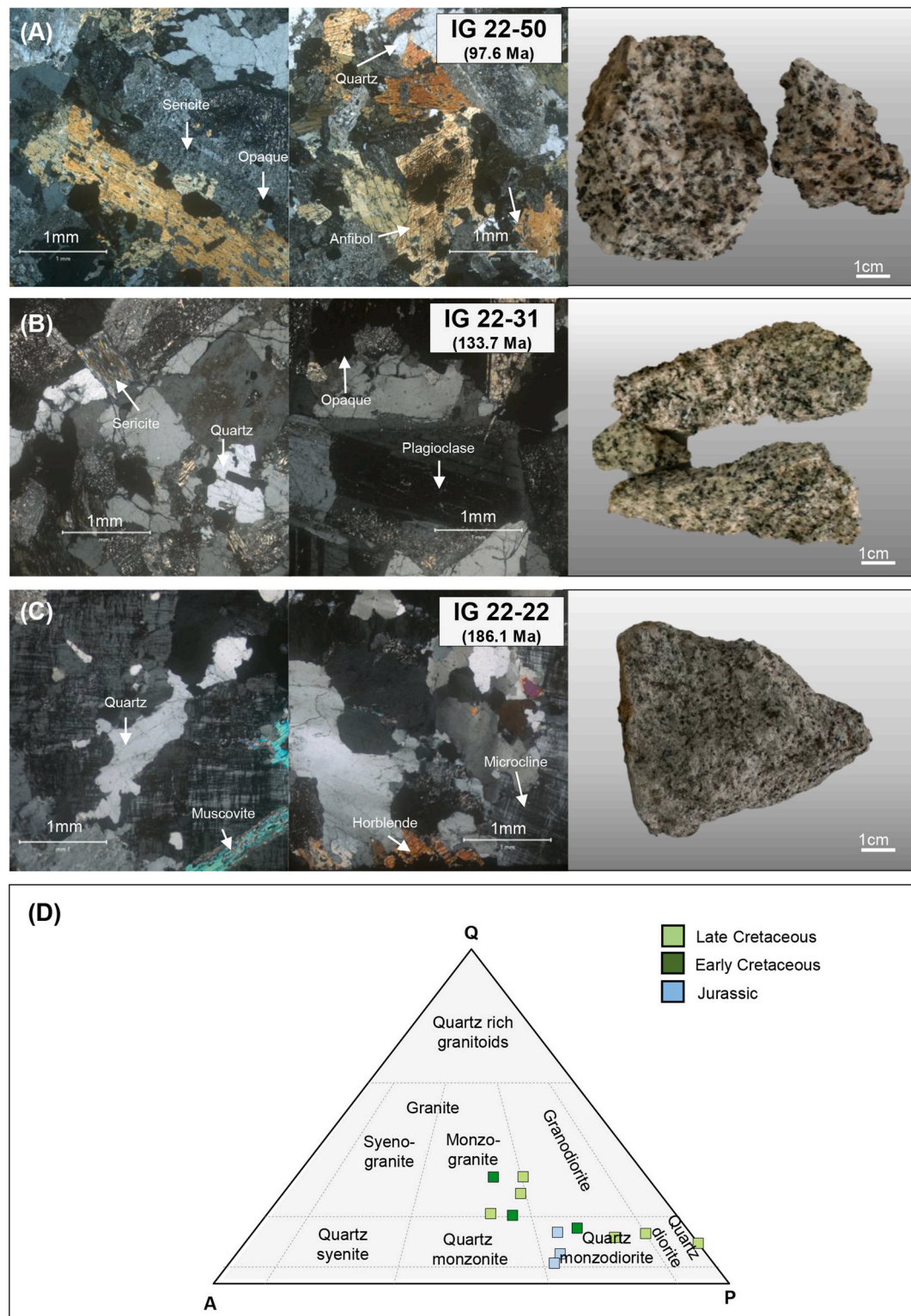


Fig. 4. (A–C) Photomicrographs of Mesozoic rocks displaying main mineral assemblages and Hand-size samples. (D) QAP diagram (Streckeisen, 1974) used to classify intrusive igneous rocks based on their mineralogy. Q, quartz. A, alkali feldspar. P, plagioclase.

Laboratory, University of Montpellier, France (AETE–ISO regional facility of the OSU OREME) using a ThermoFinnigan Neptune+MC–ICP–MS (multicollector–inductively coupled plasma–mass spectrometer) coupled with a Photon-Machine Analyte G2 Excimer laser (193 nm wavelength); where ablation was performed using a 50 μm spot size, the laser frequency was 6 Hz and a fluence of 4.5 J/m². During the measurements, three zircon standards (91,500, GJ1 and Plešovice) with

reference values taken from Blichert-Toft (2008); Morel et al. (2008); and Sláma et al. (2008); were treated as unknown in order to check the quality and the reproducibility of the data. All values were found to be in agreement with their references: 91,500 ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282305 \pm 0.000020$, $n = 31$), GJ1 ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282005 \pm 0.000036$, $n = 23$), and Plešovice ($^{176}\text{Hf}/^{177}\text{Hf} = 0.282486 \pm 0.00001$, $n = 21$).

Hafnium isotopic data are expressed with the epsilon notation

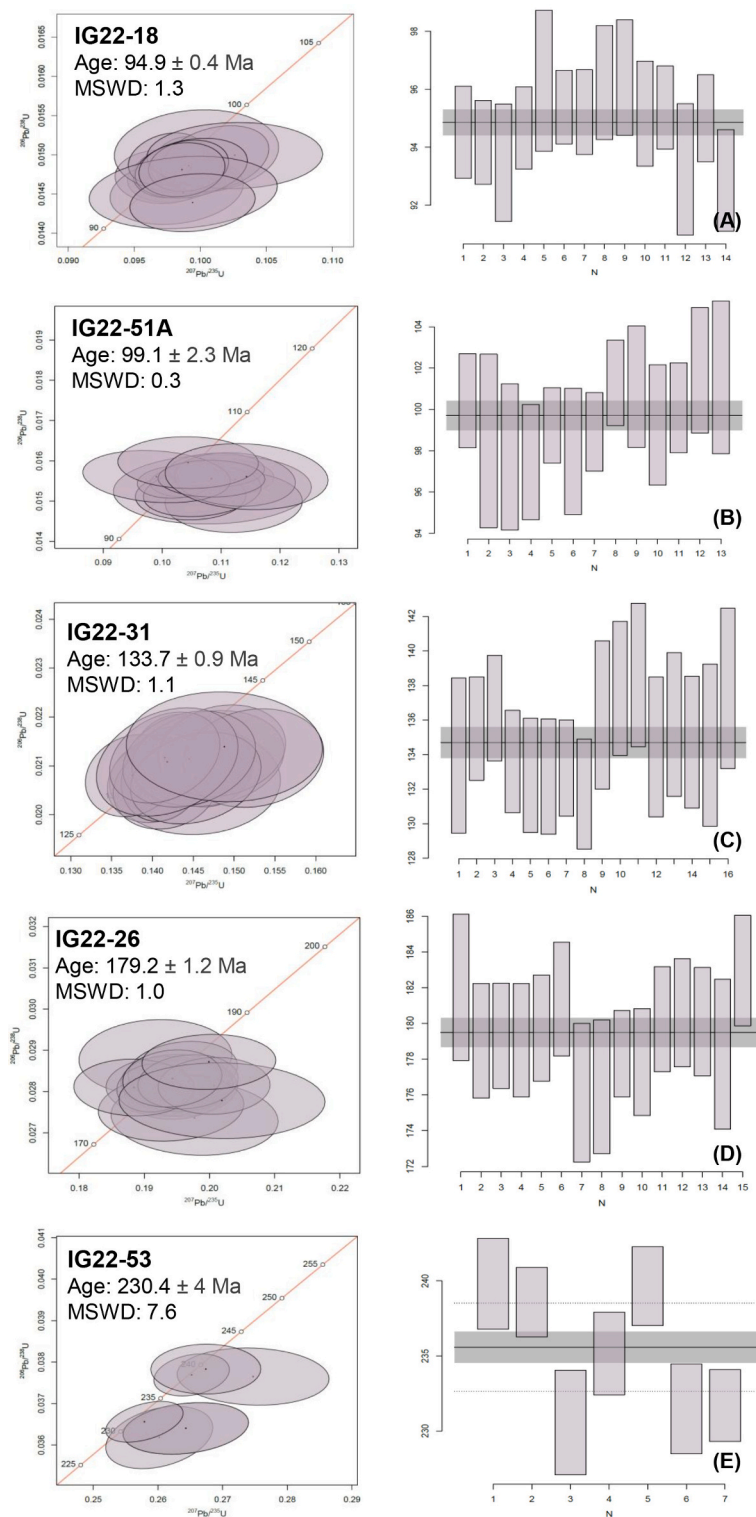


Fig. 5. Concordia (left) and weighted mean age (right) diagrams for selected samples, showing representative ages. Errors are expressed at 2σ . Plots were generated using ISOPLLOT (Ludwig, 2003). (A) Sample IG22–18. (B) Sample IG22–51 A. (C) Sample IG22–31. (D) Sample IG22–26. (E) Sample IG22–53.

($\epsilon\text{Hf}_{(t)}$), representing the deviation of $^{176}\text{Hf}/^{177}\text{Hf}$ measured in a sample from the chondritic uniform reservoir (CHUR; Vervoort and Blichert-Toft, 1999), and presented in Table S9 within errors at 2 sigma level.

3.5. $\delta^{18}\text{O}$ analysis

Analysis of $\delta^{18}\text{O}$ in zircons are able to trace crust-mantle interaction

through time and intracrustal recycling. This record is especially sensitive because oxygen isotope ratios of igneous rocks are highly affected by the incorporation of supracrustal materials into melts, which usually have $\delta^{18}\text{O}$ values higher than primitive mantle magmas (Valley et al., 2005).

Oxygen isotopic compositions in zircon were measured using a Cameca IMS 1270 E7 ion microprobe at the Centre de Recherches

Péetrographiques et Géochimiques (CRPG, CNRS), Université de Lorraine, Nancy (France) using a Cs + primary ion beam accelerated at 10 kV with an intensity of 2.5 nA. The detection mode was FC/FC (Faraday cup) multicollection. Instrumental mass fractionation from 4.41 ‰ to 6.418 ‰ using BrF5 extraction and a gas source mass spectrometer.

Measured $^{18}\text{O}/^{16}\text{O}$ ratios were normalized using Vienna Standard Mean Ocean Water compositions (VSMOW, $^{18}\text{O}/^{16}\text{O} = 0.0020052$; Gonfiantini et al., 1995), then corrected for the instrumental mass fractionation factor (IMF), and reported within 1 sigma error (Table S10); further technical information can be found in Witt et al. (2023).

3.6. Trace elements analysis in Zircon

Zircon is a robust mineral known for its capacity to incorporate trace elements into its crystal lattice (Belousova et al., 2002; Grimes et al., 2007). This mineral demonstrates a remarkable resistance to chemical alteration, making it a powerful geochemical tracer for studying geological processes (Belousova et al., 2002). Rare Earth Elements found in zircons can provide insights into the conditions during which zircon crystallized, revealing information about the composition of parental magmas (Grimes et al., 2007; and references therein).

Zircon trace-element concentrations were measured at Géosciences Montpellier (University of Montpellier, AETE-ISO regional facility of the OSU OREME) using LA-ICP-MS, whose analytical platform includes a 193 nm ArF excimer laser (Teledyne G2) coupled to a Thermofinnigan Element XR mass spectrometer modified by the addition of an 80 m³/h Edwards primary pump in the interface to enhance sensitivity. The laser was operated at a repetition rate of 6 Hz, using a 50 µm spot size and a fluence of 4.5 J/m². The total analysis time was 120 s with the first 80 s used for background measurement prior to sample ablation. NIST 612 was used for external calibration with reference values from Pearce et al. (2007). The accuracy and long-term reproducibility of the measurements were ensured by analyzing three zircon standards (91,500 $n = 20$; GJ1 $n = 11$ and Plešovice $n = 11$). Finally, data reduction was carried out with the software package Glitter (van Achterberg et al., 2001), and is presented in Table S11.

Data was further filtered to exclude measurements that may have been influenced by the presence of inclusions, following the criteria proposed by Attia et al. (2020), which involve excluding analyses with high counts of Y (>5000 ppm), and LREE ([Ce] > 200 ppm; [Sm] > 300 ppm; [Eu] > 15 ppm and [Gd] > 150 ppm).

4. Results

4.1. Petrographic analyses

Twelve thin sections from monzogranite, quartz diorite, and quartz-monzodiorite samples were examined for petrographic characterization (Table S3). All samples displayed phaneritic textures (Figs. 4 and S3), with crystal sizes ranging from 0.8 to 2.7 mm (Fig. 4). The primary mineral assemblage was composed of quartz, orthoclase, microcline, plagioclase, muscovite, and biotite phenocrysts, accompanied by minor amounts of hornblende, apatite, and opaque minerals. The rocks are relatively pristine, with well-preserved grain boundaries and limited evidence of alteration. This is supported by their loss on ignition (LOI) values, which range from 0.85 to 1.94 (Table S8). However, minor plagioclase sericitization and slight biotite chloritization were observed locally.

The rocks are predominantly felsic in composition. Jurassic samples plot in the quartz monzodiorite field, while Early Cretaceous rocks fell into the monzogranite and quartz monzodiorite fields. In contrast, Late Cretaceous rocks exhibited a wider compositional range, with samples falling into the quartz diorite, quartz monzodiorite, and monzogranite fields (Fig. 4D; The geochronological framework for these age groups is presented in Section 4.2).

4.2. Zircon U–Pb geochronology

Nineteen new zircon U–Pb ages were obtained in this study, supplemented by two previously published Triassic ages from Sandoval-Espinel et al. (2025): samples CT013 (222.8 ± 1.2 Ma) and CZ105 (229.2 ± 1.4 Ma).

Sample IG22–53 (Fig. 5E) clearly exhibits two distinct age populations. Given the magmatic nature of the rock, the best estimate for its maximum crystallization age was based on the youngest coherent population ($n = 3$), yielding a weighted mean age of 230.4 ± 4 Ma.

The Mesozoic ages obtained in this study were distributed as follows: i) one Triassic sample (230.4 ± 4) from the ATB; ii) five Jurassic samples from the eastern Ecuadorian and western Peruvian Cordilleras, with ages ranging from 191.4 ± 5.3 Ma (IG22–23) to 157.7 ± 4.2 Ma (IG22–32); iii) four Early Cretaceous samples (also from the Cordilleras), with ages ranging from 139.8 ± 1.8 Ma (SAN18) to 126.1 ± 3.6 Ma (IG22–30); and iv) nine Late Cretaceous samples from the Celica–Lancones arc, ranging from 100.8 ± 1.8 Ma (IG22–51B) to 87.8 ± 1.7 Ma (IG22–49).

4.3. Whole rock geochemistry

Fifteen samples were selected for whole-rock geochemical analysis (Table S8). Only one Triassic sample was analyzed in this study due to the extensive geochemical data available in the literature for this period (e.g., Cochrane et al., 2014; Mišković et al., 2009). In the total alkali versus silica (TAS) classification scheme (Fig. 6A), Triassic samples—both published data and those analyzed in this study—plot within the granite, granodiorite, and quartz monzonite fields. Jurassic samples fall predominantly within the granodiorite field, while Early Cretaceous samples are classified as granite, granodiorite, and quartz monzonite. In contrast, Late Cretaceous samples exhibit greater compositional diversity, ranging from granites and granodiorites to diorites and gabbros. In general, most samples analyzed were felsic in composition, with only a few exhibiting intermediate to mafic characteristics.

In general, the felsic rocks possessed compositions that ranged between 63.4 and 75.1 wt% SiO₂, 13.5–17.1 wt% Al₂O₃, 0.24–3.9 wt% MgO, and 0.62–7.98 wt% CaO, while the intermediate to mafic rocks possessed composition ranges between 49.1 and 59.9 wt% SiO₂, 18.1–19.5 wt% Al₂O₃, 1.7–7.8 wt% MgO, and 7.2–14.1 wt% CaO (all values recalculated to an anhydrous basis; Table S8).

The La/Yb and Sr/Y ratios, which are commonly used as proxies for crustal thickness (Chapman et al., 2015; Profeta et al., 2015), show a consistent trend from the Triassic to the Cretaceous (Fig. 7).

4.4. Zircon isotopic data

A total of 130 $\epsilon\text{Hf}_{\text{t}}$ analyses are presented in Table S9, with results illustrated in Fig. 8A. The $\epsilon\text{Hf}_{\text{t}}$ values in the Triassic samples range between -12.8 and 1.2 , while the Jurassic samples range between 4.5 and 7.5 , with an outlier at -17.8 . Early Cretaceous $\epsilon\text{Hf}_{\text{t}}$ values vary from 4.4 to 11.8 , while samples from the Late Cretaceous exhibit the highest $\epsilon\text{Hf}_{\text{t}}$ values, fluctuating between 8.5 and 14.8 , with three outliers at -10.1 , -1.9 , and 3.1 . In general, the $\epsilon\text{Hf}_{\text{t}}$ values are indicative of long-term depletion from about 200 to about 85 Ma (Fig. 8A). It should be noted that the samples reach their maximum values in the Late Cretaceous (~ 100 Ma), with values approaching depleted mantle signatures before slightly decreasing toward ca. 85 Ma, although this trend is subtle.

A total of 44 $\delta^{18}\text{O}$ measurements are reported in Table S10, with results illustrated in Fig. 8B. The $\delta^{18}\text{O}$ values for the Triassic samples show supracrustal signatures ranging from 8.3 to 11 ‰, with an outlier at 4.7 ‰. Samples from the Jurassic exhibit relatively uniform $\delta^{18}\text{O}$ values (5.3 – 6.2 ‰), which are close to mantle compositions, with one higher outlier at 9.5 ‰. Early Cretaceous $\delta^{18}\text{O}$ values range between 3.9 and 6.5 ‰, while Late Cretaceous samples exhibit ranges from 3.3 to 5 ‰.

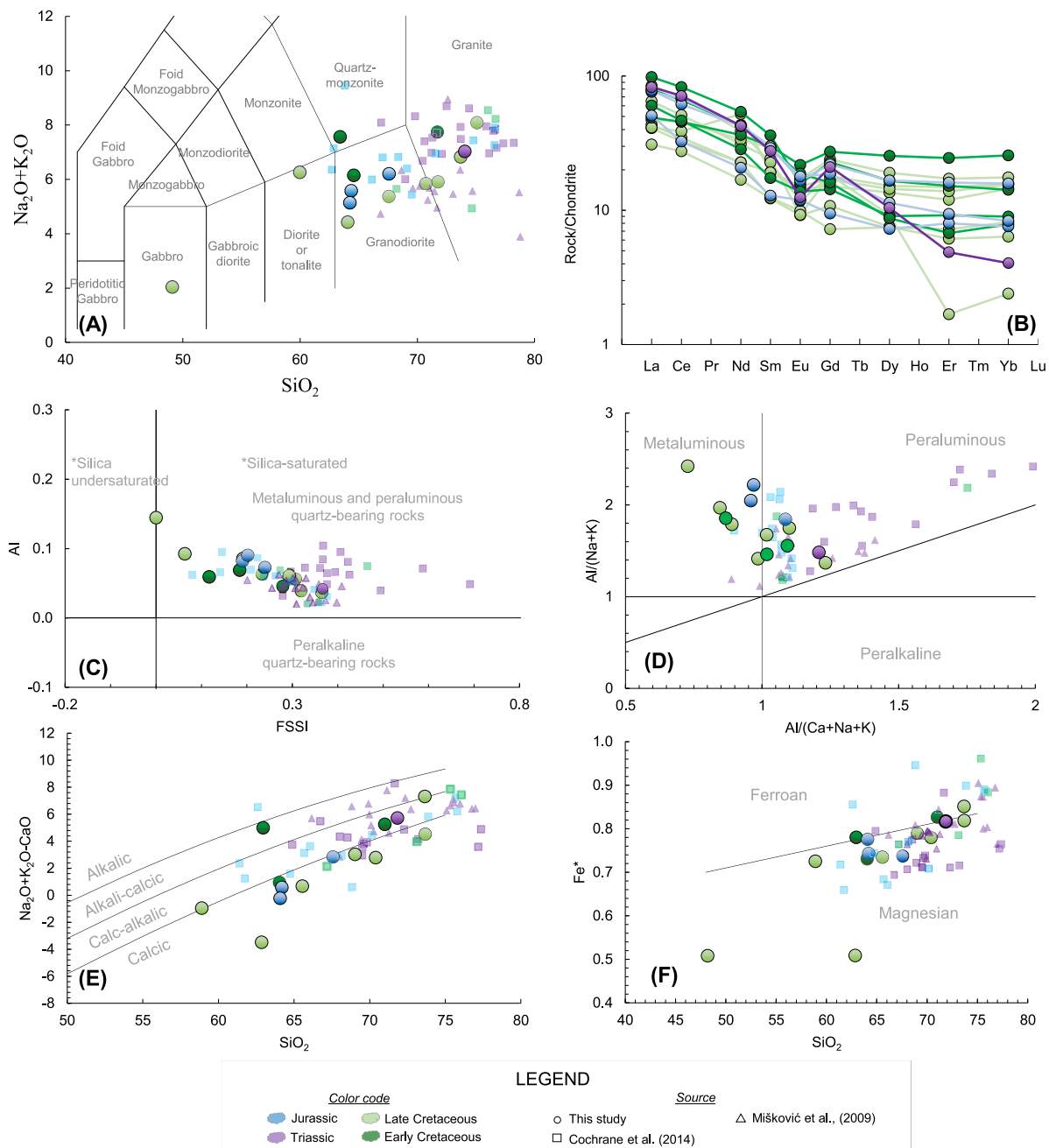


Fig. 6. Whole rock classification diagrams. (A) Total alkali versus silica plot (Middlemost, 1994). (B) Chondrite-normalized rare element plot, normalizing values are from Sun and McDonough (1989). (C) Plot of alkalinity index (AI) vs feldspathoid silica-saturation index (FSSI). (D) Molar A/CNK versus molar A/NK plot. (E) $\text{Na}_2\text{O} + \text{K}_2\text{O}-\text{CaO}$ as a function of SiO_2 , fields are from Frost and Frost, 2008. (F) Fe^* versus SiO_2 plot (Frost et al. 2001).

‰, with two outliers exceeding 7 ‰. There is a clear decrease in $\delta^{18}\text{O}$ values over time, with values trending toward mantle-like signatures (Fig. 8B).

4.5. Zircon geochemistry

The zircon geochemical dataset comprises 121 measurements that exhibit considerable variability in several trace elements, including Dy (25–864 ppm), Gd (3–231 ppm), U (42–8130 ppm), and Y (285–9140 ppm) (Table S11). The chondrite-normalized trace element patterns exhibited trends that were typical of continental arc samples (Fig. 9A; Hoskin and Schaltegger, 2003) with significant enrichment in HREE relative to LREE ($(\text{Yb}/\text{Sm})_{\text{CN}} = 44\text{--}118$; $(\text{Yb}/\text{Gd})_{\text{CN}} = 13\text{--}39$) and negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.20\text{--}0.31$).

The zircons exhibited Th/U ratios ranging from 0.03 to 2.5 (Fig. 9B), indicative of magmatic origins. However, some crystals from the Triassic exhibited low Th/U values (0.03–0.06), which can be indicative of metamorphic environments ($\text{Th}/\text{U} < 0.1$; Grimes et al., 2007). The majority of zircon grains are derived from felsic rocks ($\text{Th}/\text{U} > 0.1$; Grimes et al., 2015; Teipel et al., 2004), with the exception of some Early Cretaceous crystals that suggest a more mafic source ($\text{Th}/\text{U} = 1.9\text{--}2.5$). In addition, most of the zircon grains possess characteristics that are consistent with continental arc formation, while a subset of the Late Cretaceous grains exhibit signatures that are consistent with a mid-ocean ridge environment (Fig. 9C and Fig. 9D).

The Triassic zircon crystals exhibit S-type to “hybrid” S-type signatures although a few plot in the I types, based on the classification scheme proposed by Roberts et al. (2024); these are consistent with the

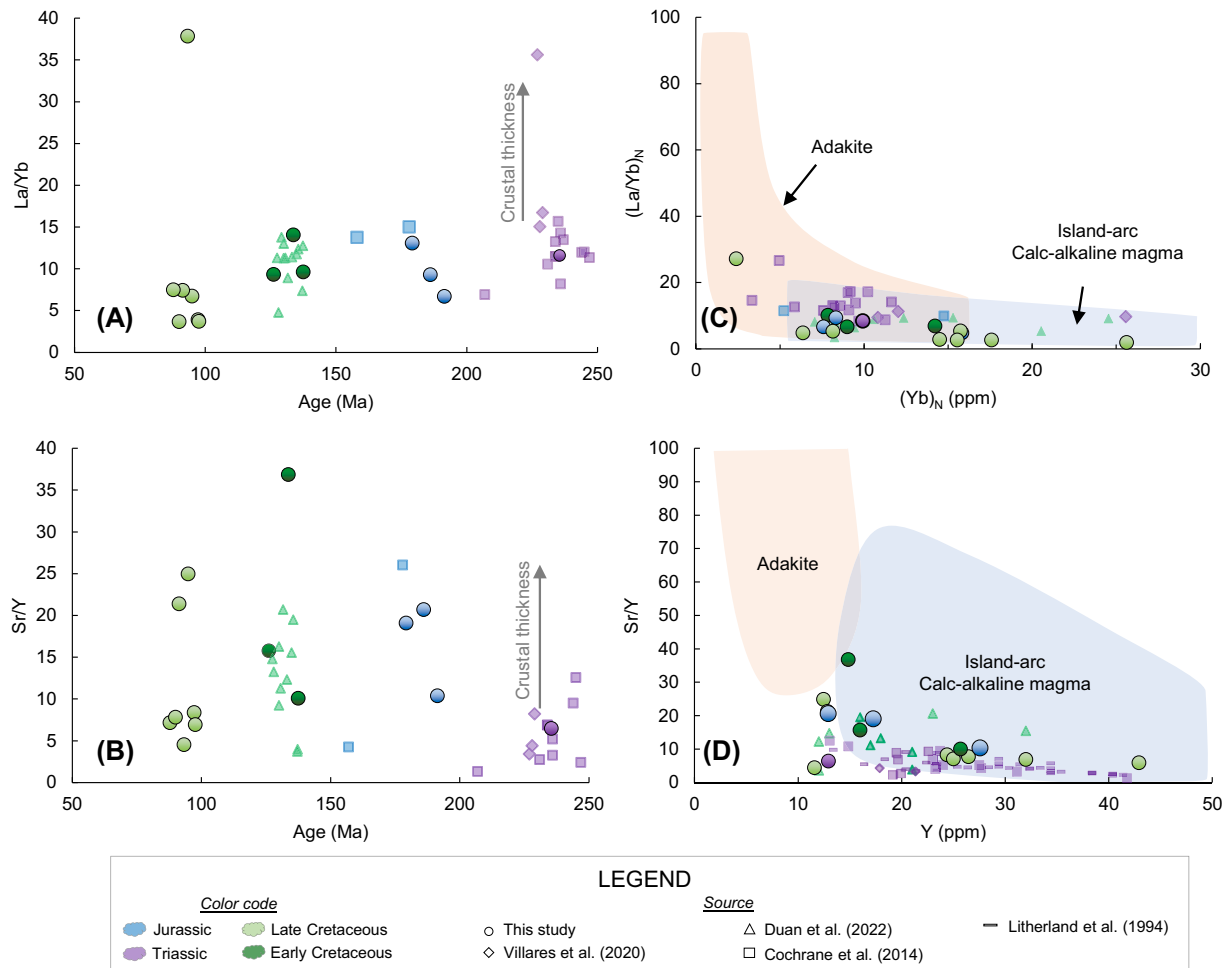


Fig. 7. Whole-rock petrogenetic proxies related to crustal thickness and adakite discrimination diagrams. (A) La/Yb vs. Age. (B) Sr/Y vs. Age. (C) $(La/Yb)_N$ vs. $(Yb)_N$ (after Martin, 1986; N = chondrite-normalized). (D) Sr/Y vs. Y (after Drummond & Defant, 1990).

findings of Aspen et al. (1992) and Riel et al. (2014). In contrast, the Jurassic and Late Cretaceous zircon grains exhibit signatures typical of I-type granitoids (Fig. 9E), while Early Cretaceous grains possess features that are characteristic of both I-type and S-type granitoids.

U/Yb ratios are used to distinguish continental and oceanic zircons and assess crustal contributions in magmas, as this ratio often reflects depletion or enrichment as well as the extent of crustal assimilation (Grimes et al., 2007; Grimes et al., 2015). There was a gradual increase in U/Yb ratios from the Triassic to the Early Cretaceous, indicative of progressive enrichment (Fig. 10A). However, this trend was disrupted in the Late Cretaceous, where zircons exhibit both high and low U/Yb values, indicating that they were derived from a mixed source. Notably, the high observed Th/U values were primarily associated with sample IG22–19, which also exhibits anomalously high U concentrations. It should be noted that IG22–19 was the most inland sample of the Late Cretaceous group.

Ratios such as Yb/Gd, Nb/Ta, and LREE/HREE can be used as indicators of melting depth, as they reflect pressure-dependent mineral fractionation in key mineral phases (e.g., garnet, amphibole, clinopyroxene, and plagioclase). Consequently, they are often used as proxies for crustal thickness (Drabon et al., 2024; Grimes et al., 2015). There is a progressive increase in Nb/Ta, LREE/HREE, and Eu/Eu ratios from the Triassic to the Early–Middle Cretaceous, though this trend is less evident in Late Cretaceous zircon grains. Dy/Yb decreases over the same interval, while Yb/Gd exhibits no distinct trends (Fig. 10).

5. Discussion

5.1. Triassic crustal reworking

Triassic magmatism, recorded between 247.2 ± 4.3 Ma and 203 ± 1.4 Ma, is associated with the Moromoro, Sabanilla, and Tres Lagunas units along the western flank of the Ecuadorian Eastern Cordillera as well as the Marcabell, La Victoria, and La Florida granitoids of the ATB (e.g., Cochrane et al., 2014; Feininger & Silberman, 1982; Litherland, 1994; Sandoval-Espinel et al., 2025). Triassic magmatism has also been identified further east in the Chinchiná unit, located at $\sim 75.5^\circ\text{W}$ (e.g., Cochrane et al., 2014; Litherland, 1994; Table S1), indicative of the existence of a broad magmatic arc. The U–Pb zircon data presented in this study support and refine these observations, with documented crystallization ages ranging from 230.4 ± 4 to 222.8 ± 1.2 Ma, which are consistent with previous ages reported for the ATB (Figs. 2, 3 and 11).

Triassic magmatism along the western margin of the Northern Andes is attributed to mantle upwelling resulting from lithospheric thinning and extension, processes interpreted to result from either continental rifting during Pangea fragmentation or changes in subduction dynamics (e.g., Riel et al., 2018; Spikings et al., 2015; Villares et al., 2020). Our dataset refines these interpretations by constraining the degree and timing of crustal involvement during this magmatic episode. The Triassic granitoids investigated in this study exhibit strong crustal assimilation as shown by high $\delta^{18}\text{O}$ values (up to 11 ‰) and low $\epsilon_{\text{Hf}(t)}$ values (–12 to +2), indicating that prolonged crustal reworking

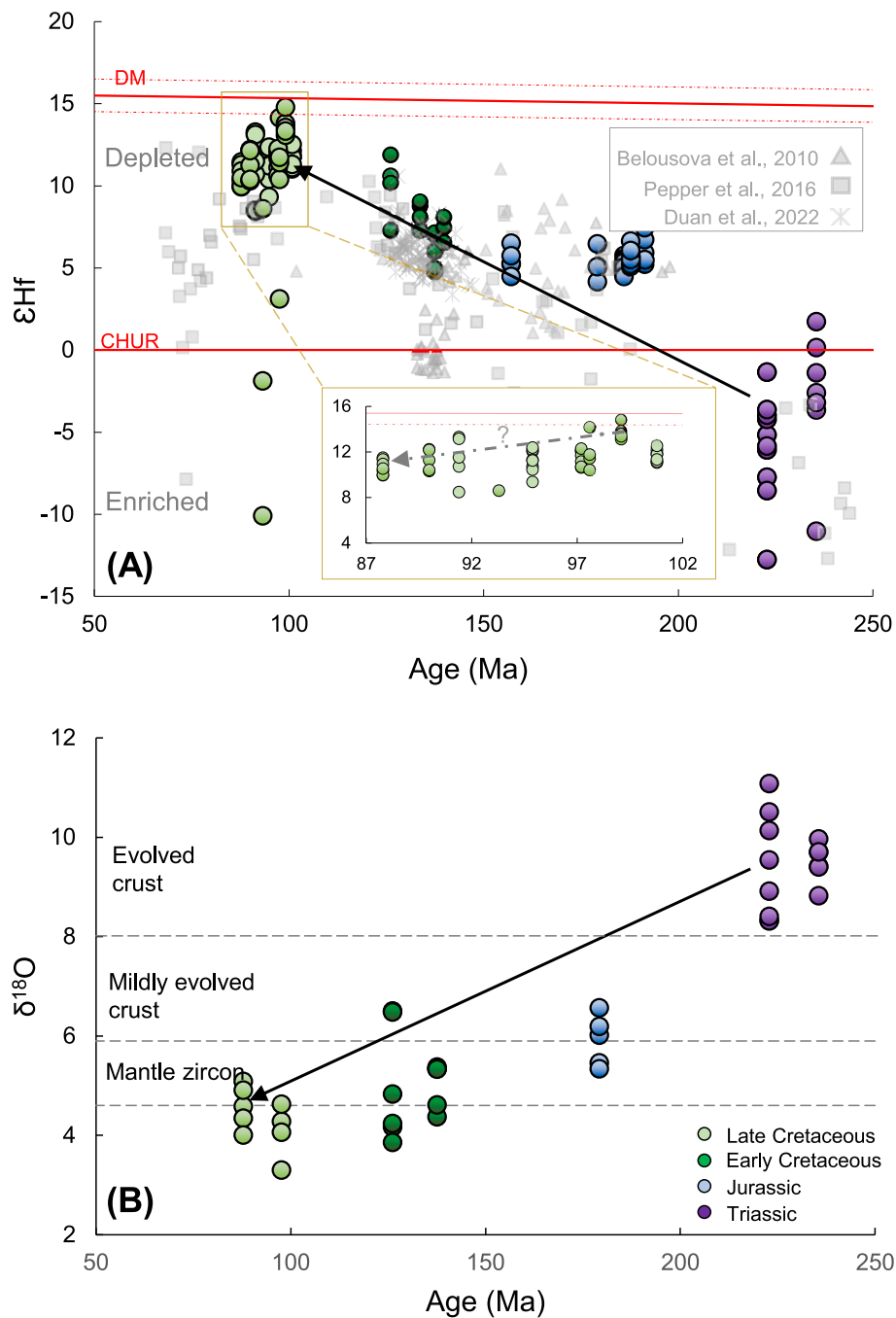


Fig. 8. Isotopic data for the study area. (A) ϵHf vs. Age, including published ϵHf isotopic data from detrital zircons by Belousova et al. (2010) and Pepper et al. (2016). (B) $\delta^{18}\text{O}$ vs. Age. Limits are from Valley et al. (2005).

persisted until at least ~ 220 Ma (Fig. 8). This is consistent with models proposed by Riel et al. (2018) and Villares et al. (2020), which documented S- and A-type magmatism along the western Gondwana margin during the same period. Our dataset also reveals a trend from S-type to hybrid S-type, and to I-type granites signature (235–222 Ma; Fig. 9E), emphasizing the significant contribution of supracrustal materials to magmatic reservoirs and providing further evidence of extensive crustal reworking.

The Triassic granitoids exhibit magnesian and calc-alkalic geochemical signatures (Fig. 6E and F) that are characteristic of arc environments (Frost and Frost, 2023; and references therein). The high Dy/Yb (Fig. 10B) and low Yb/Gd (Fig. 10C) ratios in the Triassic zircons are indicative of garnet stability in the source residue, consistent with

deep crustal melting in a thickened crust (Drabon et al., 2024; and references therein). Some Triassic samples also display elevated whole-rock La/Yb ratios (Fig. 7A and C), which are compatible with magma derivation from a thick crust. In contrast, whole-rock Sr/Y ratios (Fig. 7B and D) do not show high values typically interpreted as evidence of crustal thickening. Recent studies, however, have shown that crustal thickness estimates based on Sr/Y can deviate substantially from geophysically determined values due to the strong influence of fractionation processes (Guo and Yang, 2023). Consequently, we suggest that Triassic magmatism was generated in an active subduction setting through partial melting and reworking of a previously thickened continental crust (Fig. 12A).

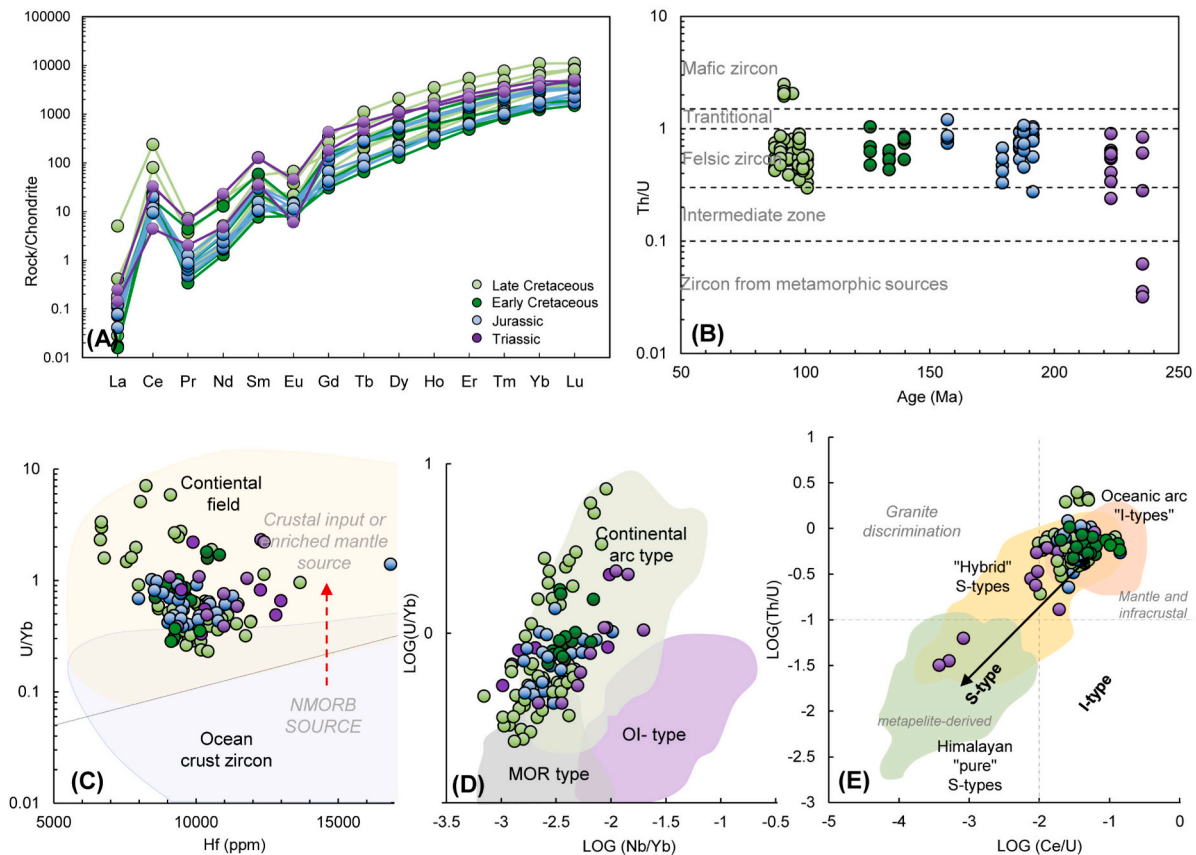


Fig. 9. Zircon-based classification diagrams. (A) Chondrite-normalized rare element plot, normalizing values are from Sun and McDonough (1989). (B) Th/U versus age plot. (C) U/Yb vs Hf, fields for continental and oceanic zircon are from Grimes et al. (2007) (D). Tectonic discrimination diagram, boundaries are from Grimes et al. (2015). (E) Th/U vs Ce/U plot defining I-type, S-type and hybrid S-type granitoids, boundaries are from Roberts et al. (2024). MOR: Mid ocean ridge. OI: ocean island.

5.2. Jurassic magmatism: From strong crustal reworking to predominantly mantle inputs

Jurassic magmatic activity in northwestern South America is recorded by Lower–Middle Jurassic batholiths in Colombia and by the Abitagua and Zamora batholiths in Ecuador (Fig. 2; Bayona et al., 2020; Bustamante et al., 2016; Cochrane et al., 2014; Leal-Mejía et al., 2019; Spikings et al., 2015).

In southern Ecuador, specifically, Jurassic magmatism is primarily represented by the Zamora Batholith. The crystallization ages for the batholith have been constrained by various geochronological techniques, including K–Ar dating on hornblendes and biotites (201–151 Ma; Gendall et al., 2000; Litherland, 1994), U–Pb dating on zircons (180–145 Ma; Chiaradia et al., 2009; Cochrane et al., 2014; Drobe et al., 2013), and ^{40}Ar – ^{39}Ar dating on hornblendes (160–150 Ma; Chiaradia et al., 2009; Codor, 2003). The U–Pb zircon ages presented in this study range from 191 ± 5 Ma to 157 ± 4.2 Ma, extending the previously known magmatic interval and suggesting that the onset of Jurassic magmatism occurred significantly earlier than previously reported. Our data also provide the first direct evidence of Jurassic magmatism in northern Peru, with samples IG22–32 and IG22–34 yielding crystallization ages of 157.7 ± 4.2 Ma and 187.8 ± 3.2 Ma, respectively. These results show that the Jurassic magmatic arc extended further south into northern Peru, at least as far as 6°S , indicating that Jurassic magmatic activity was more widespread than previously recognized.

Furthermore, samples IG22–22, IG22–23, IG22–26, and IG22–34 have Early Jurassic crystallization ages ranging from ca. 191 to 179 Ma, overlapping with the crystallization ages of the Norosí and San Martín

batholiths (189–182 Ma) as well as the Mocoa-Garzón batholith (180–172 Ma) in Colombia (e.g., Leal-Mejía et al., 2019; and references therein). These results call for a re-evaluation of the southward-younging model of magmatism proposed by Spikings et al. (2015), which was based on data available at that time.

Jurassic isotope data reveal intermediate ϵHf_t values (4.2–7.5; Fig. 8A) and a shift from >8 ‰ to 5.3–6.5‰ $\delta^{18}\text{O}$ values (Fig. 8B). This trend indicates a transition toward more juvenile compositions as well as increasing mantle contribution over time. Jurassic magmatism exhibits a compositional change from peraluminous to metaluminous (Fig. 6C and D) as well as magnesian and calcic geochemical signatures (Fig. 6E and F) indicative of less evolved magma sources (e.g., Frost and Frost, 2008). This geochemical evolution is also expressed as a shift from S-type to I-type granitoids (Fig. 9E), accompanied by decreasing Dy/Yb zircon ratios (Fig. 10B and F), indicating melting in a garnet-free, plagioclase-stable source at relatively shallow crustal levels (Drabon et al., 2024; Grimes et al., 2015). We interpret Jurassic magmatism (191 ± 5 Ma to 157 ± 4.2 Ma) as the product of lithospheric thinning associated with intra-arc extension, which facilitated mantle-derived magmatism with limited crustal recycling (Fig. 12B). Furthermore, our data do not support a thick Jurassic crust (190–180 Ma) proposed by Chavarria et al. (2022), given the geochemical evidence for crustal thinning and shallow-level melting.

Jurassic extensional tectonics have already been documented in the Northern Andes (e.g., Bustamante et al., 2016; Cochrane et al., 2014; Spikings et al., 2015). For instance, Spikings et al. (2015) and Cochrane et al. (2014) investigated Jurassic magmatism in the Ecuadorian Andes and suggested that, based on older arc-related rocks dated between 209

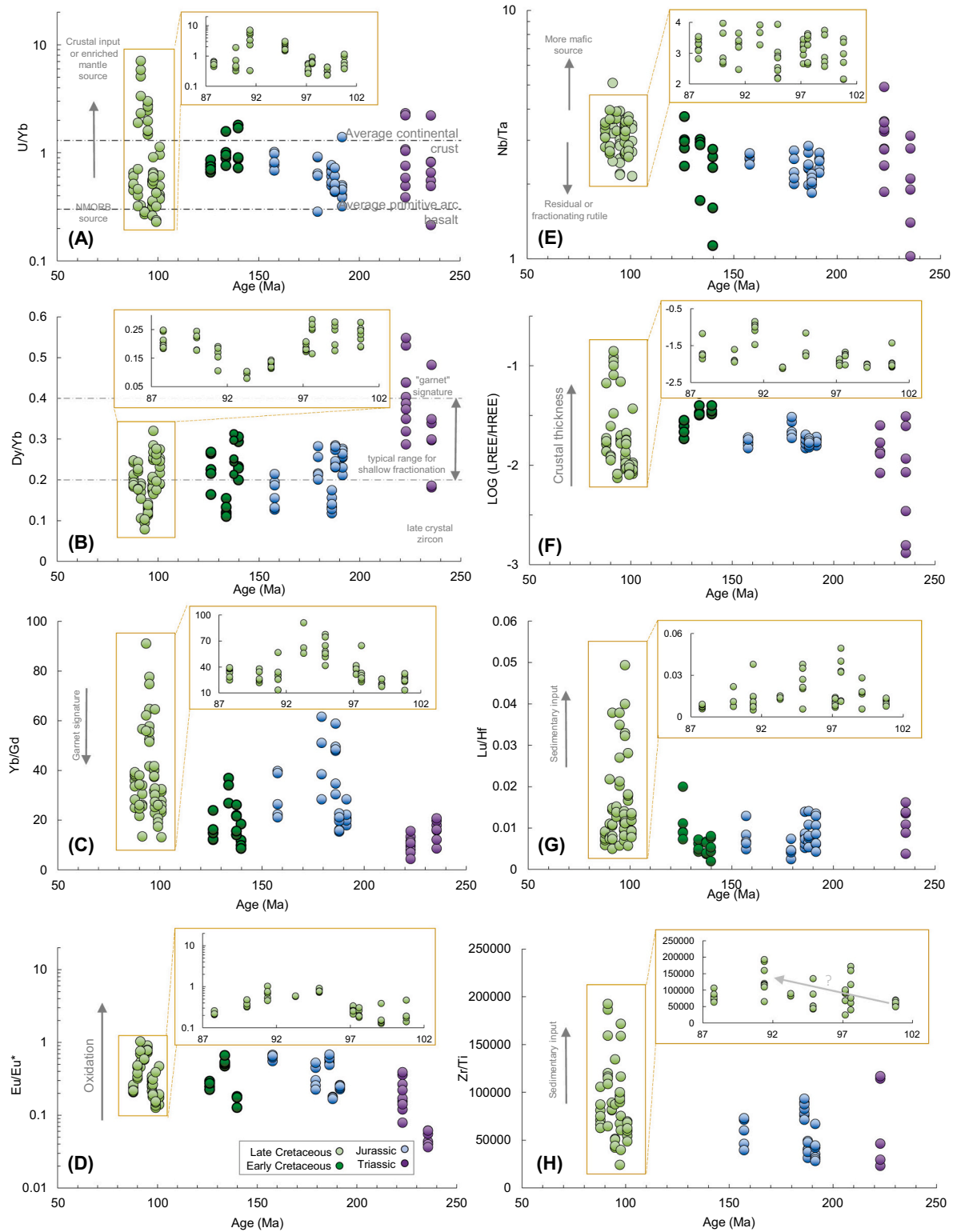


Fig. 10. Zircon bivariate plots showing various proxies. (A) Age vs. U/Yb as a proxy for melt maturity, with domains from Grimes et al. (2015). (B–F) plots of proxies for crustal thickness, including (B) Dy/Yb vs. Age, (C) Yb/Gd vs. Age, (D) Eu/Eu* vs. Age, (E) Nb/Ta vs. Age, and (F) LREE/HREE vs. Age. (G–H) plots of proxies for sediment input, including (G) Lu/Hf vs. Age, and (H) Zr/Ti vs. Age.

and 194 Ma in the Santander Massif of Colombia, the arc axis migrated oceanward between 194 and 189 Ma (Van der Lelij, 2013). Slab rollback induced a westward arc migration from the Cordillera Real to the Western Cordillera (Fig. 1), resulting in the emplacement and

development of a long-lived magmatic arc that persisted until ~140 Ma. This arc migration is attributed to crustal extension above a retreating subduction zone, leading to the progressively reduced continental contamination of mantle-derived magmas. While we agree with an

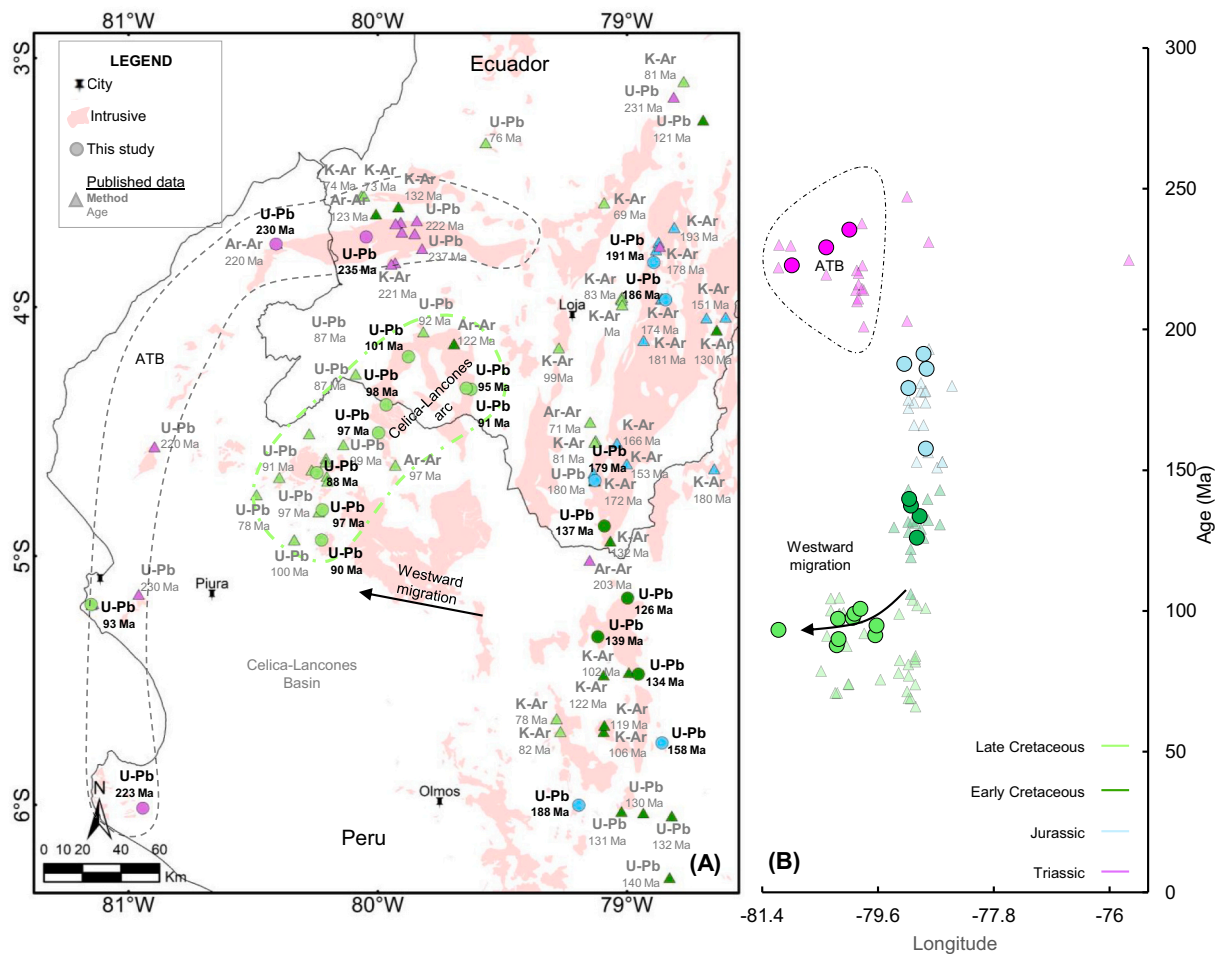


Fig. 11. (A) Sketch of the area showing arc position during Mesozoic. (B) Latitude vs age of the Mesozoic samples.

overall decrease in crustal input, our U–Pb zircon ages do not support such an early timing for arc migration (see Section 5.3).

The petrological characterization of Jurassic magmatism in the Colombian Andes by Bustamante et al. (2016) concluded that oblique convergence of the Farallon Plate (~170–130 Ma) limited the incorporation of fusible sediments into the mantle, resulting in a more refractory mantle with a primitive isotopic signature, consistent with the isotopic signatures observed in this study (Fig. 8). This allows us to suggest that, during the Jurassic, the southernmost Northern Andes was subject to similar geodynamic conditions and mantle source characteristics as the Colombian Andes.

5.3. Early–Middle Cretaceous dynamics: Westward magmatic migration and the evolution of the Celica-Lancones basin

Early Cretaceous magmatism in the Peruvian Western Cordillera has primarily been dated by whole-rock K–Ar, yielding ages ranging from 122 ± 6 Ma to 102 ± 5 Ma (Hama, 1990), while limited U–Pb dating in the region reveals ages ranging from 140 Ma to 130 Ma (CGS_INGEMMET, 2017). Similarly, Early Cretaceous magmatism in southern Ecuador has primarily been constrained by whole-rock K–Ar dating (119 ± 6 to 106 ± 5 Ma; Hama, 1990), $^{40}\text{Ar}/^{39}\text{Ar}$ dating on hornblende (126 ± 4 to 122 ± 1 Ma; Ulrich, 2005), and a few U–Pb zircon ages ranging from 131 ± 1 Ma to 104 ± 2 Ma (Cochrane, 2013; Winter, 2008). Our study supplements this information with new U–Pb zircon ages ranging from 140 ± 2 Ma to 126 ± 4 Ma.

Early Cretaceous magmatism coincided with a major change in subduction direction from WSW to NNE around 145–140 Ma (Riel et al.,

2014), followed by basal accretion of the Raspas Ophiolitic Complex between 130 and 120 Ma (Gabriele, 2002; Riel et al., 2014). During this process, oceanic lithosphere (MORB crust $\pm$ seamount/oceanic plateau fragments) was subducted, metamorphosed at high pressure, and subsequently underplated to the lower crust before being exhumed in the ATB during the Late Cretaceous (Riel et al., 2014; and references therein).

Early Cretaceous magmatic reservoirs (140–126 Ma) are characterized by zircon $\delta^{18}\text{O}$ values within and near the mantle array and mid-enriched to depleted $\varepsilon\text{Hf}(t)$ values (+4.4 to +11.8), indicating a predominantly mantle-derived source. Additionally, their trace-element compositions, including low Dy/Yb ratios, elevated LREE/HREE ratios, and low Yb/Gd values (Fig. 10), suggest that differentiation occurred under upper amphibolite-facies conditions (Drabon et al., 2024; and references therein). We suggest that the Early Cretaceous magmatism developed in an extensional subduction setting, where progressive crustal thinning enhanced the influx of mantle-derived melts into the magmatic system. A minor contribution from the underplated oceanic materials at the base of the crust remains possible and cannot be excluded (Fig. 12C; Riel et al., 2014). The proposed extensional regime is reflected in the regional stratigraphy, with a widespread Early Cretaceous angular unconformity as well as the development of deep sedimentary basins such as the Chicama Basin in northern Peru (Jaillard and Soler, 1996), and the Celica-Lancones in southern Ecuador north Peru (Jaillard et al., 1999).

Intrusive bodies dated between 100 and 88 Ma are systematically located to the west of intrusions dated as late as ~126 Ma (see former section). This distribution supports the interpretation of a westward

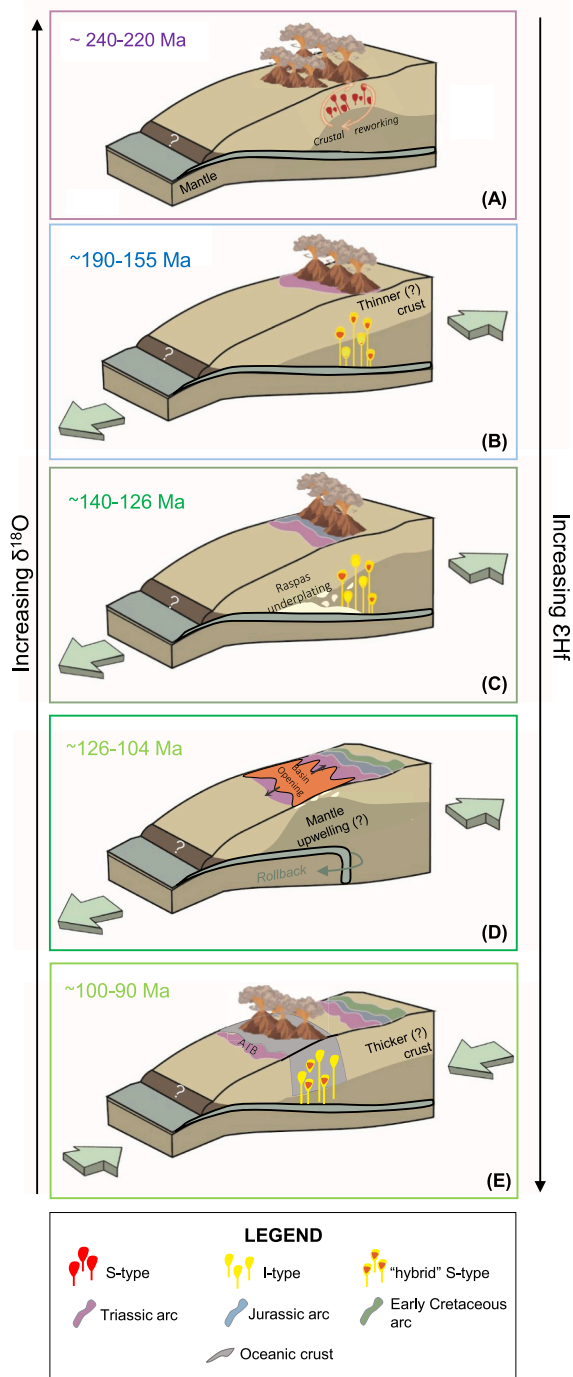


Fig. 12. Generalized time-slice sketches illustrating the Mesozoic tectono-magmatic evolution of southern Ecuador and northern Peru, as constrained by this study. (A) 240–220 Ma: arc magmatism and crustal reworking; (B) 190–155 Ma: extensional arc development; (C) 140–126 Ma: subduction of oceanic Rapas complex and underplating to the lower crust; (D) 126–104 Ma: rollback and opening of the Celica–Lancones basin; (E) 100–90 Ma: onset of compression and establishment of a new western arc emplaced on oceanic crust.

migration of magmatism during the Middle to Late Cretaceous. We constrain the younger limit of this migration to ~104 Ma based on the oldest age reported by Winter et al. (2010) in the Celica–Lancones arc, located to the east. The westward shift marks the relocation of a previously stationary arc set at ~79°W (present-day coordinates) that was active between ~190 and ~126 Ma (Fig. 11). This migration is coeval with the opening of the NE–SW trending Celica–Lancones Basin

(~110–100 Ma; Fig. 12D; Jaillard et al., 1999; Mourier, 1988; Winter, 2008). During this rifting setting, the ATB block detached from the South American margin and underwent a ~65° clockwise rotation (Mourier, 1988; Riel et al., 2014).

Given the accentuated extensional deformation in the basin, and considering the relatively old age of the subducting slab (~60 Ma; Maloney et al., 2013), we propose that slab rollback, occurring at the same time as the formation of the Celica–Lancones Basin around 110 Ma, was the main cause of arc migration. Rollback-related processes likely also contributed to within-plate alkaline magmatism (110–82 Ma) in the Ecuadorian Oriente Basin, consistent with our interpretation (Barragán et al., 2005).

A westward arc migration has also been documented in Colombia, Ecuador, and northern Peru (Cochrane et al., 2014; Duan et al., 2022; Leal-Mejía et al., 2019; Ramos, 2009; Spikings et al., 2015). Some studies suggest that this magmatic shift began in northern Peru at around ~145 Ma (Duan et al., 2022), while studies in northern-Central Ecuador have settled on a broader time frame (e.g., Cochrane et al., 2014; Spikings et al., 2015), with migration thought to have occurred between the Jurassic and Early Cretaceous (see Section 4.2). These interpretations are based on the presence of Early Cretaceous magmatic units located west of older arc remnants. For example, the Peltetec Complex, which has traditionally been interpreted as Early Cretaceous (~134 Ma) based on $^{40}\text{Ar}/^{39}\text{Ar}$ dating on hornblende, muscovite, and biotite (Gabriele, 2002; Spikings et al., 2015), is emplaced to the west of Jurassic batholiths. However, Villares et al. (2020) proposed a Triassic age of 228.1 ± 1.7 Ma for the Complex using U–Pb dating and suggested that the $^{40}\text{Ar}/^{39}\text{Ar}$ ages reflect a Cretaceous thermal overprint associated with high-pressure metamorphism (~130 Ma; Gabriele, 2002; Riel et al., 2014), challenging the previously proposed Jurassic timing (~194 Ma) for arc migration.

Further south (8°–18.4°S), Martínez-Ardila et al. (2023) identified a progressive eastward migration of the Mesozoic arc through central and southern Peru (see Fig. 3C). The ages of Mesozoic rocks became increasingly younger toward the foreland between 200 and 66 Ma. This trend, in opposition to the westward migration observed in our study area, highlights the complex geodynamic evolution of the Andean arc as well as the regional variability in subduction processes during the Mesozoic.

5.4. Middle-late cretaceous evolution: The formation of a distinct arc

During the Albian (~100 Ma), active seafloor spreading in the South Atlantic Ocean and the westward drift of the South American Plate marked a shift from a predominantly extensional regime toward a compressional, Andean-type subduction system. This change in plate dynamics promoted the establishment of a new continental arc (Fig. 12E; Jaillard et al., 2000). This interpretation is supported by our U–Pb data (Fig. 3; Table 5), which records ages (100.8–87.8 Ma) that are consistent with those reported by Winter (2008) (U–Pb in zircon; 100.2 ± 0.5 to 78.6 ± 1.9 Ma).

Late Cretaceous magmatism produced rocks with a broad range of SiO_2 contents (Table S8), ranging from metaluminous to peraluminous rocks (Fig. 6D) from diorite to granite as well as minor occurrences of silica-undersaturated gabbros (Fig. 6A). Notably, the gabbro sample (IG22–18), one of the easternmost samples in the Late Cretaceous dataset, stands out due to its primitive character. Despite its juvenile isotopic signature ($\epsilon\text{Hf} > +10$; Table S9), zircon analyses reveal very high U/Yb ratios (~5–7), typical of crustal assimilation and fluid-enriched mantle sources. These paradox results suggest that this gabbro is an enigmatic product of hydrous mantle melting in a continental arc setting, akin to tholeiitic gabbros in the Eastern Pontides Orogenic Belt (NE Turkey), where similar primitive but high-U/Yb magmas are attributed to bimodal arc magmatism (Temizel et al., 2022). Alternatively, the combination of high ϵHf and elevated U/Yb in this gabbro may reflect a juvenile parental magma generated under garnet- or

amphibole-controlled melting conditions that suppressed Yb.

The whole-rock compositions of these samples are characteristic of calc-alkaline and calcic signatures (Fig. 6E), with magnesian affinities (Fig. 6F). This marks a change from the Early Cretaceous, when compositions ranged from magnesian to ferroan. These geochemical trends may reflect the influence of the newly established compressional setting, which likely contributed to increased crustal thickening and differentiation, thus favoring magnesian, calcic-alkalic compositions (e.g., Frost and Frost, 2008). However, Dy/Yb ratios in zircon remain consistently low, while LREE/HREE ratios remain highly variable, with samples exhibiting particularly high values, indicative of a magmatic source formed under conditions where garnet was absent (Fig. 10B). Nevertheless, the Dy/Yb ratios increase around 93 Ma, suggesting higher-pressure melting conditions consistent with the stabilization of garnet in the residue, and therefore with magma generation at greater crustal depths. This combination may reflect progressive crustal thickening and differentiation under a developing compressional regime. While these geochemical shifts are potential evidence of a tectonic transition, additional data are required to determine whether significant crustal thickening occurred during this period.

Zircon Th/U ratios (Fig. 9B) can be categorized into two distinct groups: (i) an intermediate group (Th/U ratios of 0.3–1) associated with felsic compositions, and (ii) a high-Th/U group (Th/U ratios >1.5), typically associated with more mafic magmatism. This distribution is consistent with the zircon Nb/Ta ratios (Fig. 10D), which possess values that are more characteristic of mafic sources, highlighting the significant influence of such components in the Late Cretaceous magmatic system. The broad distribution of U/Yb ratios (Fig. 10A) is indicative of contributions from both MORB sources and enriched mantle or crustal inputs. The coexistence of oceanic and continental zircon signatures (Fig. 9C and D), as well as I-type and hybrid S-type granitoid affinities, provides further support for a mixed-source model. This is also evidenced by zircon isotopic data: highly depleted $\epsilon\text{Hf}_{(t)}$ values, in some cases approaching the depleted mantle (DM) field (Fig. 8A), occur together with predominantly mantle-like $\delta^{18}\text{O}$ signatures, while a few low $\delta^{18}\text{O}$ values (<4.4 ‰) are present as outliers. These features are best explained by mantle input combined with limited assimilation or partial melting of gabbroic photoliths (Valley et al., 2005), mixing model, consistent with a mixing scenario.

Consequently, our data indicate that the Late Cretaceous arc was constructed on an oceanic basement. Potential origins for this basement include: (i) the underplated Early Cretaceous Rospas Ophiolitic Complex (Riel et al., 2014); (ii) inherited Paleozoic–Triassic oceanic crust, preserved as fragments of lithosphere generated during the Late Permian–Triassic breakup of Pangea, consistent with models proposed for the Western Peruvian Trough (ca. 9–12°S; Polliand et al., 2005); or (iii) new oceanic crust formed through mantle upwelling and melting during the opening of the Celica–Lancones Basin. The third scenario is considered less likely, as the Celica–Lancones arc occupies a forearc position where basaltic magmatism is typically linked to incipient subduction, an interpretation that conflicts with the evidence presented here for continuous subduction since the Triassic. Ultimately, the spatial distribution of our dataset remains insufficient to unambiguously resolve the precise origin of this oceanic basement.

Regardless of mechanism, the Celica–Lancones arc spans the Late Albian to Turonian (100–88 Ma) and could be considered to be the northern counterpart of the Aptian–Albian volcanic arc of Peru due to their coeval magmatism. However, these arcs differ in terms of their basement characteristics: the central–southern Peruvian arc was emplaced on continental crust (Martínez-Ardila et al., 2023; Soler, 1991), while it is clear that the Celica–Lancones Arc is emplaced on oceanic crust. Despite their similar timing, these differences suggest that the two arcs evolved under distinct tectonic conditions, highlighting the complexity of magmatic arcs along the same subduction margin.

This work shows that the integration of U–Pb geochronology, whole-rock geochemistry, and zircon ϵHf and $\delta^{18}\text{O}$ isotopic data is a

powerful tool for reconstructing the spatial and temporal evolution of magmatic arcs. The analyses presented here demonstrate that this approach is particularly effective in highly dynamic subduction systems, where the formation of distinct crustal domains can strongly influence arc geochemistry.

6. Conclusions

The U–Pb zircon data presented in this study refine the existing geochronological framework of Mesozoic magmatism in southern Ecuador and northern Peru, providing new insights into the spatiotemporal evolution of the arc. Triassic magmatism occurred in an active subduction setting. Between 240 and 220 Ma, magmatism was characterized by significant crustal recycling and the formation of S-type granitoids as indicated by zircon Hf–O isotopic data that indicate sustained crustal assimilation until at least 220 Ma. Post-Triassic magmatism marked a transition to voluminous I-type granitoids emplacement, while Jurassic magmatism (201–157 Ma) occurred under an extensional arc system, characterized by a shift toward less radiogenic isotopic compositions, reflecting an increasing contribution from juvenile mantle sources. In addition, the new Jurassic ages obtained in this study challenge the interpretation of a missing Jurassic arc in northern Peru, suggesting that magmatic activity may have been more widespread than previously thought. Furthermore, the synchronous nature of the Jurassic magmatism in southern Ecuador, northern Peru, and Colombia challenges the previously proposed southward-younging trend for the region.

Changes in subduction geometry in the Early Cretaceous had an influence on magmatic activity during this period, favoring the melting of primarily mantle sources. The magmatic arc remained stationary and active between ~190 and ~126 Ma, but by the Middle Cretaceous, the arc had migrated westward, likely due to slab rollback. This coincided with the formation of the Celica–Lancones Basin, contradicting previous interpretations of Jurassic–Early Cretaceous arc migration.

During the Late Cretaceous (~100 to ~88 Ma), magmatism evolved within a compressional regime and involved contributions from oceanic-like components. This oceanic signature may have been derived from (i) the melting of a lower crustal material, possibly linked to the underplated Early Cretaceous Rospas Ophiolitic Complex; (ii) direct input from an upwelling depleted mantle, forming an oceanic-like basement during the opening of the Celica–Lancones Basin; or (iii) melting of preserved fragments of lithosphere generated during the Late Permian–Triassic breakup of Pangea.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.lithos.2025.108389>.

Funding sources

This work was supported by the PhD scholarship awarded to Leidy Carolina Sandoval Espinel by the University of Padova (Grand: 2077712).

CRediT authorship contribution statement

Leidy Carolina Sandoval Espinel: Writing – original draft, Visualization, Methodology, Formal analysis, Conceptualization. **Cesar Witt:** Writing – review & editing, Supervision, Formal analysis, Conceptualization. **Jorge Iglesias:** Writing – review & editing, Methodology. **Massimiliano Zattin:** Writing – review & editing, Supervision, Formal analysis. **Olivier Bruguier:** Writing – review & editing, Data curation. **Marc Poujol:** Writing – review & editing, Data curation. **Pablo Samaniego:** Writing – review & editing. **Mauricio Bermudez:** Writing – review & editing, Supervision, Formal analysis. **John Jairo Sandoval Espinel:** Writing – review & editing, Visualization, Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We thank Leonardo Tauro for his assistance with the preparation of thin sections at the University of Padova. We are also grateful to Editor-in-Chief Greg Shellnutt, reviewer Alina Tibaldi, and an anonymous reviewer for their thoughtful and constructive comments, which greatly improved the quality and clarity of this manuscript.

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