

N° d'ordre :

IMT LILLE-DOUAI



LABORATOIRE DE  
GÉNIE CIVIL ET DE GÉO-  
ENVIRONNEMENT



UNIVERSITÉ DE LILLE 1



## Thèse

présentée en vue d'obtenir

### L'Habilitation à Diriger des Recherches (HDR)

en

Spécialité : Géosciences

par

**Vincent THIÉRY**

**HABILITATION À DIRIGER DES RECHERCHES  
DE L'UNIVERSITÉ DE LILLE 1**

Titre de la thèse :

What can a hardrock geologist bring to a civil & environmental engineering laboratory in geomaterials characterization (and vice-versa)?

Soutenue le 20 juin 2017 devant le jury d'examen :

*Arnaud GAUTHIER, Pr., IMT- Lille-Douai, garant*

*Catherine DAVY, Pr., École Centrale de Lille, rapporteur*

*Philippe LE COUSTUMER, Dr. HDR, Université de Bordeaux, rapporteur*

*Béatrice LEDÉSERT, Pr., Université de Cergy-Pontoise, rapporteur*

*Maarten A.T.M. BROEKMANS, Dr., Geological Survey of Norway (NGU), examinateur*

*Bernard GUY, DR, Mines Saint-Étienne, examinateur*

Laboratoire d'accueil : Département de Génie Civil et Environnemental de Mines Douai  
École Doctorale SMRE 104 (Lille 1)



# TABLE OF CONTENTS

<b>1</b>	<b>RÉSUMÉ FRANÇAIS ÉTENDU.....</b>	<b>5</b>
<b>2</b>	<b>INTRODUCTION AND BACKGROUND – WHAT IS A GEOMATERIAL? .....</b>	<b>13</b>
2.1	HARDROCK GEOLOGY VS. CONCRETE .....	13
2.2	THE ELUSIVE CONCEPT OF GEOMATERIALS .....	13
2.3	SUMMARY.....	15
<b>3</b>	<b>NATURAL GEOMATERIALS: FIELD AND LABORATORY BASED RECOGNITION TOWARDS FUNDAMENTAL GEOLOGICAL KNOWLEDGE.....</b>	<b>17</b>
3.1	GENERAL GEOLOGY.....	18
3.1.1	<i>Characterization of controversial inclusions: the case of diamond .....</i>	<i>18</i>
3.1.2	<i>Cordierite growth in cumulative migmatites – melt /restite segregation .....</i>	<i>21</i>
3.2	METALLOGENY, FROM PRIMARY ORE TO ALTERATION.....	22
3.2.1	<i>Improvements in the characterization of deposits: the case of an antimony district - see also the reprint of the article at the end of the manuscript .....</i>	<i>22</i>
3.2.2	<i>Specific mineralogy: case of the fibrous mimetite - see also the reprint of the article at the end of the manuscript.....</i>	<i>24</i>
3.3	SUMMARY.....	25
<b>4</b>	<b>SELECTED ANTHROPOGENIC GEOMATERIALS IN CIVIL ENGINEERING .....</b>	<b>27</b>
4.1	INVESTIGATION OF 19 <sup>TH</sup> CENTURY BINDERS FROM RAILWAY STRUCTURES (TO BE PRESENTED DURING THE 16 <sup>TH</sup> EMABM, LES DIABLERETS, SWITZERLAND, MAY 2016).....	27
4.1.1	<i>Introduction .....</i>	<i>27</i>
4.1.2	<i>Materials and methods .....</i>	<i>29</i>
4.1.3	<i>Results.....</i>	<i>30</i>
4.1.4	<i>Discussion and conclusions .....</i>	<i>31</i>
4.2	CONCRETE DURABILITY: A BRIEF OVERVIEW OF PATHOLOGIES .....	31
4.3	OIL SHALE AND ITS HIGH TEMPERATURE TRANSFORMATIONS.....	32
4.3.1	<i>Characterization of burnt oil shale – see also the reprint at the end of the manuscript .....</i>	<i>32</i>
4.3.2	<i>An example of the use of BOS in concrete to prevent ASR .....</i>	<i>34</i>
4.4	BURNT OIL SHALE SLAG AND ASSOCIATED UNUSUAL PARAGENESSES .....	34
4.5	BURNT COLLIERY SPOIL .....	35
4.6	SUMMARY.....	36
<b>5</b>	<b>THE MISSING LINK PROVIDED BY THE COMMON METHODS.....</b>	<b>39</b>
5.1	SAMPLING AND SAMPLE PREPARATION .....	39
5.2	THE ADVENT OF PETROGRAPHY AND MICROSCOPY OF CEMENTITIOUS MATERIALS: FROM FUNDAMENTAL TO APPLIED PETROGRAPHY .....	40
5.3	WHICH MICROSCOPY? .....	42
5.4	ENHANCING IMAGES: THE MULTIFOCUS TECHNIQUE - SEE ALSO THE REPRINT OF THE ARTICLE AT THE END OF THE MANUSCRIPT.....	43
5.5	SUMMARY.....	44
<b>6</b>	<b>ANALOGIES BETWEEN NATURAL AND ANTHROPOGENIC MATERIALS .....</b>	<b>45</b>
6.1	DIVERSITY IN CONSTRUCTION AND BUILDING MATERIALS.....	45
6.2	MINERALS OR SYNTHETIC SUBSTANCES? .....	45
6.3	NATURAL ANALOGUES OF CEMENTITIOUS PHASES: AN ORIGINAL APPROACH TO THE STUDY OF DURABILITY .....	46
6.3.1	<i>Geological context .....</i>	<i>47</i>
6.3.2	<i>Anhydrous high temperature minerals similar to clinker .....</i>	<i>49</i>
6.3.3	<i>Analogues of cement hydrates.....</i>	<i>50</i>
6.3.4	<i>Laboratory study of hydration of analogues.....</i>	<i>51</i>
6.4	ETTRINGITE: NATURAL MINERAL, USEFUL ANALOGUE (PART OF THIS SECTION HAS BEEN SUBMITTED TO THE “JOURNAL OF MICROSCOPY”) ..	53
6.4.1	<i>General considerations .....</i>	<i>53</i>
6.4.2	<i>Ettringite in cement media: considerations about its microscopy and microanalysis.....</i>	<i>55</i>

6.4.3	<i>The ettringite group minerals</i> .....	55
6.4.4	<i>Crystal chemistry</i> .....	56
6.4.5	<i>Beam damage</i> .....	57
6.5	ANTHROPOGENIC ANALOGUES OF NATURAL PHENOMENA: BURNT COLLIERY SPOIL AND MINERALOGY OF BURNT COAL HEAPS .....	59
6.5.1	<i>Coal heaps</i> .....	59
6.5.2	<i>The coal heap burning phenomenon</i> .....	60
6.6	THE BURNING COAL HEAP OF LA RICAMARIE (WORK IN PROGRESS).....	61
6.6.1	<i>Geographical &amp; geological context</i> .....	61
6.6.2	<i>Historical coal fires in the Stephanian coal seams</i> .....	61
6.6.3	<i>The Ricamarie heap – history</i> .....	64
6.6.4	<i>Prismation of paralavas – first worldwide occurrence?</i> .....	65
6.7	SUMMARY.....	66
<b>7</b>	<b>CONCLUSIONS AND RESEARCH PERSPECTIVES</b> .....	<b>67</b>
7.1	WHAT HAVE I DONE SO FAR.....	67
7.2	CURRENT WORK AND PERSPECTIVES.....	68
7.2.1	<i>Stabilization of antimony in cementitious phases</i> .....	68
7.2.2	<i>Alkali-activation of mine tailings</i> .....	68
7.2.3	<i>Diamond pollution in garnet during polishing: fact or fiction?</i> .....	69
7.2.4	<i>Summary and perspectives about the devices used</i> .....	69
7.2.5	<i>Perspectives in the study of mimetite</i> .....	70
7.2.6	<i>A new occurrence of katoptrite (Mn<sup>2+</sup>;Mg)<sub>13</sub>(Al; Fe<sup>3+</sup>)<sub>4</sub>Sb<sup>5+</sup><sub>2</sub>Si<sub>2</sub>O<sub>28</sub></i> .....	70
7.2.7	<i>General geology, ore geology</i> .....	70
7.3	GENERAL CONCLUSION: “WHAT CAN A HARDROCK GEOLOGIST BRING TO A CIVIL & ENVIRONMENTAL ENGINEERING LABORATORY IN GEOMATERIALS CHARACTERIZATION (AND VICE-VERSA)?” .....	71
7.3.1	<i>Fundamental &amp; applied thermometry</i> .....	71
7.3.2	<i>Microscopy and microanalysis</i> .....	71
7.3.3	<i>Durability of construction and building materials as seen through natural analogues</i> .....	71
<b>8</b>	<b>CURRICULUM VITAE</b> .....	<b>79</b>
8.1	BACKGROUND .....	79
8.2	REVIEWS OF SCIENTIFIC PAPERS .....	79
8.3	TEACHING .....	79
8.4	SUPERVISION .....	80
8.5	PROFESSIONAL OR SCIENTIFIC SOCIETY MEMBERSHIP .....	80
8.6	ORGANIZATION OF CONFERENCES .....	80
8.7	LIST OF PUBLICATIONS .....	80
8.7.1	<i>International peer-reviewed journals</i> .....	80
8.7.2	<i>Geological maps and booklets</i> .....	82
8.7.3	<i>Edited book chapters</i> .....	82
8.7.4	<i>Publications in French peer-reviewed journals</i> .....	82
8.7.5	<i>Conference proceedings</i> .....	83
8.7.6	<i>Conference without proceedings (abstracts only)</i> .....	84
8.7.7	<i>Popular science</i> .....	84
8.8	SELECTED REPRINTS .....	86

## LIST OF FIGURES

FIGURE 1 : ACCORDING TO ONE’S BACKGROUND, THE VERY SAME GEOMATERIAL WILL BE APPRECIATED DIFFERENTLY .....	13
FIGURE 2 : GEOMATERIALS RANKED BY RESEARCH AREA, SOURCE: WEB OF KNOWLEDGE (2017/03/28).....	14
FIGURE 3 : USSEL GEOLOGICAL MAP (THIÉRY ET AL., 2010), WHICH I HAVE ENTIRELY DRAWN, COORDINATED AND PARTLY MAPPED .....	18
FIGURE 4 FROM THIÉRY ET AL. (2015) A, TYPICAL INCLUSION RICH GARNETS IN METAPELITE. THE RECTANGLE INDICATES THE FIELD OF MICROGRAPH B. TRANSMITTED LIGHT, UNCROSSED POLARS. B, DETAIL OF A BOUNDARY BETWEEN AN INCLUSION-RICH CORE AND A CLEAR, INCLUSION FREE RIM. THE SQUARE INDICATES THE FIELD OF MICROGRAPHS C AND D. TRANSMITTED LIGHT, UNCROSSED POLARS. C, CLOSE-UP VIEW OF A DIAMOND (Dia) IN TRANSMITTED LIGHT, UNCROSSED POLARS. D, SAME FIELD OF VIEW AS C, IN REFLECTED LIGHT. E, THE SAME DIAMOND SEEN UNDER THE SEM IN BSE MODE (90° CLOCKWISE ROTATION). ....	19
FIGURE 5 FROM THIÉRY ET AL. (2015). LEFT: TYPICAL RAMAN SPECTRA SHOWING THE CHARACTERISTIC DIAMOND PEAK AT 1332 CM <sup>-1</sup> AND BROAD PEAKS AROUND 1600 CM <sup>-1</sup> INDICATING GRAPHITE-LIKE AMORPHOUS CARBON (FREZZOTTI ET AL., 2011). RIGHT: RAMAN ANALYSES OF DIAMOND INCLUSIONS IN GARNET IN THE DEPTH OF THE THIN SECTION. A, PLOT PROFILE OF DIAMOND PEAK INTENSITY FROM THE SURFACE TO THE DEPTHS OF THE THIN SECTION. B, 3D REPRESENTATION OF DIAMOND (RED) AND GRAPHITE (GREEN) ENCLOSED IN GARNET (NOT SHOWN FOR CLARITY) .....	20
FIGURE 6 FROM THIÉRY (2011A) : CONCEPTUAL SKETCH OF THE SUCCESSIVE STAGES OF THE CORDIERITITE EVOLUTION .....	21
FIGURE 7 FROM THIÉRY & CARTANNAZ (2013): PHOTOMICROGRAPH OF ORE MINERALS FROM MÉRINCHAL, TAKEN USING A METALLOGRAPHIC MICROSCOPE WITH REFLECTED LIGHT UNDER CROSSED POLARS EXCEPTED WHEN MENTIONED. APY: ARSENOPYRITE, CCP: CHALCOPYRITE, GN: GALENA, SP: SPHALERITE, TTR: TETRAHEDRITE (ABBREVIATIONS AFTER WHITNEY AND EVANS, 2010), BRT: BERTHIERITE; PYR: PYRARGYRITE. A: MYRIAD OF MINUTE PYRARGYRITE CRYSTALS IN THEIR QUARTZ MATRIX, STEREO-MICROSCOPE VIEW, B: POLYPHASED ASSEMBLAGE OF ARSENOPYRITE, GALENA AND SPHALERITE, THE LATTER SHOWING STRONG BROWN INTERNAL REFLECTIONS, C: BERTHIERITE VEIN, D: ARSENOPYRITE CONTAINING A SUBEHEDRAL TETRAHEDRITE CRYSTAL, E: CLOSE-UP VIEW OF A TETRAHEDRITE CRYSTAL CONTAINING VERMICULAR CHALCOPYRITE AND GALENA, F: DYSCRASITE AND PYRARGYRITE.....	23
FIGURE 8 FROM THIÉRY (2014A): SEM (SECONDARY ELECTRON MODE) OF FIBROUS MIMETITE .....	24
FIGURE 9 : LOCATION OF THE STUDIED RAILWAY IN FRANCE AND DETAIL OF THE ITINERARY ALONG THE CHAVANON VALLEY. THE LOCATIONS OF THE TWO STRUCTURES ON WHICH SAMPLING HAVE BEEN CARRIED OUT HAVE A LIGHT GREY FRAME .....	28
FIGURE 10 : A STEAM TRAIN ON THE RANDONNIÈRE BRIDGE, GETTING OUTSIDE THE RANDONNIÈRE TUNNEL. PICTURE FROM VILAIN (1982) .....	28
FIGURE 11 : STRUCTURES FROM WHICH THE MORTARS HAVE BEEN SAMPLED .....	29
FIGURE 12: GROUND SLAB OF MORTAR FROM THE SOUTHERN ENTRANCE OF THE CONFOLENT TUNNEL.....	30
FIGURE 13: FEATURES OBSERVED IN BINDERS AS SEEN IN OPTICAL MICROSCOPY, TRANSMITTED LIGHT AND CROSSED POLARS EXCEPT WHEN INDICATED. A: CEMENT PARTICLE COMPOSED OF PSEUDOWOLLASTONITE AND POTASSIUM SILICATE (CONFIRMED BY EDS) FROM THE PONT BIAIS BRIDGE, B: PSEUDOWOLLASTONITE DOMINATED ASSEMBLAGE, CONFOLENT TUNNEL (SOUTHERN ENTRANCE), C: SEM (BSE) IMAGE OF A CEMENT PARTICLE COMPOSED OF HYDRATED ALITE (DARK), HYDRATED BELITE (DARK) AND INTERSTITIAL FERRITE (BRIGHT), D: COAL ASH (REFLECTED LIGHT), E: LIMESTONE FILLER, CONFOLENT TUNNEL.....	30
FIGURE 14 FROM THIÉRY ET AL. (2015): SCHEMATIC DIAGRAM SUMMARIZING THE FABRICATION AND USE OF BOS .....	33
FIGURE 15 FROM THIÉRY ET AL. (2015): HIGH-TEMPERATURE EVOLUTION OF THE POSIDONIA SHALE. A) TYPICAL PYRITE FRAMBOIDS FROM THE UNBURNT, RAW POSIDONIA SHALE. REFLECTED LIGHT, CROSSED POLARS. B) HEMATITE PSEUDOMORPHS AFTER PYRITE FRAMBOIDS IN THE BURNT OIL SHALE. REFLECTED LIGHT, CROSSED POLARS .....	33
FIGURE 16 FROM BOURDOT ET AL. (2016) : EFFECT OF BURNT OIL SHALE ON EXPANSION DUE TO ALKALI-SILICA REACTION .....	34
FIGURE 17 : BOS PARTICLE IN CEMENT PASTE ; A) TRANSMITTED LIGHT, CROSSED POLARS B) REFLECTED LIGHT.....	34
FIGURE 18 FROM GATEL ET AL. (2015) : OIL-SHALE PROCESSING AT THE LAPANOUSE PLANT. SHALE, WITH AN AVERAGE OIL CONTENT OF 4,4%, WAS EXPLOITED IN A LARGE OPEN-PIT BY BLASTING. AFTER CRUSHING, THE TWO FRACTIONS (FINE AND COARSE) WERE SEPARATED. THE FINE FRACTION WAS NOT PROCESSED AND WAS DIRECTLY DEPOSITED ON A WASTE HEAP. THE WASTE HEAP THUS CONTAINS UNPROCESSED, FINE PARTICLES OF OIL SHALE (I.E., STILL CONTAINING ORGANIC MATTER), THE SOLID RESIDUE OF COARSE PROCESSED OIL SHALE, AND SOME ADMIXED LIMESTONE. A SHORT TIME AFTER THE PLANT WAS CLOSED (1951), THE HEAPS BEGAN TO BURN AND THE COMBUSTION LASTED FOR AT LEAST 10 YEARS. ....	35
FIGURE 19: BURNT COLLIERY SPOIL USED AS DECORATIVE AGGREGATE ON SIDEWALKS (IMAGE FROM GOOGLE STREET VIEW) .....	35
FIGURE 20 FROM THIÉRY & GUY (2015): MACROSCOPIC SAMPLES OF BURNT COLLIERY SPOIL FROM VARIOUS LOCALITIES. A) BAKED SANDSTONE, RIEULAY, NORTH OF FRANCE; B) BAKED ARGILLITE, SAME PROVENANCE; C) PRESERVED FOSSIL LEAVES ON A BAKED SHALE, GERMIGNIES, NORTH OF FRANCE; D) POROUS PARALAVA WITH FLOW TEXTURE, RIEULAY, NORTH OF FRANCE; E) ROPY PARALAVA, LA RICAMARIE, CENTER OF FRANCE; F) EXTREMELY VACUOLAR PARALAVA, SAME PROVENANCE. ....	36
FIGURE 21: THE MOUNTAIN VS. THE DAM. LEFT: OISANS MOUNTAINS SOMEWHERE IN THE VÉNÉON VALLEY (FRENCH ALPS), RIGHT: BORT-LES-ORGUES DAM, FRENCH MASSIF CENTRAL. THE AMOUNT OF SAMPLE AVAILABLE FOR STUDY IS NOT THE SAME. ....	39
FIGURE 22 FROM GARY LARSON’S « THE FAR SIDE GALLERY »: EARLY MICROSCOPE .....	40
FIGURE 23 : TWO GREAT SCIENTISTS HISTORICALLY LINKED TO THE STUDY OF THIN SECTIONS. A) THE ENGLISH GEOLOGIST HENRY CLIFTON SORBY (1826-1908), THE INVENTOR OF THIN SECTIONING OF ROCKS B) THE FRENCH CHEMIST HENRY LE CHATELIER (1850-1936), FIRST SCIENTIST TO STUDY AND DESCRIBE PORTLAND CLINKER AND CEMENT HYDRATION UNDER THE MICROSCOPE IN THIN SECTION. IMAGES FROM WIKIPEDIA. ....	41
FIGURE 24 FROM THIÉRY ET AL. (2016): (A) THE ORIGINAL DRAWING OF HENRY LE CHATELIER (1887), REPRESENTING THE MICROSTRUCTURE OF PORTLAND CLINKER AS SEEN IN THIN SECTION, SCAN FROM THE ORIGINAL DOCUMENT COURTESY OF THE BIBLIOTHÈQUE PATRIMONIALE NUMÉRIQUE DE L’ÉCOLE NATIONALE DES MINES DE PARIS (B) MODERN CLINKER AS SEEN IN THIN SECTION, CROSS-POLARIZED LIGHT (C) TYPICAL MICROSTRUCTURE OF CLINKER AS SEEN IN REFLECTED LIGHT (CROSS-POLARIZED LIGHT) (D) SAME FIELD OF VIEW AS (C) AFTER ETCHING OF THE SURFACE WITH NITAL (E) ALITE, TERMED C <sub>3</sub> S – TRICALCIUM SILICATE (F) BELITE, TERMED C <sub>2</sub> S – DICALCIUM SILICATE (G) THE INTERSTITIAL PHASE BETWEEN CALCIUM SILICATES, CONSISTING OF DARK- GREY TETRACALCIUM ALUMINOFERRITE (TERMED C <sub>4</sub> AF) AND GREY TRICALCIUM ALUMINATE (TERMED C <sub>3</sub> A). ....	41
FIGURE 25 FROM THIÉRY & GREEN (2012) : A MULTIFOCUS STACK OF A SET OF 21 IMAGES OF A SINGLE PYROXENE CRYSTAL; THE SCALE BAR IS 100 μm. A 3D RENDERING OF THE INCLUSIONS LOCATED IN THE CRYSTAL WITH A SECTION ALONG AB THROUGH THE INCLUSIONS.....	43

FIGURE 26: DIVERSITY IN CONSTRUCTION AND BUILDING MATERIALS .....	45
FIGURE 27 : TIMESCALE BETWEEN PORTLAND CEMENT AND ITS NATURAL ANALOGUE AND FAMOUS BUILDINGS.....	47
FIGURE 28 FROM ROCHELLE & MILODOWSKI (2013): THE DOLERITE PLUG OF SCAWT HILL .....	48
FIGURE 29: THE LOKBATAN MUD VOLCANO (AZERBAIJAN).....	49
FIGURE 30: THE LANDMARK CHAPTER BY Y. KOLODNY (1979), DESCRIBING NATURAL ANALOGUES .....	49
FIGURE 31 : ORIGINAL PUBLICATIONS DESCRIBING THE NATURAL ANALOGUES OF $C_2S$ , LARNITE (TILLEY, 1929), AND $C_3S$ , HATRURITE (GROSS, 1977) .....	50
FIGURE 32 : ORIGINAL PUBLICATION DESCRIBING PORTLANDITE ( $Ca(OH)_2$ ) IN A NATURAL CONTEXT (TILLEY, 1933) .....	51
FIGURE 33 A&B FROM THIÉRY ET AL. ICMA 2014 ORAL PRESENTATION, C&D FROM THIÉRY (2013). COMPARISON OF NITAL ETCHING OF A LARNITE-BEARING ROCK (A/B, BEFORE/AFTER) AND A PORTLAND CEMENT CLINKER (C/D, BEFORE/AFTER). .....	52
FIGURE 34 FROM THIÉRY ET AL. (2014): XRD COMPARISAON BEFORE AND AFTER HYDRATION OF A LARNITE-BEARING ROCK .....	53
FIGURE 35 : ETTRINGITE CRYSTALS FROM THE N'CHWANING MINE .....	54
FIGURE 36: CRYSTAL STRUCTURE OF ETTRINGITE ; DATA FROM (GOETZ-NEUNHOEFFER & NEUBAUER, 2006) DRAWN USING VESTA SOFTWARE (MOMMA & IZUMI, 2011) .....	55
FIGURE 37 FROM THIÉRY ET AL., SUBMITTED TO "JOURNAL OF MICROSCOPY": EDS MAPS OF ETTRINGITE CRYSTALS FROM THE N'CHWANING MINE, SHOWING VARIATIONS IN COMPOSITION. THE CORE OF THE CRYSTAL IS COMPOSED OF ALMOST PURE ETTRINGITE (CA, AL, S) WHILE THE RIMS SHOW VARIATIONS TOWARDS OTHER END-MEMBERS WITH MORE COMPLEX CHEMISTRY (STURMANITE $Ca_6(Fe^{3+}, Al, Mn^{3+})_2(SO_4)_2[B(OH)_4](OH)_{12} \cdot 25H_2O$ OR CHARLESITE $Ca_6(Al, Si)_2(SO_4)_2[B(OH)_4](OH, O)_{12} \cdot 26H_2O$ ) .....	57
FIGURE 38: TRIPLETS OF IMAGES SHOWING AN AREA BEFORE AND AFTER ANALYSIS AND A CLOSE-UP VIEW OF THE RESULTING BEAM DAMAGE. A, B, C: 7kV; D, E, F: 10 kV; G, H, I: 15 kV; J, K, L: 20 kV. COUNTING TIME 60s. ....	58
FIGURE 39 : DIVERSITY IN THE FILLING OF COAL HEAPS: FINE PARTICLES FROM THE CLEANING OF COAL, DEMOLITION WASTES.....	59
FIGURE 40 FROM THIÉRY ET AL. (2013): SYNTHETIC CROSS-SECTION THROUGH A BURNING COAL HEAP .....	60
FIGURE 41: THE EVOLUTION OF THE RICAMARIE BURNING COAL HEAP THROUGH TIME .....	63
FIGURE 42 FROM GUY ET AL (IN REVISION) : (A) GENERAL VIEW OF THE COLUMNAR "SILL" FROM THE BURNING HEAP. (B) ANOTHER GENERAL VIEW OF THE COLUMNAR ZONE SHOWING THE PART OF THE HEAP OVERLYING THE COLUMNS. THIS PART IS MADE OF BLOCKS SINTERED TOGETHER BECAUSE OF BURNING AND PARTIAL MELTING OF THE PRIMARY MATERIAL. THE LENGTH OF THE COLUMNS IS ABOUT TWO TO FOUR METERS. CONDENSATE MINERALS ARE RESPONSIBLE FOR THE WHITE COLOR ON THE SURFACE OF SOME OF THE ROCKS.(C) GENERAL VIEW OF THE COLUMNAR ZONE SEEN FROM ABOVE, AS REVEALED BY DIGGING OF THE HEAP. THE POLYGONAL SECTIONS OF THE COLUMNS CAN BE SEEN. THE DIAMETER OF THE PRISMS IS AROUND 30 TO 50 CM. THE VISIBLE LENGTH OF THE COLUMNS IS APPROXIMATELY 2 METERS HERE. PICTURE TAKEN IN 2011. (D) PARTIAL VIEW OF THE BASE OF THE COLUMNS: PARALAVAS ARE FOUND, SHOWING HORIZONTAL LAYERING (HAMMER GIVES THE SCALE); THIS "LAYERED" STRATA MAY SHOW VERTICAL FRACTURES IN CONTINUITY WITH THE UPPER LYING COLUMNS. THE UNDERLYING PART OF THE COLUMN IS NOT VISIBLE AT THE MOMENT. PICTURE TAKEN IN 2011. (E)CLOSE-UP VIEW OF THE COLUMNAR STRUCTURES. SOME COLUMNS ARE INTERRUPTED BY HORIZONTAL OR NEARLY HORIZONTAL FRACTURES THAT MAY MAKE LARGE VOIDS APPEAR. SOME COLUMNS MAY ALSO BE SEPARATED FROM ADJACENT ONES BY VERTICAL VOIDS, SEE ALSO FIG. 4F. (F) CLOSE-UP VIEW OF THE COLUMNS. SOME VERTICAL VOIDS MAY BE SEEN BETWEEN ADJACENT COLUMNS; THE CONTOURS OF ONE COLUMN MAY NOT FIT WITH THAT OF THE NEIGHBORING ONE. THE INTERNAL PART OF THE COLUMNS IS RED, WHEREAS THE RIM IS GREY-BLACK. ALL PICTURES WERE TAKEN IN NOVEMBER 2014 UNLESS SPECIFIED. ....	65
FIGURE 43 : FROM THE FIELD SCALE TO THE MICROSCOPIC SCALE – SIMILARITY IN THE METHODOLOGY OF STUDY FOR ROCKS AND CIVIL ENGINEERING MATERIALS.....	67
FIGURE 44 : TAILING FROM THE ASAREL MINE IN BULGARIA, JULY 2012. ....	68

## LIST OF TABLES

TABLE 1 : SUMMARY OF MY FIELD WORK ACTIVITIES .....	17
TABLE 2 : PEER-REVIEW PROCESS FOR THE PAPER DESCRIBING THE FIRST OCCURRENCE OF METAMORPHIC MICRODIAMOND IN THE FRENCH MASSIF CENTRAL (THIÉRY, ROLIN, ET AL., 2015) .....	20
TABLE 3: SUMMARY OF MICROSCOPICAL INVESTIGATIONS IN MORTARS FROM 2 STRUCTURES BUILT AROUND 1880. -: NOT OBSERVED, X: MINOR, XX: ABUNDANT ...	31
TABLE 4 : SOME EXAMPLE OF CONCRETE PATHOLOGIES .....	32
TABLE 5: BRIEF REVIEW OF THE TYPES OF MICROSCOPIES APPLIED TO NATURAL AND ANTHROPOGENIC GEOMATERIALS .....	43
TABLE 6: EXAMPLES OF MINERALS WHICH NAMES HONORS SCIENTISTS HAVING BEEN INVOLVED IN CEMENT SCIENCE .....	46
TABLE 7 : THE ETTRINGITE GROUP MINERALS (EGM).....	56
TABLE 8 : HISTORICAL DESCRIPTIONS OF MINERAL EFFLORESCENCES ASSOCIATED TO COAL SEAMS FIRES IN THE LOIRE COAL BASIN .....	64

# 1 RÉSUMÉ FRANÇAIS ÉTENDU

## *Qu'est-ce qu'un géologue peut apporter à un département de génie civil et environnemental du point de vue de la caractérisation des géomatériaux (et vice-versa) ?*

Ce travail d'habilitation à diriger des recherches couvre mon parcours universitaire puis professionnel et dresse des perspectives sur des thématiques et outils de recherche.

### **Parcours universitaire, thématiques de recherches abordées et outils utilisés**

Sans entrer non plus dans une démarche autobiographique, ma découverte du monde de la recherche s'est faite très tôt, lorsqu'étudiant en DEUG j'avais sympathisé avec un doctorant qui durant sa thèse avait mis au point une machine pour éroder des galets (une immense cuve de plusieurs mètres de diamètre).

Cet aparté fait, mes premières expériences de recherche ont eu lieu à partir de 2004, en première année de « maîtrise de sciences et technologies » (équivalent de la 3<sup>ème</sup> année de licence actuelle). J'ai commencé à réaliser des stages de cartographie géologique pour le BRGM. Si la cartographie géologique est un outil, les implications des levés contribuent à la connaissance géologique d'une région, qui est une thématique de recherche. Ces premiers travaux ont été encadrés par Charles Cartannaz durant sa thèse de doctorat sur le massif de Guéret (Cartannaz, 2006), sous la responsabilité de Patrick Rolin, maître de conférences à l'université de Franche-Comté.

Durant ma première année de master (2004-2005), j'ai continué les travaux de terrain en levant la moitié est de la feuille de Felletin (Rolin et al., 2008) qui ont débouché sur la thématique de recherche que j'ai abordée au cours de ma seconde année de master (2005-2006) : la reconnaissance géologique d'un granite pouvant potentiellement être le lieu d'implantation d'un éventuel stockage profond de déchets nucléaires. Ceci a fait appel aux outils suivants :

- Cartographie (2 fois 2 mois : avril-mai et juillet-août 2005),
- Pétrographie : étude de lames minces,
- Géochimie sur les granitoïdes étudiés,
- Géochronologie.

Mes travaux de doctorat (novembre 2006-avril 2010), intitulés « Métamorphismes et déformations des séries cristallophylliennes du Chavanon, de la Sioule et d'Ussel (Massif Central français). Discussion du modèle de nappes du Massif Central », ont fait appel aux outils suivants :

- Cartographie intensive (coordination de la feuille « Ussel » n°715 au 1/50 000) : 2 mois en 2006, 2007 et 2008, durées plus réduites en 2009 (2-3 semaines),
- Pétrographie des formations étudiées,
- Géochimie des formations étudiées,
- Géochronologie.

## **Cheminement scientifique**

À l'issue de mon doctorat, j'ai obtenu un poste de chargé de recherches, ayant depuis évolué en maître-assistant, en minéralogie appliquée aux matériaux naturels et anthropiques, au sein du département « génie civil et environnemental » de l'École des Mines de Douai. Cette thématique, vaste, couvre en fait mon domaine d'intervention sur les différents axes de recherche menés au département :

- Valorisation de déchets et sous-produits industriels (granulats de démolition, sédiments, laitiers...) dans les matériaux de construction,
- Impact environnemental,
- Étude de la durabilité des matériaux de construction (pathologies d'ouvrages).

J'ajouterai un dernier point, indépendant de ces axes de recherches : la poursuite d'une activité propre liée à la géologie, principalement dans la suite de mes travaux de thèse. Plusieurs aspects sont à considérer vis-à-vis de cette volonté de poursuivre cette thématique :

- Conserver la maîtrise d'un certain nombre d'outils (travail de terrain notamment),
- Maintien à niveau des connaissances et veille bibliographique sur les sujets qui m'intéressent,
- Continuer à publier des données issues de mes travaux de thèse.

Au cours de ce manuscrit, nous verrons comment certains travaux, à priori très fondamentaux, s'intègrent dans la démarche de recherche plus large que je mène et peuvent faire écho à des travaux plus appliqués.

Le titre de ce manuscrit, un peu provocateur, reflète une position qui peut paraître un peu ambiguë de prime abord. En effet, les caractérisations des matériaux dans le domaine des sciences appliquées, et en particulier dans le cas du génie civil, sont plus souvent faites par des physico-chimistes. L'intérêt et l'originalité de l'approche naturaliste du géologue sur ces matériaux sont discutés dans ce manuscrit.

Ce manuscrit est organisé de la manière suivante :

### **Introduction – que sont les géomatériaux ?**

Ce court chapitre introductif replace les matériaux décrits dans ce manuscrit dans un cadre plus général. Dans la mesure où j'ai fait le choix de mélanger les thématiques fondamentales et appliquées, et donc les géomatériaux naturels (roches, minéraux) et anthropiques (sous-produits industriels), il m'a paru intéressant de livrer quelques explications sur les visions que peuvent avoir les scientifiques du terme « géomatériaux ».

Ainsi, on peut facilement mettre en évidence que pour un même géomatériau, sa perception sera différente suivant le parcours de la personne qui l'étudie. Prenons le cas d'un granite : un géologue verra le résultat de l'évolution d'une dynamique orogénique, un géochimiste appréciera



les éléments présents, un ingénieur géotechnicien quant à lui se focalisera sur les aspects mécaniques.

La diversité d'utilisation de ce terme est reflétée dans les journaux scientifiques référencés dans le Web of Science ayant publié des articles contenant le terme « geomaterials ». Contre toute attente, les journaux qui référencent le plus ce terme sont axés sur l'ingénierie (mécanique des roches). Le journal « Geology » n'apparaît pas.

## **Chapitre 1 – Les géomatériaux naturels : reconnaissance sur le terrain et au laboratoire pour des applications en géologie fondamentale.**

Ce chapitre reprend des aspects fondamentaux abordés au cours de mon parcours universitaire (master et doctorat) et après. Il est divisé en deux sous-parties principales : géologie générale et métallogénie.

La section « géologie générale » est consacrée à la présentation de deux résultats liés à l'étude de la série du Chavanon menée durant ma thèse de doctorat (Thiéry, 2010).

Le plus important de ces résultats, la découverte de microdiamants d'origine métamorphique (Thiéry, Rolin, et al., 2015) est ainsi abordée. Sans entrer dans un luxe de détails sur les implications géodynamiques (potentiellement nombreuses), cette découverte est présentée ici sous l'œil de la préparation des échantillons et de la nécessité de combiner plusieurs techniques analytiques afin de s'assurer de la présence (ou de l'absence) de certains minéraux ou certaines phases, d'autant plus quand les implications sont importantes. Dans le cas présent, la découverte (controversée) de ces microdiamants a donné lieu à discussion (Berger, 2016; Thiéry, Rolin, et al., 2016) sur les aspects de géodynamique mais également sur la préparation des échantillons : celle-ci faisant appel à des produits diamantés (lame de scie, abrasifs de polissage), l'éventualité d'une pollution est fréquemment abordée dans ces contextes (Perraki et al., 2009; Nasdala et al., 2016). Signalons ainsi une controverse majeure sur une pollution aux diamants dans les plus vieux zircons de la Terre (conglomérats de Jack Hills, Australie) : initialement décrits et interprétés à la lumière des connaissances sur la présence de diamants, symptomatiques de contextes de ultra-haute pression (Menneken et al., 2007), il a par la suite été démontré que leur présence résultait d'une pollution liée à la préparation des échantillons (Dobrzhinetskaya et al., 2014).

Le second de ces résultats, toujours au sein du même ensemble géologique (la série du Chavanon) concerne des estimations géothermométriques sur la base de la description de roches riches en cordiérite (Thiéry, 2011a). L'intérêt est d'utiliser des techniques de microanalyse élémentaire (microsonde électronique) pour alimenter des géothermomètres basés sur des équilibres minéraux. Cette section est présentée car il est également question de cordiérite dans le chapitre consacré aux analogues anthropiques des phénomènes naturels, à savoir les terrils (chapitre 4).

La section « métallogénie » quant à elle reprend des résultats de caractérisation menés sur des gîtes minéraux antimonifères (Thiéry & Cartannaz, 2013) : cartographie, étude des paragenèses et des minéraux d'altération, ainsi que la caractérisation d'une forme particulière de mimérite associée aux minéraux secondaires d'un gîte plombifère (Thiéry, 2014a). De la même manière que pour les microdiamants, l'accent est mis sur les méthodes de caractérisation plutôt que sur les

implications. Dans les deux cas présentés ici, une approche multi-échelle et donc multi-technique est abordée : terrain, microscopie optique (loupe binoculaire et microscope pétrographique), microscopie électronique à balayage (imagerie et microanalyse EDS) voire spectroscopie Raman. La caractérisation des gîtes d'antimoine de la région de Mérinchal (Creuse) sur la base d'échantillons prélevés dans le cadre de levés géologiques sur la carte d'Aubusson (Cartannaz et al., 2008) a permis d'affiner la connaissance de la minéralisation ainsi que celle des minéraux secondaires. Concernant les travaux menés sur la mimétite, l'étude de la micromorphologie de cristaux aciculaires au MEB, jusqu'à présent jamais menée, a permis de mettre en évidence la présence d'aiguilles de diamètre inférieur au micromètre ; l'étude Raman quant à elle a permis d'affiner la connaissance chimique de cette mimétite au sein de la solution solide mimétite-pyromorphite (Bajda et al., 2011).

## **Chapitre 2 – Exemples de géomatériaux anthropiques en génie civil**

Ce chapitre est divisé en deux parties : d'une part, une étude sur des liants hydrauliques anciens est présentée, et d'autre part des caractérisations de matériaux de haute température sont menées.

Des mortiers d'ouvrages d'art (pont, tunnel) de la fin du 19<sup>ème</sup> siècle (environ 1880) sont caractérisés au microscope optique et électronique afin de reconnaître les phases en présence. Il s'agit de ciments Portland relativement primitifs (Gosselin & Pintér, 2016; Rayment, 1986) au sein desquels l'étude des phases met en évidence l'hétérogénéité des températures dans le four au cours de la cuisson (Dariz et al., 2017).

Les sous-produits industriels de haute température que j'ai été amené à étudier sont d'une part liés à une thématique étudiée au sein du département GCE (réaction alcali-silice) et d'autre part à mon installation dans le Nord de la France :

- Les schistes calcinés sont des ajouts cimentaires qui permettent de se prévenir contre la réaction alcali-silice,
- Les résidus de la distillation de schistes bitumineux, stockés en terrils et étant entrés en combustion fournissent des matériaux de haute température originaux,
- Les « schistes houillers » sont quant à eux des résidus de l'exploitation du charbon.

Les schistes calcinés sont des résidus de la combustion de schistes bitumineux, dans le cas présent des marnes Toarciennes, dans une centrale thermique en lit fluidisé. Leur minéralogie ainsi que leur caractère pouzzolanique étaient déjà bien connus dans la littérature (Weislehner, 1983; Peters, 1987; Riedhammer, 1985). Mon apport concerne leur caractérisation microstructurale fine, multi-technique (microscope optique, MEB-EDS et MET-EDS) couplée à une étude par DRX de l'évolution du schiste non calciné au schiste calciné.

Les résidus de combustion de terril de schistes bitumineux stockés en terril, exploités localement comme granulats, présentent une double évolution thermique : lors de la distillation, aux alentours de 500°, et lors de la combustion, autour de 1000°. Les phénomènes de pyrométamorphisme (voir au chapitre 4) sur ces matériaux sont à l'origine de sous-produits (on ne peut pas réellement parler de roches, bien qu'il s'agisse d'assemblages minéraux) originaux,

partiellement voire totalement fondus et recristallisés (les « paralavas »). Les minéraux secondaires, issus de l'interaction avec l'atmosphère ou avec des fluides météoriques circulant dans le terril, peuvent présenter des analogies avec les matériaux cimentaires – ce point est discuté au chapitre 4.

Le terme « schiste houiller » est courant concernant le tout-venant des terrils (Raoul et al., 2008; Guy et al., 2008). On distingue le « schiste noir », non brûlé, du « schistes rouge », brûlé (le phénomène de combustion des terrils est abordé au chapitre 4). Ce sont des matériaux largement exploités dans les anciennes régions minières, pour diverses applications (voir à ce sujet le rapport EUR 5736E de la commission européenne, 1977, « utilisation of colliery spoil in civil engineering applications »): granulats pour béton (Runguphan & Guthrie, 2009), substitution au cru du clinker, granulats décoratifs. Mon apport sur ces matériaux concerne essentiellement leur description pétrographique, assez peu répandue dans la littérature.

### **Chapitre 3 – Le chaînon manquant : les méthodes de caractérisation identiques**

Aussi surprenant que cela puisse paraître, les similitudes entre les méthodes de caractérisations appliquées aux géomatériaux naturels et anthropiques sont telles que l'on parle même de « pétrographie du béton », largement répandue dans la littérature internationale (St John et al., 2016; Mielenz, 1962). Ce chapitre confronte les méthodes d'investigation traditionnelles appliquées à la caractérisation microstructurales tant des géomatériaux naturels qu'anthropiques : microscopies optiques, électroniques, microtomographie à rayons X...

Depuis les premières lames minces de 1849 du géologue anglais Henry Clifton Sorby (Humphries, 1992) à la première description des phases du clinker Portland à l'aide de lames minces par le chimiste français Henry Le Chatelier (Le Chatelier, 1882, 1887), cet aperçu historique montre que les deux familles de matériaux ont rapidement été étudiées par des méthodes communes.

Après avoir insisté au chapitre 1 sur la nécessité de procéder à une préparation rigoureuse des échantillons afin d'éviter tout artefact (cas des inclusions de diamants dans les grenats ou autres minéraux) dans le cas de géomatériaux naturels pour des études à vocation fondamentale, le chapitre 3 aborde également l'aspect de la préparation des échantillons. En effet, comme souligné par Fernandes et al. (Fernandes et al., 2009), « *le prix d'une carotte de béton comprend les coûts liés à l'extraction, au transport, à la manutention, au stockage et la préparation ainsi que des coûts éventuellement liés à une fermeture de route ou à des échafaudages. Calculé au kilogramme, une carotte peut valoir son poids d'or, presque littéralement. Ainsi, il est important de prendre des précautions pour minimiser l'introduction d'artefacts à n'importe quel moment avant l'analyse, également durant l'extraction* ».

Pour un géologue, la quantité d'échantillon disponible pour un prélèvement est pratiquement illimitée (sauf dans le cas de minéraux ou de fossiles rares, par exemple) ; pour l'étude d'un ouvrage d'art il n'en est pas de même. Les prélèvements doivent être faits intelligemment en sachant qu'il n'y a pas de droit à l'erreur.

Enfin, un complément à ce chapitre présente une technique d'amélioration d'images : l'imagerie multifocale. Elle permet de combiner des images prises avec des mises au point différentes en une seule image parfaitement nette. Bien connue chez les photographes de microminéraux (Green, 2005), cette technique étendue à la pétrographie (Thiéry & Green, 2012) offre également des perspectives intéressantes telles que la possibilité de réaliser des modèles 3D d'inclusions, d'objets archéologiques (Figueiredo et al., 2013)... En génie civil, elle a été appliquée pour obtenir des modèles 3D de fractures de béton (Štukovnik et al., 2014).

## Chapitre 4 – Analogies entre les matériaux naturels et anthropiques

Après avoir décrit des matériaux très contrastés dans les chapitres 1 et 2, puis avoir montré dans le chapitre 3 qu'ils s'étudient de la même manière, ce chapitre présente des analogues de deux manières :

- Analogues naturels de phases cimentaires (minéralogie de ultra-haute température ainsi que minéraux secondaires semblables à ceux formés lors de l'hydratation des ciments,
- Analogues artificiels de phénomènes naturels, en particulier phénomènes associés à la combustion des terrils.

Les analogues naturels des phases cimentaires sont connus de longue date, qu'il s'agisse des anhydres similaires aux phases du clinker Portland ou des produits d'hydratation. La larnite,  $\text{Ca}_2\text{SiO}_4$ , est l'analogue naturel de la bélite ( $\text{C}_2\text{S}$  des cimentiers), elle a été décrite dès 1929 à Scawt Hill (Tilley, 1929). Ce gisement, situé en Irlande du Nord, est intéressant à plus d'un titre. Géologiquement parlant, il s'agit d'une intrusion de dolérite au contact de formations sédimentaires (calcaires à nodules de silex, Rochelle & Milodowski, 2013). Parmi les autres analogues de phases cimentaires dont Scawt Hill est la localité-type, mentionnons la portlandite  $\text{Ca}(\text{OH})_2$ ,

Minéral	Analogue cimentaire	Références
Larnite $\text{Ca}_2\text{SiO}_4$	$\text{C}_2\text{S}$ - C'est l'une des phases principales du clinker Portland	(Tilley, 1929)
Rankinite $\text{Ca}_3\text{Si}_2\text{O}_7$	Connue dans des laitiers utilisés comme ajouts cimentaires	(Leslie & Hughes, 2004; Duée et al., 2015)
Portlandite $\text{Ca}(\text{OH})_2$	CH – Elle se forme par hydratation de la chaux $\text{CaO}$	(Tilley, 1933)
Hydrocalumite $\text{Ca}_2\text{Al}(\text{OH})_6[\text{Cl}_{1-x}(\text{OH})_x].3\text{H}_2\text{O}$	C'est le modèle structural de la phase AFm qui se forme lors de l'hydratation du ciment Portland.	(Matschei et al., 2007; Tilley et al., 1934)

Les analogues anthropiques (ou semi-anthropiques) de phénomènes naturels, plus précisément les analogies de certains phénomènes volcaniques, peuvent être observés au sein des terrils en combustion. Signalons à titre de curiosité scientifique que le chimiste Jean Pierre Louis Girardin (1803-1884), dans son ouvrage « Considérations générales sur les volcans et examen critique des diverses théories qui ont été successivement proposées pour expliquer les phénomènes

volcaniques » (1831) mentionnait déjà les analogies entre les phénomènes des « houillères embrasées » (feux de couches de charbon en place) et les volcans.

La combustion des terrils est un phénomène généralement accidentel, provoqué le plus fréquemment par la foudre, un feu de forêt à proximité ou encore par un court-circuit (Nichol & Tovey, 1998).

L'auto-inflammation et la combustion spontanée des résidus riches en charbon, ainsi que l'apport de chaleur lié à la décomposition exothermique de la pyrite, sont les causes internes et typiques de la combustion de la majorité des terrils de par le monde. De plus, la nature faiblement compactée des dépôts facilite les appels d'air ainsi que sa circulation vers les parties internes. La moisissure sur les morceaux de bois peut également contribuer à l'élévation interne de température (Limacher, 1963). Il a été estimé, dans le Nord-Pas-de-Calais, qu'un terril sur trois entrainait en combustion, ce qui, au début des années 1980, représentait 74 terrils (Ghouzi, 1982). L'entrée en combustion d'un terril est donc un phénomène complexe, dont on trouvera une discussion dans l'article de Misz-Kennan & Fabiańska (2011).

## **Conclusions et perspectives de recherche**

### ***Synthèse des travaux effectués jusqu'à présent***

Ce chapitre, sur la base des précédents, va tenter de répondre à la question posée en titre de ce manuscrit, à savoir « *Qu'est-ce qu'un géologue peut apporter à un département de génie civil et environnemental du point de vue de la caractérisation des géomatériaux (et vice-versa) ?* ».

La lecture des 2 premiers chapitres montre deux domaines contrastés a priori difficiles à réconcilier : outre l'aspect de la recherche fondamentale plus ou moins opposée à la recherche appliquée, on peut également opposer le côté naturaliste à une vision très anthropique.

En tentant une approche naturaliste précisément, on réalise que les analogues entre ces matériaux sont à rechercher de deux manières : analogues naturels de phases cimentaires (ou autres produits industriels) ou à l'inverse analogues semi-anthropiques de phénomènes naturels, comme par exemple la combustion des terrils qui fournit un bon exemple d'analogues de phénomènes magmatiques : prismation des *paralavas* (Guy et al., soumis, voir chapitre 4) mais également différenciation magmatique (Gawęda et al., 2011).

### ***Synthèse sur l'approche proposée***

Les travaux présentés dans ce mémoire, combinant les approches naturalistes et appliquées, comme décrit ci-dessus, s'alimentent mutuellement.

Ainsi, la maîtrise d'une technique expérimentale dans un domaine est grandement bénéfique à l'autre, comme par exemple :

- L'approche pétrographique, très marquée en géologie fondamentale, permet de résoudre des problématiques purement appliquées (nature d'une pathologie d'ouvrage, type de liant utilisé...),
- Toujours dans le domaine de la pétrographie mais avec une démarche plus spécifique telle que celle adoptée dans les études ayant trait au métamorphisme : l'étude d'une paragenèse d'un sous-produit industriel tel que les schistes calcinés permet de retracer

leur « histoire » (disons plutôt leur évolution) lors de la calcination, de la même manière que l'étude d'une roche métamorphique permet de retracer son évolution au cours des épisodes qu'elle a vécu,

- A l'inverse, l'emploi de techniques microanalytiques sur des matériaux complexes (changements de chimie à l'échelle nanométrique, présence de porosités à cette même échelle) tels que les matériaux cimentaires permet de prendre du recul sur les analyses effectués sur des matériaux naturels, là encore les deux domaines s'alimentent mutuellement comme par exemple dans le cas de l'ettringite naturelle qui fournit un analogue de choix pour l'étude des ettringites formées lors de l'hydratation des ciments.

### *Et maintenant ?*

L'intégration dans un laboratoire traitant de thématiques liées au génie civil et à l'environnement m'a permis d'élargir mon champ de vision ainsi que la gamme des matériaux auxquels je m'intéresse. Tout en restant fidèle à mes racines de géologue, mes projets de recherche en cours, ou mes projets futurs, comprennent par exemple :

- L'étude de l'impact sur l'environnement d'anciennes mines d'antimoine : ayant effectué des relevés cartographiques autour d'anciens sites miniers (Cartannaz et al., 2008; Thiéry & Cartannaz, 2013) je souhaiterais mettre à profit cette connaissance pour voir à une échelle plus vaste quelles sont les éventuelles pollutions associées,
- Élargir mes connaissances des pathologies du béton et notamment par des études *in situ* plutôt qu'en laboratoire,
- M'intéresser à la caractérisation de mortiers historiques, comme par exemple dans le cas de travaux en cours sur des mortiers utilisés en maçonnerie ferroviaire sur des ouvrages construits dans les années 1870,
- Enfin, le dernier (mais non le moindre) concerne autant un souhait que des projets de recherche, à savoir maintenir une activité de terrain régulière dans le Massif Central qui est un terrain d'étude merveilleux pour la majorité des thématiques abordées dans ce manuscrit...

## 2 INTRODUCTION AND BACKGROUND – WHAT IS A GEOMATERIAL?

### 2.1 Hardrock geology vs. concrete

Even if some concrete scientist recognize that « concrete is, in essence, ‘man made geology’ » (Idorn, 2005), the so called « hard rock geologist » - usually working on metamorphic rocks or ore geology (Hall, 1988) - seem to be rarely involved in both fields at the same time. Indeed, if the petrography of the aggregates used in concrete is studied, the implications are not the same that in geodynamics. On another hand, concrete tend to be disregarded from the geoscientists involved in more fundamental topics.

However, it is well known that some causes of concrete failure have a pure geological cause (French, 2005). Concrete pathologies such as alkali-aggregate reaction (§ 4.2) are directly linked to the nature and the mineralogy of the aggregate used (Diamond, 1976; Broekmans, 2012).

### 2.2 The elusive concept of geomaterials

It might be a little tricky to find a universal definition for geomaterials – as well as to switch, in a single manuscript, from metamorphic microdiamond to high temperature industrial by-products. But thanks to the link provided by their common means of characterization, we will try to bridge (sic) the gap between them.

Geomaterials do not have the same meaning for a civil engineer, a material engineer or a geologist– the first will see a hard rock suitable for building on it, the second will see a microstructural imbrication of various feldspars, micas and quartz whereas the last one will see a peraluminous granite resulting from the collapse of an overthickened mountain root (Figure 1).



This is...

- Rich in Si, Al, Ca, Fe, Mg
- A hard rock suitable to build on
- A microscopic mix of quartz, feldspar and biotite
- The result of the collapse of a thickened orogenic root
- All of the above
- None of the above

**Figure 1 :** according to one’s background, the very same geomaterial will be appreciated differently

It is worth noting that neither the *Oxford Dictionary* nor the *Cambridge Dictionary* proposes (January 2017) any definition for the word « geomaterial ». More specialized dictionaries such as the *Dictionary of Civil Engineering* (Kurtz, 2004) do not contain this entry either.

On Elsevier's Science Direct portal, the first appearance of this term was in 1957 (Wardani, 1957) and was related to the geochemistry of germanium in various rocks. Other scientific publishers have published this term later (1970's-1980's). It corresponds to the contraction of «geological materials » and once again this meaning will be different according to various scientific cultures.

A published description of the term is as follows: “*processed or unprocessed soils, rocks or minerals used in the construction, including man-made construction materials manufactured from soils, rocks or minerals*” (Fookes, 1991).

Another way to study statistically the occurrence of geomaterials within the scientific literature is to rank it according to the research area (Figure 2).

Field: Research Areas	Record Count	% of 1494	Bar Chart
ENGINEERING	979	65.529 %	█
MECHANICS	382	25.569 %	█
GEOLOGY	372	24.900 %	█
MATERIALS SCIENCE	317	21.218 %	█
MATHEMATICS	98	6.560 %	█
GEOCHEMISTRY GEOPHYSICS	81	5.422 %	█
PHYSICS	77	5.154 %	█
COMPUTER SCIENCE	75	5.020 %	█
MINING MINERAL PROCESSING	61	4.083 %	█
CONSTRUCTION BUILDING TECHNOLOGY	46	3.079 %	█
AGRICULTURE	38	2.544 %	█
CHEMISTRY	32	2.142 %	█
ENVIRONMENTAL SCIENCES ECOLOGY	27	1.807 %	█
MINERALOGY	26	1.740 %	█
TRANSPORTATION	25	1.673 %	█
WATER RESOURCES	25	1.673 %	█
SCIENCE TECHNOLOGY OTHER TOPICS	21	1.406 %	█
METALLURGY METALLURGICAL ENGINEERING	20	1.339 %	█
ENERGY FUELS	16	1.071 %	█
INSTRUMENTS INSTRUMENTATION	12	0.803 %	█
ACOUSTICS	11	0.736 %	█
THERMODYNAMICS	7	0.469 %	█
METEOROLOGY ATMOSPHERIC SCIENCES	6	0.402 %	█
IMAGING SCIENCE PHOTOGRAPHIC TECHNOLOGY	5	0.335 %	█
NUCLEAR SCIENCE TECHNOLOGY	4	0.268 %	█
OPERATIONS RESEARCH MANAGEMENT SCIENCE	4	0.268 %	█
SPECTROSCOPY	4	0.268 %	█
ARCHAEOLOGY	3	0.201 %	█
AUDIOLOGY SPEECH LANGUAGE PATHOLOGY	3	0.201 %	█
MICROSCOPY	3	0.201 %	█
OPTICS	3	0.201 %	█
PHYSICAL GEOGRAPHY	3	0.201 %	█
AUTOMATION CONTROL SYSTEMS	2	0.134 %	█
EDUCATION EDUCATIONAL RESEARCH	2	0.134 %	█
OCEANOGRAPHY	2	0.134 %	█
PUBLIC ADMINISTRATION	2	0.134 %	█

**Figure 2 :** Geomaterials ranked by research area, source: Web of Knowledge (2017/03/28)

Surprisingly, geology appears only as the third research area dealing with geomaterials, being surpassed by mechanics and engineering. An analysis of the occurrence of “geomaterials” ranked according to the source title (not shown here) reveals that the field of mechanical testing of materials, rock mechanics... are the first journals in this rank. The “European Journal of Mineralogy” and “American Mineralogist” are ranked #74 and 77 respectively. “Geology” is not even present!



## 2.3 Summary

The present manuscript is a review of my research activities and center of interests in both fundamental and applied geosciences which can be briefly be summarized as follows:

- Materials characterization at the microscopic scale, with emphasis on natural geomaterials,
- Ageing of cementitious materials,
- Mining and post-mining activities (field recognition of deposits, history of mining activities, environmental impact),
- Geological mapping and general geology,
- Mineralogy.

Some specific field-based case studies are presented in this manuscript based on my own experience; the map recalling the places in which I have worked and sampled is presented in the appendix.

The present manuscript is organized as follows:

**Chapter 1** entitled “Natural geomaterials: field and laboratory based recognition towards fundamental geological knowledge” presents rocks, minerals and ore characterization from the strict point of view of their characterization, without too much emphasis on the implications.

**Chapter 2** entitled “Selected anthropogenic geomaterials in civil engineering” focuses on selected high temperature, industrial by-products and their use in concrete as well as in artificial aggregates, and also an incipient work on 19<sup>th</sup> century binders.

**Chapter 3** entitled “The missing link provided by the common methods of investigation” documents the use of microscopy in its broad sense (i.e. *microscopies*) in both fundamental and applied geosciences in order to emphasize on their similarities.

**Chapter 4** entitled “Analogies between natural and anthropogenic materials” presents cases studies of analogies between natural and anthropogenic geomaterials, and vice-versa, and how they can be useful to each other.

**Chapter 5** entitled “Conclusions and perspectives” summarizes all of the present manuscript and gives insights of what I would like to do in the future.

**Appendices** contain my detailed resume and list of publications as well as reprints of the most representative articles I have published, and finally a map presenting the places where I have carried out field work.



### 3 NATURAL GEOMATERIALS: FIELD AND LABORATORY BASED RECOGNITION TOWARDS FUNDAMENTAL GEOLOGICAL KNOWLEDGE

Field work is a major aspect of earth sciences, and especially in geology. It can take the form of sampling only, but it is the fundamental tool to establish geological maps, which are 2D representations of the geology on a topographic map. Geological maps are fundamental data in the understanding of the geology of an area. The multidisciplinary “Journal of Maps”, published since 2005 by Taylor & Francis, recalls on its “aims and scope” page that *“back in the geological and geographical journals of the late-1800s and early 1900s [...] the investigative research during this period was based strongly around fieldwork and the observation of phenomena”*.

Thus, as a geologist, I have carried out a lot of field work, and especially in the 2004-2010 period corresponding to several training period for the French geological survey (BRGM) and during my PhD. The majority of this field work has been carried out within the framework of the regular geological mapping of France at the 1:50 000 scale. Moreover, some field work for specific research purposes has also been carried out, and some samples taken during the mapping have also sometimes been used in other studies. The Table 1 summarizes this activity.

Thematic	Year	Duration	Resulting publications (if relevant)
Training on the geological mapping in <b>granitic terranes</b> .	2004	1,5 month	(Cartannaz et al., 2008)
Detailed mapping of the eastern part of the Felletin geological map. Emphasis on the Crocq-Fernoël <b>granitic massif</b> .	2005	4 months	(Rolin et al., 2008; Thiéry & Cartannaz, 2013; Thiéry, 2014b)
Geological mapping on the Ussel and Felletin geological map ( <b>mainly metamorphic rocks</b> ), geological survey in the Sioule sequence.	2006	2 months	(Thiéry et al., 2010; Rolin et al., 2008; Thiéry, 2012, 2011b)
	2007	2 months	
	2008	2 months	
Training on the BRGM Geomodeller software with field work on the Alès coal basin, southern France. Field work on cataclasites and pseudotachylites from the Ivrea-Sesia zone (northern Italy)	2009	1 week	
Visit of <b>active mines</b> and tailings deposits in Bulgaria	2012	1 week	
<b>Burning coal heaps</b> from the North of France and Massif Central, <b>former mining sites</b> .	2010-2017		(Thiéry & Guy, 2015; Thiéry et al., 2013)

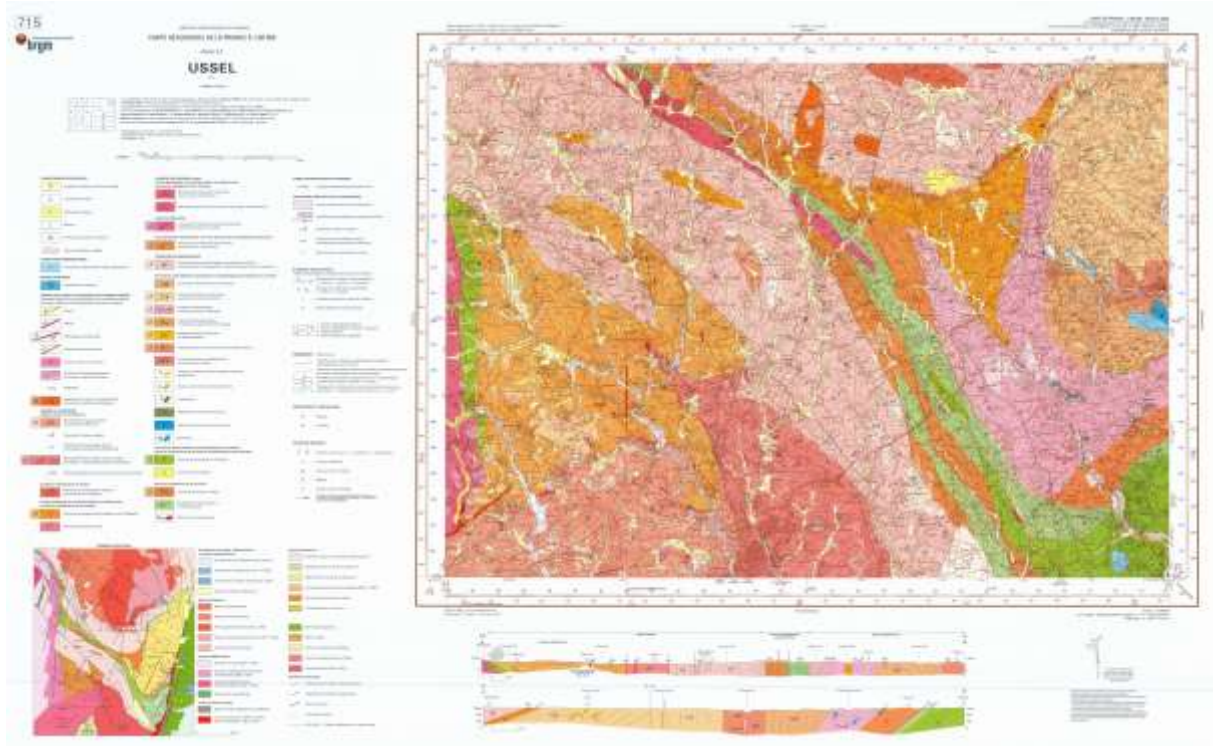
Table 1 : summary of my field work activities

I have published several articles presenting the work resulting from these field work experiences. However, the purpose of the present manuscript is not to enter into details into complex geodynamical considerations but rather to present some geomaterials characterization from the point of view of fundamental geosciences or with applications in ore geology.

Two sections will focus on general geology on the one hand, and one section will be devoted to metallogeny on the other hand.

### 3.1 General geology

In the course of the realization of geological maps, I have sampled and studied many rocks. The representation on a geological map is one thing (Figure 3), but the thorough characterization of rock mineralogy is another.

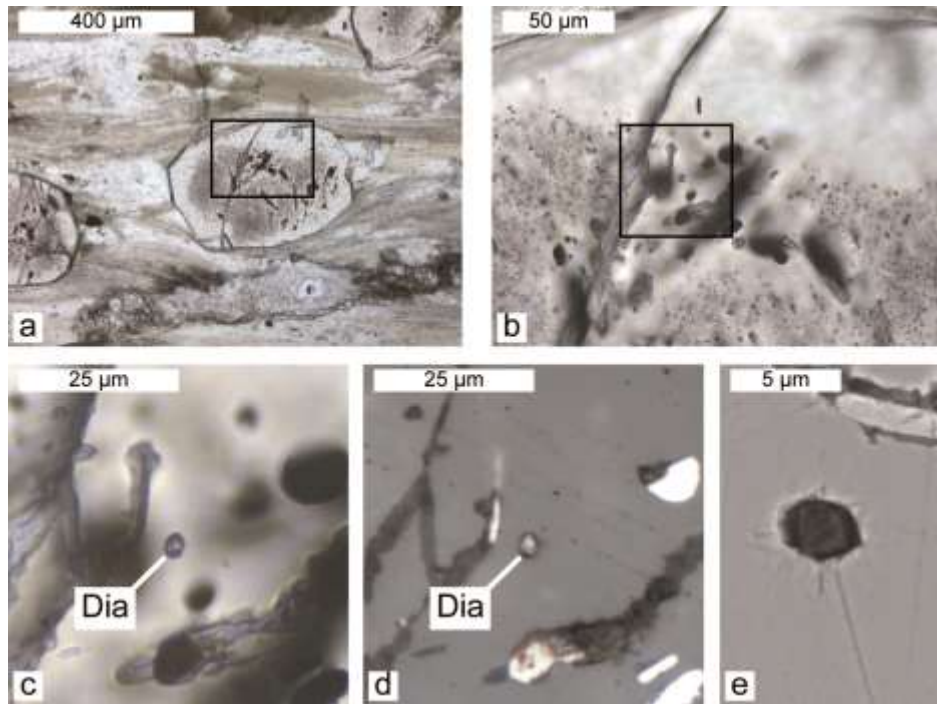


**Figure 3 :** Ussel geological map (Thiéry et al., 2010), which I have entirely drawn, coordinated and partly mapped

The study of rocks in the laboratory is necessary in the realization of such maps in order to group them when possible; in some cases, unexpected mineralogy can be discovered and will need further investigation, as presented below.

#### 3.1.1 *Characterization of controversial inclusions: the case of diamond*

I will review here the very specific case of the (unexpected) discovery of microdiamond inclusions in micaschists from the French Massif Central (Thiéry, Rolin, et al., 2015). As shown in Figure 4, microcrystals of diamond (a few micrometers across) occurs as inclusions in garnet. Such diamond can only form in ultra-high pressure contexts (Ogasawara, 2005; Dobrzhinetskaya, 2012) and it is thus absolutely necessary to ensure that they are present naturally and are not the result of any type of pollution from cutting or polishing devices (Perraki et al., 2009; Nasdala et al., 2016). In the present case, diamond forms so small crystals that it is quite difficult to ensure their nature only under the optical microscope.



**Figure 4 from Thiéry et al. (2015)** a, typical inclusion rich garnets in metapelite. The rectangle indicates the field of micrograph b. Transmitted light, uncrossed polars. b, detail of a boundary between an inclusion-rich core and a clear, inclusion free rim. The square indicates the field of

micrographs c and d. Transmitted light, uncrossed polars. c, close-up view of a diamond (Dia) in transmitted light, uncrossed polars. d, same field of view as c, in reflected light. e, the same diamond seen under the SEM in BSE mode (90° clockwise rotation).

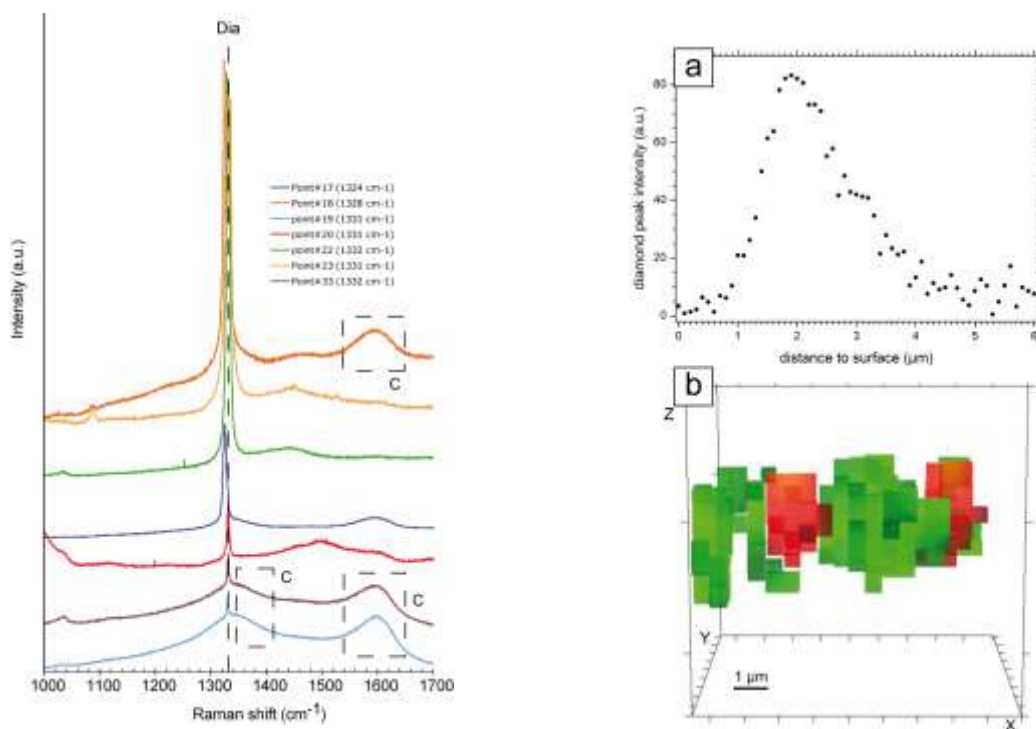
The only way to ensure that diamond was present among the minute fluid inclusions was Raman spectroscopy. Indeed, SEM reveals that some of them consist of a light element since they are almost black in BSE mode on thin sections (figure 4e). An EDS analysis (not illustrated here) has revealed a C peak, which is not enough to ensure completely that this is a diamond (even if optically there is some indication that the mineral is not graphite: it is translucent and has a very high optical relief).

Another indication concerning the potential diamondiferous nature of part of the inclusions is the presence of scratches around them (figure 4d to a small extent, figure 4e), as already described in diamondiferous gneisses from the Erzgebirge (Massonne et al., 1998). However, in the present case, the striation pattern is not as obvious as in the aforementioned gneisses, and is thus questionable.

Thus, Raman spectroscopy has been carried out in order to ensure the presence of diamond. This mineral is characterized by a typical peak around  $1332\text{ cm}^{-1}$  (Solin & Ramdas, 1970). In the present case, several micrometric inclusions at the surface of the thin section have been assigned to this mineral thanks to their unambiguous peak (figure 5a). However, during the peer-review process of the paper (Table 2), one of the reviewers has expressed his doubts about the presence of the inclusions at the surface since they may result from the filling of porosities by polishing products.

Thus, confocal Raman spectroscopy, allowing to study inclusions even under the surface of the sample (i.e. inside it), has been carried out on the same sample, on inclusions firstly observed using optical microscopy and specifically chosen because they were not present at the surface of the sample. Raman spectroscopy has been carried out in two ways:

- A linear penetration through the sample from its surface to a depth of 6 micrometers (figure 4a), shows an increase in the diamond peak intensity plotted as a function of the depth, then a decrease, indicating that a diamond has been crossed,
- A 3D representation of an inclusion (figure 5b) shows the intimate association of diamond and graphite contained inside garnet.



**Figure 5 from Thiéry et al. (2015).** Left: Typical Raman spectra showing the characteristic diamond peak at 1332  $\text{cm}^{-1}$  and broad peaks around 1600  $\text{cm}^{-1}$  indicating graphite-like amorphous carbon (Frezzotti et al., 2011). Right: Raman analyses of diamond inclusions in garnet in

the depth of the thin section. a, plot profile of diamond peak intensity from the surface to the depths of the thin section. b, 3D representation of diamond (red) and graphite (green) enclosed in garnet (not shown for clarity).

It is of interest to recall here the peer-review process of the paper in order to highlight the advancement of the study (Table 2).

Author	Reviewers
1 <sup>st</sup> submission: only traditional Raman spectroscopy.	
	1 <sup>st</sup> round: both reviewers wanted the proof that diamond was a real inclusion and not a polishing artifact.
2 <sup>nd</sup> submission: confocal Raman spectroscopy to study inclusions in the depth of the sample.	
	2 <sup>nd</sup> round: one reviewer was convinced while the other was still dubious – anyway, the paper was accepted.

**Table 2 :** peer-review process for the paper describing the first occurrence of metamorphic microdiamond in the French Massif Central (Thiéry, Rolin, et al., 2015)

Without discussing the geodynamical implications of such a discovery (which are otherwise debated by Berger, 2016; and discussed subsequently by Thiéry, Rolin, et al., 2016), metamorphic microdiamond indicates that those rocks have endured ultra-high pressure metamorphism, which was unlikely here. Tiny minerals such as diamonds may thus change the overall geological models for this area.

### 3.1.2 Cordierite growth in cumulative migmatites – melt / restite segregation

Those quite unusual rocks have been discovered in the course of the field work for the geological map of Felletin (Rolin et al., 2008) and have been investigated and described subsequently (Thiéry, 2011a).

They crop out as dark boulders of various sizes, from 10-20 cm to 3-4 meters across. The contact between such boulders and their host rocks has not been seen on the field, but they appear cartographically embedded in various migmatites from the Chavanon sequence.

Unlike the surrounding rocks, they are not foliated but are rather massive, fine grained and generally very dark. Under the microscope, they have a cumulative texture characterized by the abundance of idiomorphic cordierite as prisms of ca. 500 x 200 micrometers. They contain inclusions which outline successive growth steps. Temperature estimation based on microprobe analysis of cordierite (Na in cordierite geothermometer, Mirwald, 1986; Wyhlidal et al., 2007) have revealed a temperature crystallization of cordierite in the 725-781°C range.

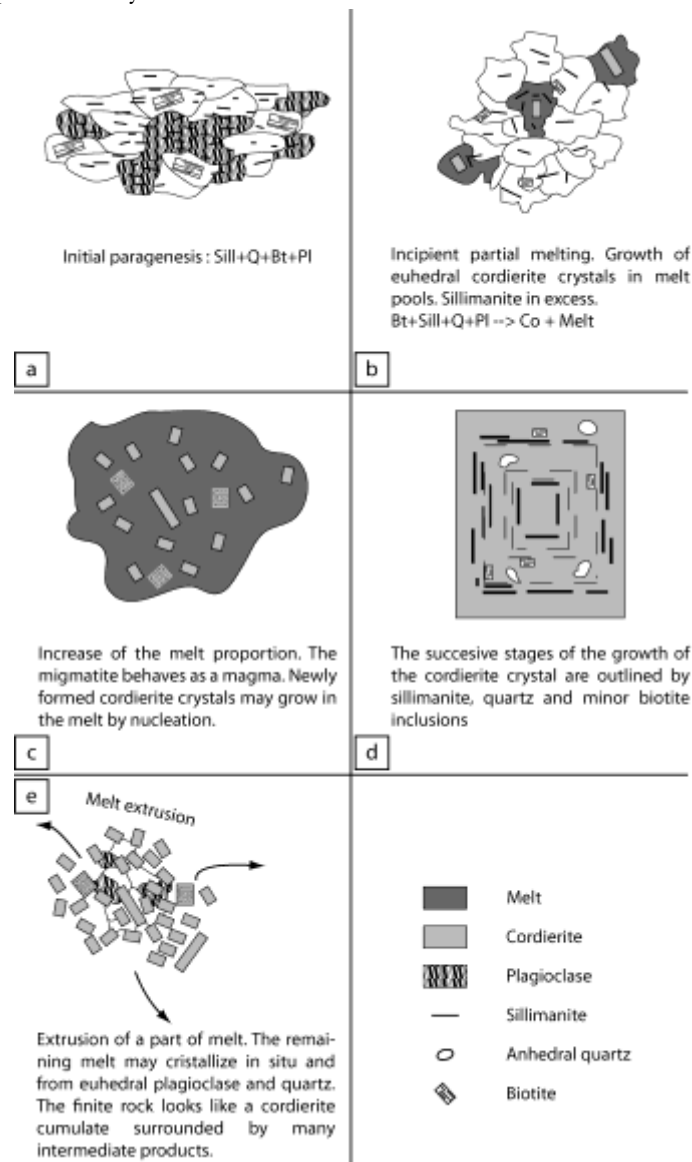


Figure 6 from Thiéry (2011a) : Conceptual sketch of the successive stages of the cordierite evolution

### 3.2 Metallogeny, from primary ore to alteration

The work that I have carried out in this domain concerns former mines or deposits that I had either the chance to recognize during the field work for geological mapping, or other places of interest.

The work that I have carried out does not concern complete metallogenic studies in the sense that I did not work on, for example, description of whole deposits, geological models and so on. My contribution is more linked to a scientific, naturalist description of samples.

Two ways of characterization are to be considered: former mining sites, more or less characterized, can still yield interesting samples to characterize the ore and the mineralization. On another way, an improvement of the knowledge of very specific minerals/parageneses can also be implemented.

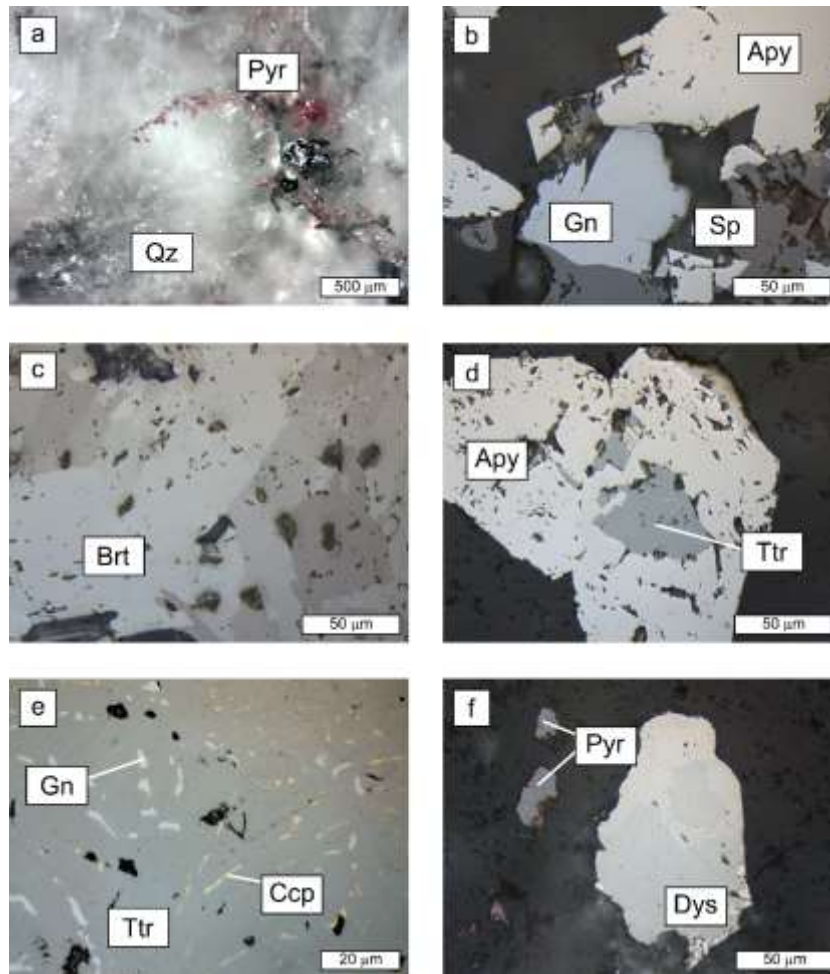
Metallic deposits which have been mined yield mining wastes; in the case of old works, some metallic concentration may still be contained in both tailings and various leftovers. Thus, the mineralogical evolution associated to mining sites has all its interest in environmental studies.

#### *3.2.1 Improvements in the characterization of deposits: the case of an antimony district - see also the reprint of the article at the end of the manuscript*

France has had a long history of mining, and especially in the Massif Central (Marignac & Cuney, 1999; Bitri et al., 1999; Bouchot et al., 2005). Gold, antimony, fluorite... has been mined in various places. Now, all those mines are closed and France is in post-mining stage (BRGM, 2007).

During the course of field work for the Aubusson geological map (Cartannaz et al., 2008). I have had the opportunity to realize the mapping on a former mining site, the Mérinchal antimony mine. Various mineralized indexes and mining sites allow the sampling of ore and thus the study of the mineralization (Figure 7).





**Figure 7 from Thiéry & Cartannaz (2013):** Photomicrograph of ore minerals from Mérinchal, taken using a metallographic microscope with reflected light under crossed polars excepted when mentioned. Apy: arsenopyrite, Ccp: chalcopyrite, Gn: galena, Sp: sphalerite, Ttr: tetrahedrite (abbreviations after Whitney and Evans, 2010), Brt: berthierite; Pyr: pyrrargyrite. a: myriad of minute

pyrrargyrite crystals in their quartz matrix, stereomicroscope view, b: polyphased assemblage of arsenopyrite, galena and sphalerite, the latter showing strong brown internal reflections, c: berthierite vein, d: arsenopyrite containing a subeuhedral tetrahedrite crystal, e: close-up view of a tetrahedrite crystal containing vermicular chalcopyrite and galena, f: dyscrasite and pyrrargyrite.

In the present case, the interest was to complement and update previous work on the area (Carroué, 1964). Antimony is one of the scarcest metals (Henckens et al., 2016) but also a toxic one (Sundar & Chakravarty, 2010; Multani et al., 2016) so a better knowledge of former mining sites is of interest for the 2 following points:

- Is there still some antimony resource in the considered site,
- What is the environmental pollution associated with mining and/or smelting?

In the case of the Mérinchal antimony district, only existing reports or new prospection may reveal the remaining resources in antimony. However, regarding the potential pollution associated with the former mining activity, the thorough study of the mineralogy of old samples has revealed the presence of important remnants of ore. Even if the bioavailability of antimony on former mining sites seems controverted (Flynn et al., 2003; Courtin-Nomade et al., 2012), in the present case, As-bearing minerals have also been described so it is worth considering metallic pollution as a whole.

3.2.2 *Specific mineralogy: case of the fibrous mimetite - see also the reprint of the article at the end of the manuscript*

Some deposits are characterized by a specific mineralogy; they might not be known as world class deposits but may be known worldwide for a specific mineral occurrence. This is typically the case for the former Molérats Pb mine in France, which is almost the only worldwide occurrence of fibrous mimetite (Thiéry, 2014a), illustrated in Figure 8. This work is independent from my experience in geological mapping but the characterization methods are similar.

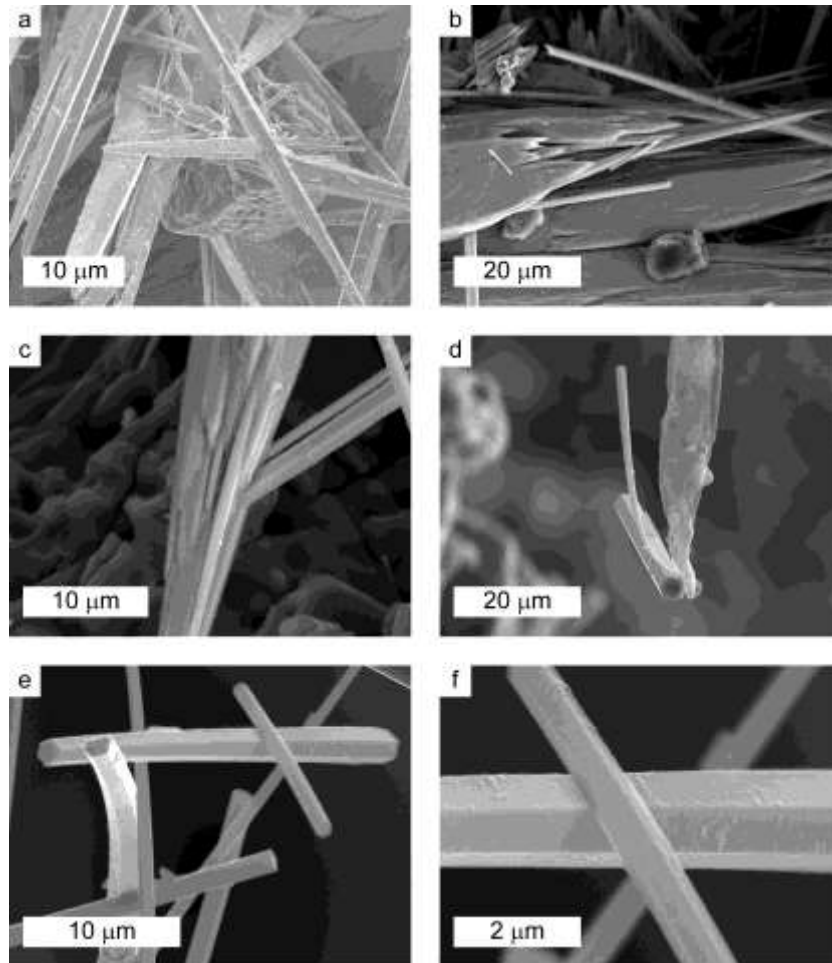


Figure 8 from Thiéry (2014a): SEM (secondary electron mode) of fibrous mimetite

Mimetite,  $Pb_5(AsO_4)_3Cl$ , is a member of the apatite supergroup (Pasero et al., 2010); described as a secondary mineral in some ore deposits (Kampf et al., 2011; Lalinská-Voleková et al., 2012) it is also of interest in environmental studies in order to stabilize Pb and As (Bajda, 2010; Kleszczewska-Zeębala et al., 2016).

The multi-technique approach in this study has involved optical microscopy, SEM-EDS on polished sections, SEM-SE on fractures and Raman spectroscopy. The micromorphology of such mimetite crystals had never been published this specifically before; the Raman study has allowed to precise the position of those crystals within the mimetite-pyromorphite solid solution (Bajda et al., 2011).

### 3.3 Summary

In the present chapter, a dramatic change in the scale of work has been presented: from the 20 x 30 km geological map presented in Figure 3 to micrometric mimetite crystals (Figure 8), there are three orders of magnitude.

The thematic presented here are also various: even if they all deal with geology, diamonds are related to ultra-high pressure metamorphism and must also be considered as a possible bias during sample preparation; cordierite is, in contrary, related to high temperature metamorphism. The two sections dealing with metallogenesis concern more environmental geosciences since they are related to former mining sites.

However, emphasize has been put on the microscopic technique, the pictures shown here are mainly micrographs, but in the corresponding publications, some data using optical cathodoluminescence, raman spectroscopy and electron microprobe (WDS) are presented.



## 4 SELECTED ANTHROPOGENIC GEOMATERIALS IN CIVIL ENGINEERING

Chapter 1 has presented some work carried out as a geologist in his (rocky) environment. The dramatic shift in the present chapter documents another stage in my career, namely, some work done after my integration in the “civil & environmental engineering laboratory”.

I have both been involved in already existing thematic, carried by other researchers, and I have also had the opportunity to realize some work on my own. The works about alkali-silica reaction (ASR) I have been involved in are not my own topic of research but I did have an input on microscopy & microanalysis. The work about burnt oil shale (§4.3.1) was a part of a wider project about ASR but I have done most of the analysis.

However, I have carried out some personal research, developing my own network of collaboration, on the following topics: the investigation of 19<sup>th</sup> century binders, burnt colliery spoil and oil shale slag.

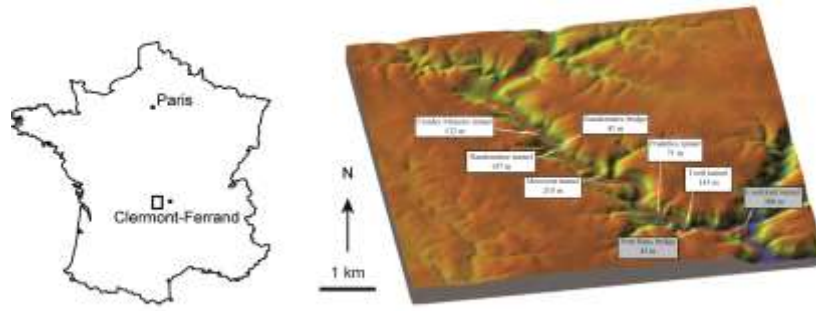
### **4.1 Investigation of 19<sup>th</sup> century binders from railway structures (*to be presented during the 16<sup>th</sup> EMABM, Les Diablerets, Switzerland, May 2016*)**

*Complete reference: Thiéry, V., Katayama, T., Ando, Y., Link, G., Bonichou, M. Marie-Victoire, E. (2017) Preliminary study of 19<sup>th</sup> century mortars from railway engineering structures abandoned since 1950, 16<sup>th</sup> Euroseminar on Microscopy Applied to Building Materials*

#### *4.1.1 Introduction*

Portland cement-based binders from the second half of the eighteenth century are known as “early age Portland cements” (Gosselin & Pintér, 2016) or “meso-Portland cement” (Rayment, 1986). They cover a compositional range broader than modern Portland cement, especially concerning a richer Al content (Dariz et al., 2017).

The present results cover an investigation of mortars from masonry structures on a 19<sup>th</sup> century railway line from the French Massif Central, built around 1880, which was subsequently totally abandoned in 1950 due to the flooding of the valley by a dam lake. The studied railway runs through the Chavanon valley located ca. a hundred kilometers to the west of Clermont-Ferrand (Figure 9), mainly constituted of various acidic metamorphic rocks (migmatites, gneisses and micaschists). The incision of the valley ranges from 180 to 250 meters in the area of interest, with locally cliffs and mainly steep slopes as well as a narrow river. The altitude of the present section ranges from 600 to 550 meters above sea level.



**Figure 9** : location of the studied railway in France and detail of the itinerary along the Chavanon valley. The

locations of the two structures on which sampling have been carried out have a light grey frame

In the ca. 8,5 km long in the more incised part of the valley (Figure 10), the railway crosses six tunnels for a total amount of 1100 meters and two bridges for a total of ca. 85 meters. All structures are in masonry and were built around 1880 since the railway line has opened in 1882. The present study documents two structures from the southern part of the line.



**Figure 10** : a steam train on the Randonnière bridge, getting outside the Randonnière tunnel. Picture from Vilain (1982)

The *Confolent* tunnel (Figure 11) is a 388 m long, curved tunnel. Its northeastern entrance is partly collapsed, the southeastern one still stands. Moss and calcite deposits are abundant on exposed surfaces; from time to time the southern entrance is partly flooded, depending on the level of the dam lake.

The *Pont Biaisi* bridge (Figure 11) cuts across the Chavanon river at an angle, hence its name (*biaisi*, in French, means “not orthogonal”). This masonry bridge is ca. 40 meters long. The intrados of the arch as well as the abutment are covered by calcite deposits forming locally some stalactites.



**Figure 11** : structures from which the mortars have been sampled

The goal of this study is to give a preliminary insight of the type of binders used since there is currently no data on those specific structures, as well as to give new descriptions to early Portland cement.

#### 4.1.2 *Materials and methods*

Sampling for this preliminary study was done on two structures, one bridge (Pont Biaï) and one tunnel (Confolent tunnel) at its two (northern and southern) entrances in May 2015. Since the study of historic mortars is greatly enhanced by the use of microscopy and microanalysis techniques (Elsen, 2006), especially concerning early Portland cements (Gosselin & Pintér, 2016), this preliminary study was based only on optical microscopy (OM) and scanning electron microscopy (SEM).

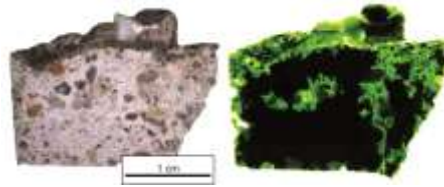
Thin sections were produced firstly at the conventional thickness (30 micrometers) to study the sand from the mortars, another sequence of thinner ones (15 micrometers) was done subsequently to study the binder.

Optical microscopy was carried out on a Zeiss Axiozoom macroscope (stereomicroscope observations under white and UV light), a Leica DMRXP microscope and a Nikon Eclipse polarizing/reflecting microscope. SEM-EDS, qualitative standardless analysis were done on a Hitachi S-4300SE/N SEM working in high vacuum mode, coupled to a ThermoScientificUltraDryEDX detector. Semi-quantitative, standard-bases SEM-EDS analysis were obtained on a JEOL JSM-7001F operating at 15 kV, 0,3 nA with a working distance of 10 mm, coupled with an Oxford Penta FETx3 detector. Data acquisition was 60s with a dead time of 20%.

### 4.1.3 Results

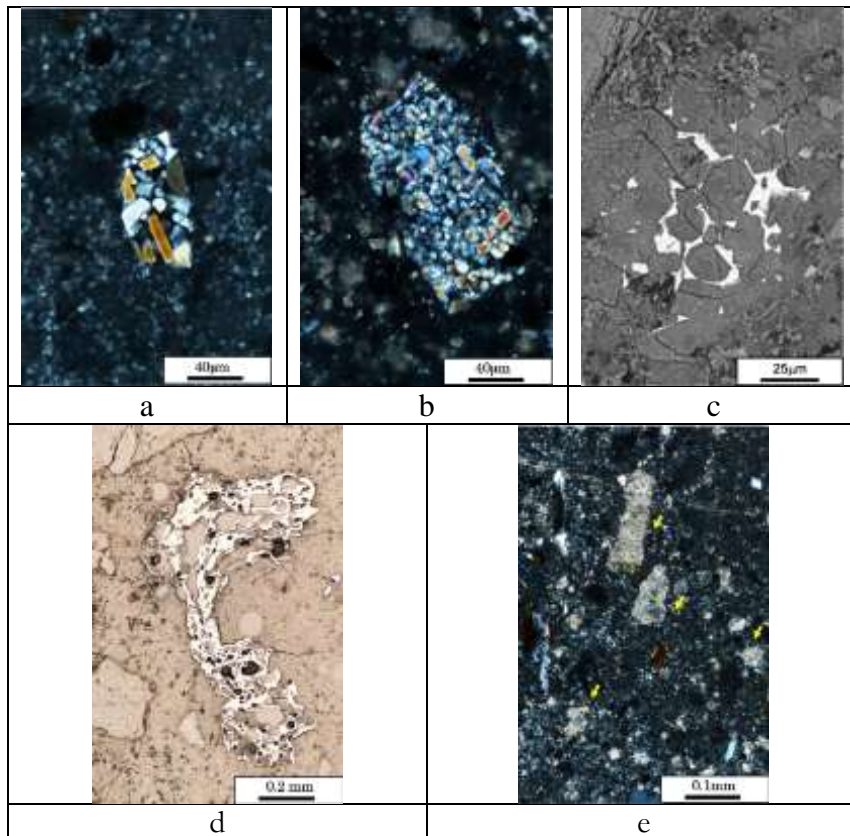
The sand of the mortars is rounded and consists of quartz grains, feldspars and various metamorphic rocks as well as volcanic ones. It corresponds most probably to sand dredged from the Chavanon river close to the works during the construction of the structures.

Hand samples are characterized by a clear, light-grey color, with a local darker patina (Figure 12).



**Figure 12:** ground slab of mortar from the southern entrance of the Confolent tunnel. Left: white light, right: UV light.

The microscopical investigation of the binder has revealed that it consists of Portland cement. Hydraulic lime was not observed in the samples. The mineralogy is variable (figure 5). It is dominated by pseudowollastonite (CS), belite ( $C_2S$ ) and alite ( $C_3S$ ), as well as rankinite ( $C_3S_2$ ) and local ye'elimite ( $C_4A_3\bar{S}$ ), according to the heterogeneity of compositions.



**Figure 13:** Features observed in binders as seen in optical microscopy, transmitted light and crossed polars except when indicated. a: cement particle composed of pseudowollastonite and potassium silicate (confirmed by EDS) from the Pont Biais Bridge, b: pseudowollastonite

dominated assemblage, Confolent tunnel (southern entrance), c: SEM (BSE) image of a cement particle composed of hydrated alite (dark), hydrated belite (dark) and interstitial ferrite (bright), d: coal ash (reflected light), e: limestone filler, Confolent tunnel



Carbonation is conspicuous in cross sections of the surface of exposed mortars. Ettringite is quite abundant, both in voids and in cracks. The main features observed microscopically in the mortars and are summarized in Table 3.

	Constituent		Biais Bridge		Confolent tunnel				
			P1	P2	Northern entrance		Southern entrance		
					N1	N2	S1	S2	
Binder	Portland cement	Isolated particle	x	x	x	x	x	x	
		Lump	x						
	Limestone powder		-	-	x	x	xx	xx	
	Coal ash		x	x	x	x	x	x	
Cement hydrates	Portlandite	Void	-	-	-	x	-	-	
		Cement paste matrix	-	-	x	x	-	-	
	Ettringite	Void	-	-	-	-	x	x	
		Crack	Fresh	-	-	-	-	xx	xx
			Carbonated	-	-	-	-	xx	xx
Carbonation	Calcite	Void	-	-	x	x	-	x	
		Cement paste matrix	x	x	x	x	x	x	
		Crack	-	-	x	-	xx	xx	

**Table 3:** summary of microscopical investigations in mortars from 2 structures built around 1880. -: not observed, x: minor, xx: abundant

#### 4.1.4 Discussion and conclusions

This railway line has been opened the very year during which the famous French chemist Henry le Chatelier published the first description of Portland cement phases under the microscope (Le Chatelier, 1882). At that time, cement was heterogeneous due to both the heterogeneity of the raw meal and the ill-defined calcination conditions (Dariz et al., 2017). The present study is in good agreement with such conclusions since several mineral assemblages, hydraulic or not, has been observed.

An excess of sulfur can be emphasized by the presence of  $C_4A_3\bar{S}$  (ye'elimité) in unhydrated cement particles relics; its source is to find in the coal used for cement production, from which ash has been observed in all of the samples. Ettringite, present in both voids and cracks, is also a manifestation of the excess of sulfur. In the present state of knowledge, the plant from which the cement came is not known so there is no indication of the sulfur amount in the clinker.

## 4.2 Concrete durability: a brief overview of pathologies

Although concrete may seem durable, because it is strong and because we live in concrete buildings, it can suffer from a number of disorders named “concrete pathologies”. Several of them are known (Table 4); a thorough review is available in the book “Concrete Petrography” (St John et al., 2016).

Name of the pathology	Cause	References
Alkali-aggregate reactions	Reaction between specific forms of silica in the aggregates and alalkies from the pore solution	(Broekmans, 2012; Diamond, 1975, 1976)
External sulfate attack	Reaction between some hydrates from the cement paste and external source of sulfates, e.g. in groundwater.	(Menéndez et al., 2013; Van Tittelboom et al., 2013)

Internal sulfate attack	Delayed ettringite formation (DEF) is due to secondary, expansive ettringite growth. The thaumasite form of sulfate attack (TSA) is more complex.	(Taylor et al., 2001)
Fire exposure	Accidental or criminal fire in concrete buildings.	(Annerel & Taerwe, 2009; Ingham, 2009)

**Table 4** : some example of concrete pathologies

The societal cost of pathologies such as alkali-silica reaction is huge considering the amount of concrete poured each year (Broekmans, 2012). Thus, laboratory studies make sense to prevent damages on structures. It can be seen in Table 4 that mineralogy plays a fundamental role in concrete evolution.

### 4.3 Oil shale and its high temperature transformations

« Oil shale is commonly defined as a fine-grained sedimentary rock containing organic matter that will yield substantial amounts of oil and combustible gas upon destructive distillation » (Dyini, 2005). This rock is known worldwide, famous deposits are currently actively mined in Estonia for example.

In the past years, I have studied oil shale, more precisely some products resulting from their exploitation:

- burnt oil shale from a German power plant, used as a supplementary cementing material,
- pyrometamorphic by-products resulting from the burning of a heap of retorted oil-shale slag

The studies that I have carried out on this material dealt with its use as a civil engineering geomaterial (especially in the case of burnt oil shale) as described below.

#### 4.3.1 *Characterization of burnt oil shale – see also the reprint at the end of the manuscript*

This material can be seen from two points of view: at first it is used in composite cements to prevent alkali-silica reaction (see § 4.2), but on a second point it can also be studied *as is*, i.e. without any consideration on its use, but only on its nature. BOS is obtained (Figure 14) when oil shale (in the present case the Posidonia Shale from Germany) is burnt to benefit from its content of organic matter.

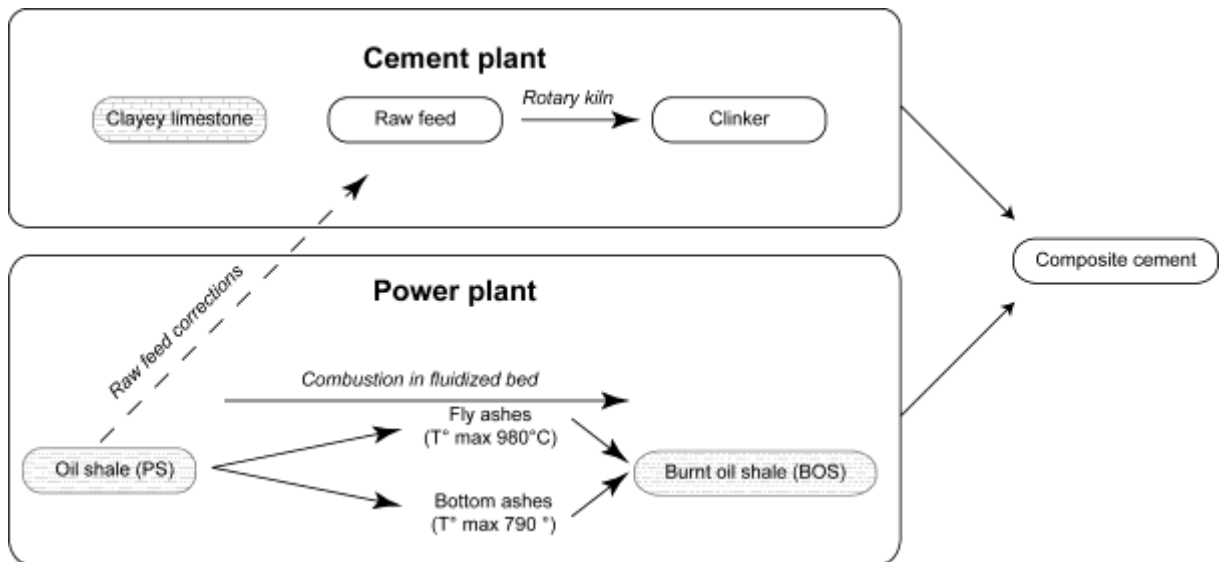


Figure 14 from Thiéry et al. (2015): schematic diagram summarizing the fabrication and use of BOS

The resulting mineral matter has suffered high temperature during the burning and its mineralogy has evolved.

During combustion, the shale keeps its initial layered texture but the mineralogy is dramatically different before and after combustion. For example, the initial framboidal pyrite shape is preserved as hematite pseudomorphs (Figure 15).

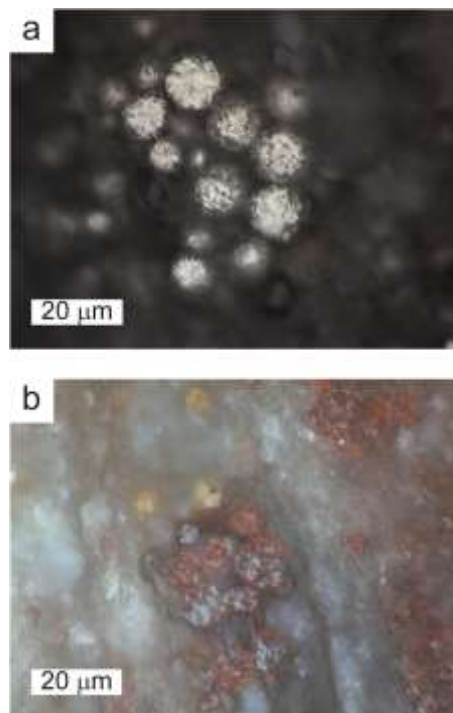


Figure 15 from Thiéry et al. (2015): high-temperature evolution of the Posidonia shale. a) Typical pyrite framboids from the unburnt, raw Posidonia shale. Reflected

light, crossed polars. b) Hematite pseudomorphs after pyrite framboids in the burnt oil shale. Reflected light, crossed polars

#### 4.3.2 An example of the use of BOS in concrete to prevent ASR

After their presentation (see above), the present paragraph will briefly document the benefit of their use in concrete. They are indeed efficient in the prevention of alkali-silica reaction (Bourdout et al., 2016) when used in blended cements. They dramatically reduce expansion in this case (Figure 16).

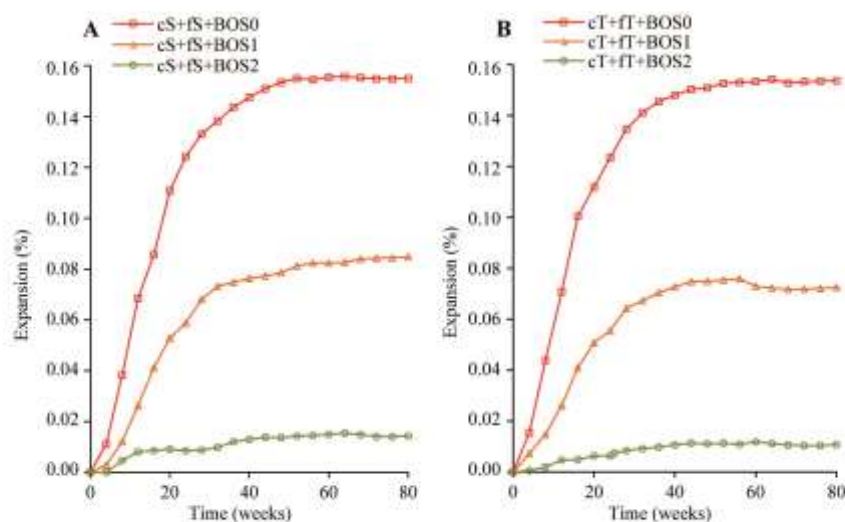


Figure 16 from Bourdot et al. (2016) : effect of burnt oil shale on expansion due to alkali-silica reaction

It has been suggested that in the present case, there is a competition between the pozzolanic reaction of the BOS and the gel growth of ASR.



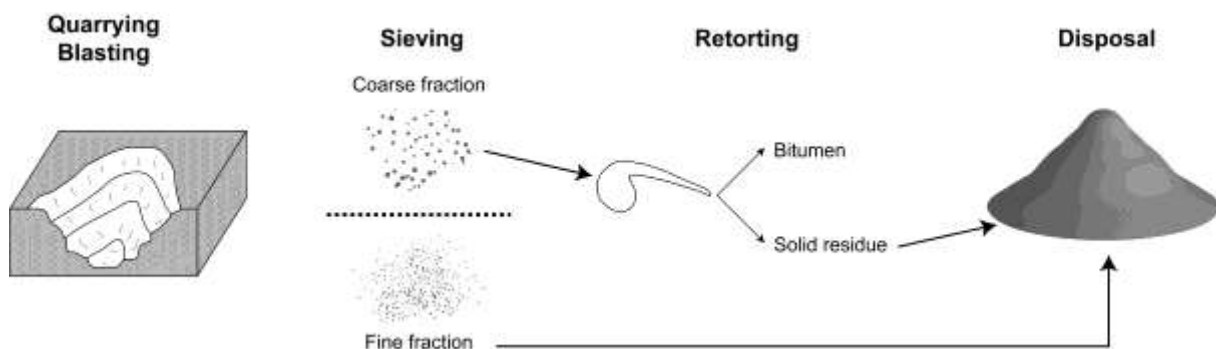
Figure 17 : BOS particle in cement paste ; a) transmitted light, crossed polars b) reflected light

#### 4.4 Burnt oil shale slag and associated unusual parageneses

I have been involved in a collective work about unusual high temperature and retrograde parageneses from an oil shale slag heap located in the south of France (Gatel et al., 2015). This work has been initiated by a scientific association, the French micromineralogical association. I

have chosen to present this section here rather than in the chapter dealing with anthropogenic analogues of natural phenomena since the materials from the heap have been used as aggregates.

It concerns residue from the retorting of oil shale, namely oil shale slag, which has been stored on heaps (Figure 18) which have subsequently been affected by inner combustion. The temperatures reached have been high enough to promote the partial melting of its content (see also §0): the rocky product, similar to lava, is termed “paralava”. However, as in any type of burning heap, melting was incomplete and some parts of the heap have been affected only by pyrometamorphism.



**Figure 18 from Gatel et al. (2015)** : Oil-shale processing at the Lapanouse plant. Shale, with an average oil content of 4,4%, was exploited in a large open-pit by blasting. After crushing, the two fractions (fine and coarse) were separated. The fine fraction was not processed and was directly deposited on a waste heap. The waste heap thus contains

unprocessed, fine particles of oil shale (i.e., still containing organic matter), the solid residue of coarse processed oil shale, and some admixed limestone. A short time after the plant was closed (1951), the heaps began to burn and the combustion lasted for at least 10 years.

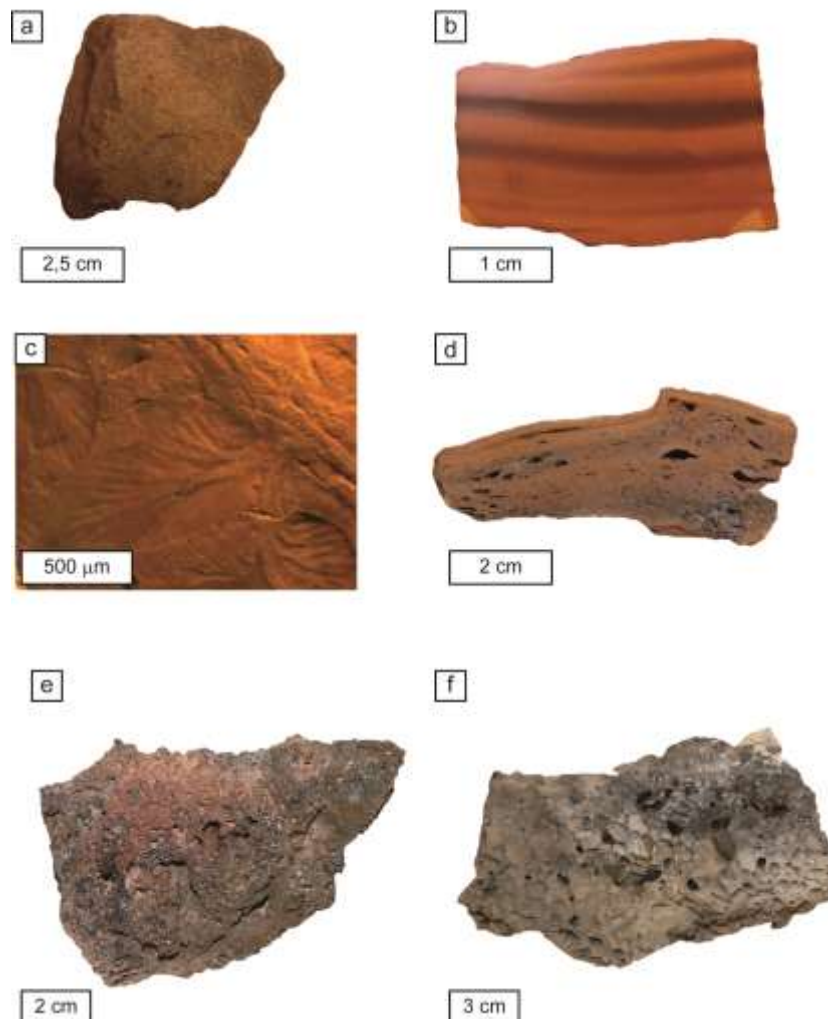
#### 4.5 Burnt colliery spoil

The phenomenon of the burning of coal heaps is documented in § 1.1. In the present part, we will review the use of the resulting material in civil engineering. The use of such waste is various (see review in Thiéry & Guy, 2015): infilling of mining galleries and shafts (Ghataora & Jarvis, 1996), aggregate source for concrete (Runguphan & Guthrie, 2009); they are also of common use as decorative aggregates on sidewalks (Figure 19).



**Figure 19:** burnt colliery spoil used as decorative aggregate on sidewalks (image from Google Street View)

A closer investigation at the microscopic scale has been made on various samples of burnt colliery spoil (Thiéry & Guy, 2015). Indeed, this denomination encloses in fact varied types of rocks and wastes having suffered from extremely heterogeneous temperatures (§ 1.1).



**Figure 20 from Thiéry & Guy (2015):** Macroscopic samples of burnt colliery spoil from various localities. a) baked sandstone, Rieulay, North of France; b) baked argillite, same provenance; c) preserved fossil leaves on a

baked shale, Germignies, North of France; d) porous paralava with flow texture, Rieulay, North of France; e) ropy paralava, la Ricamarie, center of France; f) extremely vacuolar paralava, same provenance.

The terminology of baked rocks and products formed during the combustion of coal tips is quite confusing and sometimes contradictory. Red, unmelted baked rocks are termed “clinker” or “glassy clinker” when they are melted but they do not display evidence of flow (Grapes et al., 2009). “Paralavas” are melted vesicular rocks and can show some evidences of flow (Grapes et al., 2011).

#### 4.6 Summary

To sum up with those various descriptions, it can be noted that the materials are linked all together by a high temperature step. Cement, and more precisely in the present case historic Portland cement (§ 4.1) is obtained from the burning of a raw meal in a kiln. Oil shale, either burnt or retorted, is also heated. The specific case of the burning of an oil shale slag heap is also

of interest, some similitudes are described in the following chapter concerning the burning of coal heaps.

High temperature is a necessary step to create cementing materials willingly or to create pozzolanic materials. The microscopic investigations of all those materials has revealed their history, both in the kiln (case of historical Portland cement), in the fluidized bed reactor or on a burning heap.





## 5 THE MISSING LINK PROVIDED BY THE COMMON METHODS

The two previous chapters have presented contrasted materials and contexts: rocks and geology on the one hand, concrete and industrial by-products on the other. At first sight they look different, and so is the context in which they are found, and also are the implications. However, we will try here to bring them closer by the way they can be studied.

### 5.1 Sampling and sample preparation

During field work for geological purposes, one can virtually collect as much samples as necessary; there will still be plenty left (exception made, of course, for rare minerals, fossils...). But sampling on a man-made structure is different. Indeed, the amount of sample available for sampling without damaging the structure, or without taking the risk to affect its integrity, is limited (Figure 21).

As outlined by Fernandes et al. (Fernandes et al., 2009), “*The total price of a concrete core comprises costs for extraction, transport, handling, storage, and preparation, and may also include peripheral expenses for road closing, and scaffolding. Calculated per kilogram, a core may be worth its own weight in gold, quite literally. Thus, precautions taken to minimize introduction of artifacts at any instance prior to analysis, including core extraction, are worthwhile*”.



**Figure 21:** the mountain vs. the dam. Left: Oisans mountains somewhere in the Vénéon Valley (French Alps),



right: Bort-les-Orgues dam, French Massif Central. The amount of sample available for study is not the same.

Seen from the point of view of a geologist, sample preparation in construction and building materials takes thus more importance than in fundamental geology, even if we have discussed above the importance of avoiding contamination during sawing and polishing (§3.1.1). Maybe this is because the steps of thin sectioning are more routinely practiced in earth sciences laboratories than in civil engineering but also maybe because of different practices. A thorough discussion of sample preparation for construction materials is given in Jana (2006).

## 5.2 The advent of petrography and microscopy of cementitious materials: from fundamental to applied petrography

For a geologist, petrography is the science describing rocks: overall grain size, mineralogy, porosity... Petrography usually begins on the field to understand the geological environment of a rock, then on a hand sample by the naked eye and subsequently with a magnifying glass. Afterwards only can the microscopic observations be carried out.

Whether Gary Larson likes it or not, microscopes do not seem to have been used by Neanderthalian to study mammoths, alas (Figure 22).

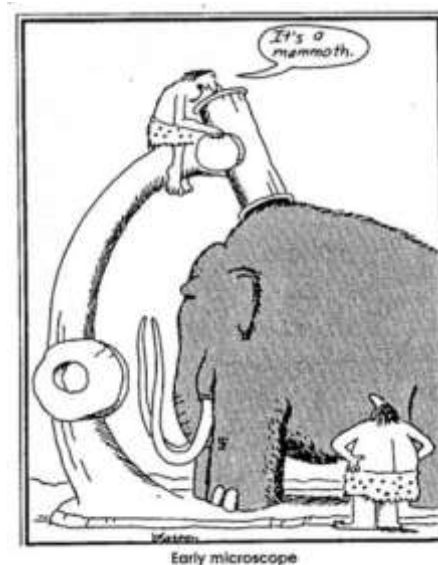
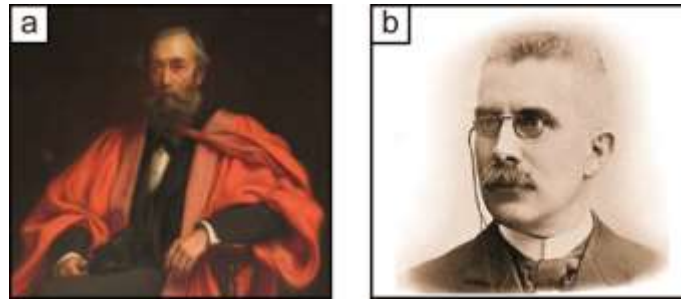


Figure 22 from Gary Larson's « the far side gallery »: early microscope

Historically, the first thin section was produced by the English geologist Henry Clifton Sorby (Figure 23a) in 1849 (see the whole story in Humphries, 1992) who rapidly took advantage of such a preparation, based on the use of polarized light, to identify rock-forming minerals, and also laid the bases of metallography by the use of reflected light.

Around forty years later, the French chemist Henry Le Chatelier (Figure 23b) was the first to use the polarizing microscope to describe the phases which form Portland clinker and their microstructure (Le Chatelier, 1882, 1887) and Figure 24a. At that time, the examination of thin sections in geology and mineralogy was common, and Le Chatelier's investigations illustrate perfectly the link between geology and cement science.

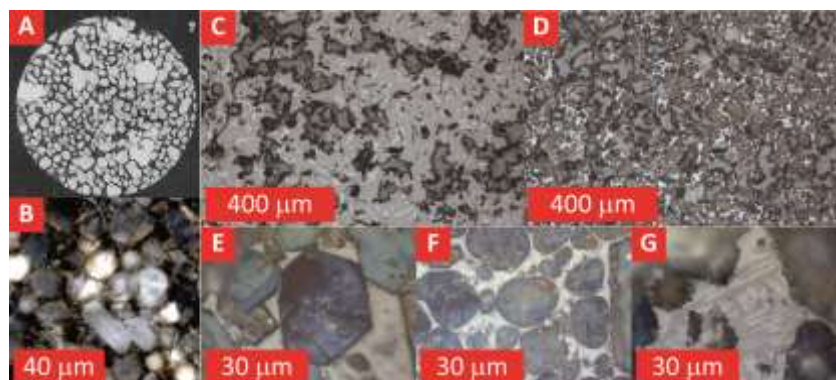


**Figure 23**: two great scientists historically linked to the study of thin sections. a) The English geologist Henry Clifton Sorby (1826-1908), the inventor of thin sectioning of rocks b) The French chemist Henry Le Chatelier (1850-

1936), first scientist to study and describe Portland clinker and cement hydration under the microscope in thin section. Images from Wikipedia.

In a landmark paper from 1882 (Le Chatelier, 1882), he described with great detail the four main phases of Portland clinker as seen in thin section. It is worth noting that those description were published in the *Comptes-Rendus Hebdomadaires des Séances de l'Académie des Sciences* – “weekly reports of the academy of science”), which at that time was designed to briefly report advances of work in progress, as also confessed by H. Le Chatelier in that paper. His description went like this:

- “*Substance with no effect on polarized light*” (direct translation from French) which he identified as a Ca-rich calcium aluminate, sometimes mixed with free lime. On the basis of its resemblance with a synthetic product that he had synthesized, he proposed this substance to be tri-calcium-aluminate, for which he identified the cubic system,
- “*Substance with weak influence on polarized light with well-formed crystal faces*”, identified as a calcium silicate. He named it “*péridot calcaire*” - limestone peridot,
- “*Strongly brow-coloured substance affecting polarized light*”. His observations on the microstructure details that this phase surrounds calcium silicate. He proposed this phase to be  $2(\text{Al,Fe})_2\text{O}_3 \cdot 3\text{CaO}$  by comparison with this very substance that he has also synthesized,
- “*Small crystals with strong effect on polarized light*”. He noted that those crystals are not abundant and are not water-sensitive. He inferred them to be magnesian in nature.



**Figure 24 from Thiéry et al. (2016)**: (a) the original drawing of Henry Le Chatelier (1887), representing the microstructure of Portland clinker as seen in thin section, scan from the original document courtesy of the *Bibliothèque Patrimoniale Numérique de l'École Nationale des Mines de Paris* (b) modern clinker as seen in thin section, cross-polarized light (c) typical microstructure of clinker as seen in reflected

light (cross-polarized light) (d) same field of view as (c) after etching of the surface with nital (e) alite, termed  $\text{C}_3\text{S}$  – tricalcium silicate (f) belite, termed  $\text{C}_2\text{S}$  – dicalcium silicate (g) the interstitial phase between calcium silicates, consisting of dark-grey tetracalcium aluminoferrite (termed  $\text{C}_4\text{AF}$ ) and grey tricalcium aluminate (termed  $\text{C}_3\text{A}$ ).

The use of microscopy applied to materials such as concrete has also greatly benefited from the discovery of concrete pathologies, the most famous one being the so-called “alkali silica reaction”. Discovered at the middle of the 20<sup>th</sup> century (Stanton, 1940). Thus, the advent of concrete petrography has logically followed, and it is not surprising that the first issue of “Reviews in Engineering Geology”, published by the Geological Society of America, contains a review on the topic (Mielenz, 1962).

A complete review covering the extent of the use of petrographic methods applied to concrete materials can be found in Jana (2005). It is worth noting that the first description of cement paste under the scanning electron microscope has been published in the prestigious journal *Nature* (Chatterji & Jeffery, 1966).

### 5.3 Which microscopy?

Whatever the method, sampling is done in order to have samples (sic) to study using different methods. Aside from the chemical, mineralogical (XRD), and so on, analysis, we will focus here on microscopy. Microscopy is a very wide field and many types of microscopes exist. Some of them are specific to some fields of investigation, but many microscopes can be used in the study of geomaterials (Table 5).

Type of microscopy	Application in geology	Application in CBM
Polarizing microscope	Virtually every rock characterization	Concrete petrography: understanding which aggregate has been used, which pathology affects the concrete (St John et al., 2016; Ingham, 2009, 2011; Gregerová & Všianský, 2009; Mielenz, 1962)...
Scanning electron microscope	Useful tool as an aid for mineral identification when accompanied with EDS, phase contrast.	Phase-contrast imaging in BSE mode on polished section with EDS analysis and hydrates morphology on fractures (Scrivener, 2004; Stutzman, 2004, 2012; Famy et al., 2002). Identification of minerals involved in degradation processes (Gregerová & Všianský, 2009).
Transmission electron microscope	Phase identification at the nanoscale, study of deformations... (Nieto K.J.T. Oberti, R., 2013)	Less common since cement hydrates are fragile under the beam. Study of Portland cement clinker (Groves, 1981), characterization of C-S-H and other hydration products (Richardson & Groves, 1993)
Confocal microscope	Porosity analysis (Mauko et al., 2009), fission track analysis (Petford & Miller, 1990), study of fluid inclusions (Petford et al., 1995)	Imaging of the porous network of cement paste and the development of hydration products (Head & Buenfeld, 2006; Yio et al., 2015; Head et al., 2006), in-situ imaging of the development of ASR products (Collins et al., 2004).

X-ray computed tomography	“Geological applications include interior examination of one-of-a-kind fossils or meteorites; textural analysis of igneous and metamorphic rocks; geometric description and quantification of porosity and permeability in rocks and soils; and any other application demanding three-dimensional data that formerly required physical serial sectioning” (Ketcham & Carlson, 2001)	Acquisition of porosity (du Plessis et al., 2014), in-situ observation of deformation (Elaqra et al., 2007).
---------------------------	---	--

Table 5: brief review of the types of microscopies applied to natural and anthropogenic geomaterials

#### 5.4 Enhancing images: the multifocus technique - see also the reprint of the article at the end of the manuscript

Tried-and-tested, routine methods may at some point still need further improvement. As an example, it can be annoying, when taking pictures using a stereomicroscope, to have only a part of the image neat and the remaining blur because of the limited depth of field. This can also be the case for SEM images even if this microscope has a very high depth of field. Moreover, in some cases, on a 30 micrometers thick thin section, tiny features of interest, studied using high power objectives, are larger than the depth of field.

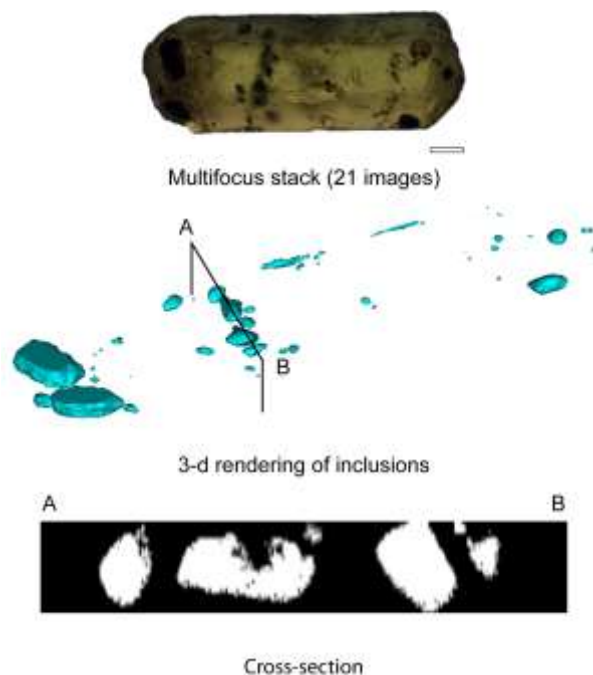


Figure 25 from Thiéry & Green (2012) : A multifocus stack of a set of 21 images of a single pyroxene crystal; the scale bar is 100  $\mu\text{m}$ . A 3D rendering of the inclusions located in the crystal with a section along AB through the inclusions

However, there is the possibility to combine images obtained at various focus points in order to obtain a single image perfectly focused. This technique is called the multifocus imaging (De et al., 2006; Betz, 2005). Besides the purely aesthetic possibilities offered by this technique since it allows perfect sharp details in microminerals imaging (Green, 2005), some practical applications

can be found such as the possibility to realize cross sections in minerals (Figure 25) as well as 3D rendering (Niederöst et al., 2003; Figueiredo et al., 2013); it has also been used to obtain 3D models of fractures in concretes (Štukovnik et al., 2014).

## **5.5 Summary**

This brief overview of microscopy has considered the study of natural and anthropogenic materials under microscopes, either optical or electronic. Since the early years of microscopy and the seminal work of the French chemist Henry Le Chatelier, optical microscopy is truly a common point, a link between fundamental and applied geomaterials science.

In my case, having begun as a field geologist and now actively involved in laboratory studies of cementitious materials, it was at first not obvious to understand this link. But since I am now aware of all the history behind the study of construction and building materials, I understand how both fields are linked.

## 6 ANALOGIES BETWEEN NATURAL AND ANTHROPOGENIC MATERIALS

I have tried to develop this activity after my integration at the *Civil and Environmental Engineering Dpt.* at the *École des Mines de Douai* in 2010. Being a geologist in such a context offered some interesting challenges. Indeed, people more engaged into the durability of built structures (whatever the material used) do not consider ageing at the same scale as geologist do. However, some natural analogues, sometimes very uncommon, exist: they offer an interesting point of view for the study of durability of their industrial, man-made analogues.

### 6.1 Diversity in construction and building materials

Construction and building materials covers such a wide range of substances (Figure 26) that a clarification is necessary to focus on the way to find analogues. Moreover, to add to the diversity, some complex admixtures can be present, more and more small (Mukhopadhyay, 2011), more and more diverse in a sustainable development trend.

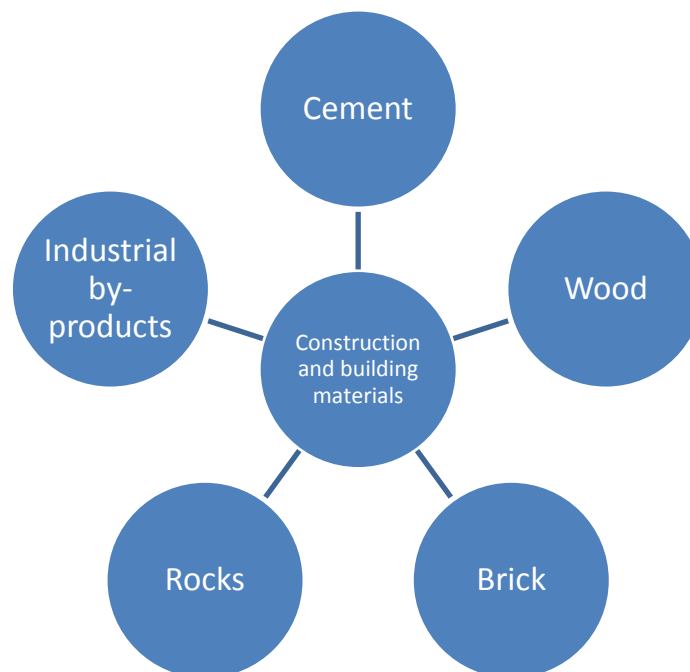


Figure 26: diversity in construction and building materials

### 6.2 Minerals or synthetic substances?

In cement s.l., we can define *phases* since they are artificial, but some of those phases are also known in nature, and thus have been recognized as *minerals*. Indeed, according to the international mineralogical association: « *a mineral is an element or chemical compound that is normally crystalline and that has been formed as a result of geological process [...] Anthropogenic substances are those produced by Man, and are not regarded as minerals. If such substances are identical to minerals, they can be referred to as « synthetic equivalents» of the minerals in question»* (E.H. Nickel, 1995). Fortunately, some recommendations have been made for such synthetic equivalents (E. H. Nickel, 1995): « *If the*

*synthetic substance has a simple formula then preference should be given to the use of a chemical formula instead of a mineral name.»*

Since the definition of a mineral implies that it is found as a natural substance, some compounds present in cement only have not (yet?) any natural analogues but the main phases of clinker do have. On the other hand, some minerals have been described as such (i.e. as natural substances) after having been known for decades in cement, such as for example portlandite (Tilley, 1933). Whatever the occurrence (natural or not), cement science since its inception is intimately linked with mineralogy, as recalled in Table 6. Several minerals have been named to honor the work of mineralogists or chemists who have dealt with cement, or simply recall their genetic link with cement-based materials.

Mineral name and formula	Context and dedication	Reference
Bredigite $\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$	The name honors Max Albrecht Bredig, a physical chemist who worked on the polymorphism of dicalcium silicate.	(Tilley & Vincent, 1948)
Brownmillerite $\text{Ca}_2(\text{Al},\text{Fe}^{3+})_2\text{O}_5$	The name honors Dr. Lorrin Thomas Brownmiller, chief chemist of the Alpha Portland Cement Company, who was among the first to identify this phase in Portland cement before the phase was recognized in a natural context.	(Hentschel, 1964; Fleischer, 1965)
Lechatelierite $\text{SiO}_2$	The name honors the French chemist Henry Le Chatelier as recognition towards his works on silica, but H. Le Chatelier is also the first scientist to have described Portland cement clinker in this section using a polarizing microscope (see § 5.2)	(Lacroix, 1915)
Tilleyite $\text{Ca}_5\text{Si}_2\text{O}_7(\text{CO}_3)_2$	The name honors Cecil Edgar Tilley, famous Australian-British petrographer, whose seminal work on the dolerite plug of Scawt Hill (see § 6.3.1.1) led to the discovery of several minerals which are analogues of Portland clinker phases or hydration products.	(Larsen & Dunham, 1933; Chinner, 1974)

**Table 6:** examples of minerals which names honors scientists having been involved in cement science

### 6.3 Natural analogues of cementitious phases: an original approach to the study of durability

Natural analogues are a common way to investigate materials when dealing with durability (Milodowski et al., 1989, 2011; Rochelle & Milodowski, 2013). This approach seems however most present in the study of natural analogues of ageing for radioactive waste disposal (Gascoyne, 2002, see also the ‘Natural Analogue Working Group’ website: [www.natural-analogues.com](http://www.natural-analogues.com)).

In cement and concrete research, the study of durability usually relies on laboratory performance tests (Alexander & Thomas, 2015; Lindgård et al., 2012). Since many minerals present in the cement paste have natural analogues it is worth trying to compare them from this point of view. But let us compare graphically the ages between cement, selected famous buildings, and geological phenomena resulting in the formation of analogues (Figure 27).



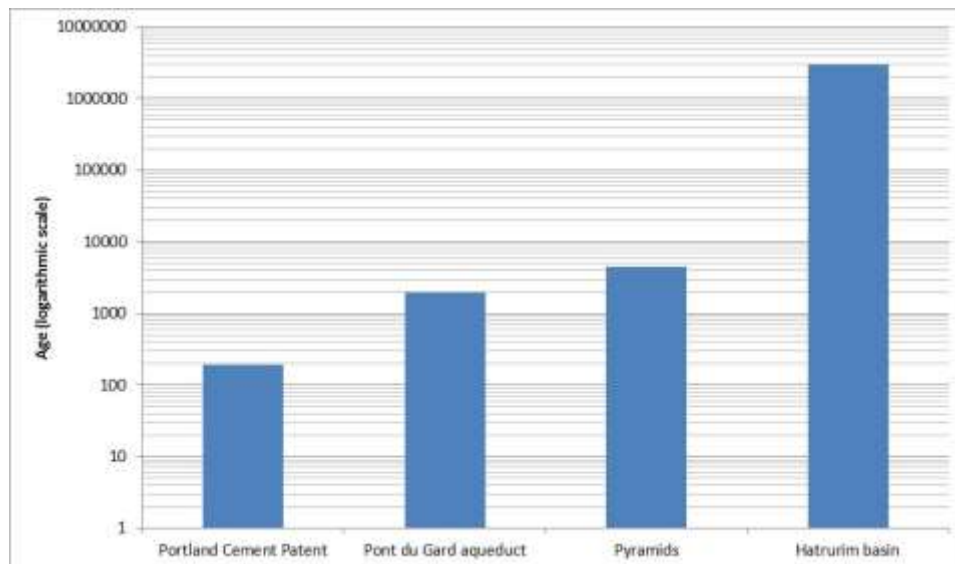


Figure 27 : timescale between Portland cement and its natural analogue and famous buildings

Portland cement was patented in 1824 by Joseph Aspdin. This is around 2000 years after the famous Roman Pont du Gard Aqueduct and 4500 years after the Egyptian pyramids. Those materials yield very interesting examples for the study of the ageing of construction and building materials. But what is left to do if we want to consider longer timescales?

Geology is the answer. From places to places, rare geological contexts have led to the formation of “cement like” rocks, which are perfect for studying the behavior of Portland-like materials through time.

### 6.3.1 Geological context

Very specific geological contexts are necessary to achieve the growth of such minerals. Indeed, contrarily to the so-called « ultrahigh temperature metamorphism» where temperatures can exceed 900°C at 7-13 kbar (Kelsey, 2008), natural analogues of clinker phases are formed at more or less ambient pressure.

Such contexts have been described throughout the world and are covered in the wide field of pyrometamorphism (R Grapes, 2011). The Russian literature usually refers to those phenomena as “combustion metamorphism” (Sokol, 2005).

#### 6.3.1.1 Contact metamorphism

Such metamorphism occurs when a high-temperature body such as an igneous intrusion is in contact (hence its name) with a geological body of lower temperature. The most famous one for a cement chemist is probably the dolerite plug of Scawt Hill, Ireland (Tilley & Harwood, 1931), where several natural analogues of cementitious mineral (anhydrous, hydrous, carbonates...) have been described (Tilley & Hey, 1930), and notably portlandite  $\text{Ca}(\text{OH})_2$  and larnite  $\text{Ca}_2\text{SiO}_4$  (natural analogue of belite, termed  $\text{C}_2\text{S}$  in cement science) for which Scawt Hill is the type locality (Tilley, 1933, 1929).

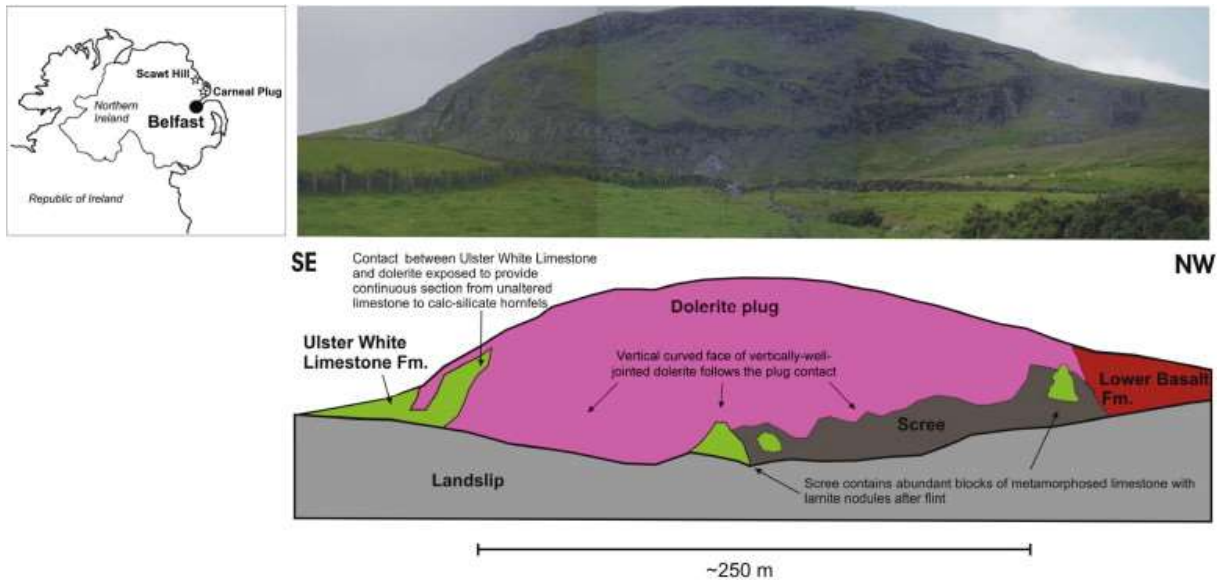


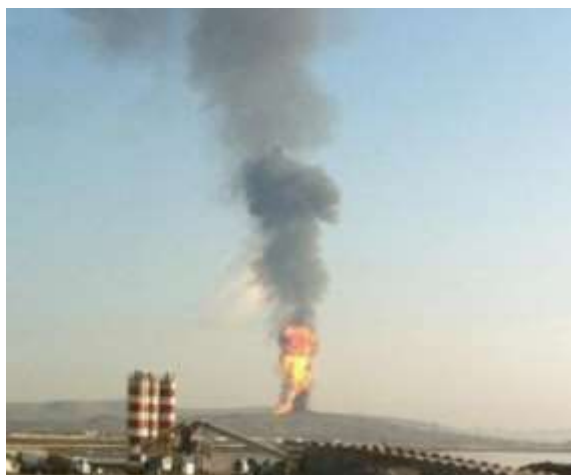
Figure 28 from Rochelle & Milodowski (2013): the dolerite plug of Scawt Hill

Secondary phases such as ettringite  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ , afwillite  $\text{Ca}_3(\text{SiO}_3\text{OH})_2\cdot 2\text{H}_2\text{O}$  and hydrocalumite  $\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{Cl}, \text{CO}_3, \text{OH})_2\cdot 4\text{H}_2\text{O}$  have also been described and are also of notable interest in cement science (see § 6.4).

#### 6.3.1.2 *Combustion metamorphism*

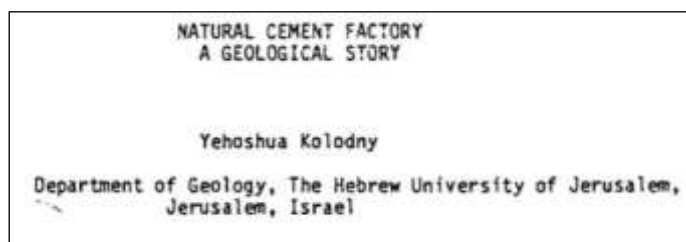
It corresponds to phenomena occurring when hydrocarbons and/or gas seeps to the surface and ignite, but also when coal seams or carbonaceous sediment burn (see review in R Grapes, 2011). Some places are famous for those phenomena:

- The Powder River basin (Wyoming and Montana, USA), characterized by unusual glass-bearing pyrometamorphic rocks (Cosca et al., 1989) and a peculiar landscape (Heffern et al., 2007), is the type locality of esseneite ( $\text{CaFe}^{3+}\text{AlSiO}_6$ ), a pyroxene typical of pyrometamorphism (Cosca & Peacor, 1987),
- The Ravat coal fire in central Tajikistan in which a coal seam, burning for more than 200 years, has formed various paralavas and clinkers (Sharygin et al., 2009, 2014) and is the type locality of a very rare organic mineral, ravatite,  $\text{C}_{14}\text{H}_{10}$  (Nasdala & Pekov, 1993), also described in various burning coal heaps (Witzke et al., 2015; Fabiańska et al., 2013),
- Various active mud volcanoes in Azerbaijan (Planke et al., 2003) such as for example the Lokbatan mud volcano (Kadirov & Mukhtarov, 2004) near Baku (Figure 29). During the 2001 eruption, a 100 m in diameter and 400 m high flame has been observed during 24 hours; the extruded mud has covered an area around the crater of 150 m in all directions and the surface temperature of baked mud was estimated to 700°-1000° (Mukhtarov et al., 2003).



**Figure 29:** the Lokbatan mud volcano (Azerbaijan) eruption in 2012 (<http://www.today.az/news/society/112652.html>)

The most famous place for such phenomena in geological times is most probably the Hatrurim basin in Israel (Negev desert). Since the seminal work of Gross (1977), numerous works have been carried out on this very unique place in which has even been called a “natural cement factory” (Figure 30).



**Figure 30:** the landmark chapter by Y. Kolodny (1979), describing natural analogues from the Hatrurim basin in a textbook about cement science

The analogies between industrial cement and rocks formed in the Hatrurim basin are indeed striking. As for Scawt Hill (§ 6.3.1.1), the Hatrurim basin is the type locality for minerals which were previously known in cementitious materials, such as hatrurite,  $\text{Ca}_3\text{SiO}_5$ , corresponding to alite ( $\text{C}_3\text{S}$ ) in Portland cement clinker, or ye’elinite,  $\text{Ca}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ , an important component of calcium sulfoaluminate cements. Within the Hatrurim formation, 141 mineral species have been described, and it’s the type locality for 10 of them (Mindat, March 2017).

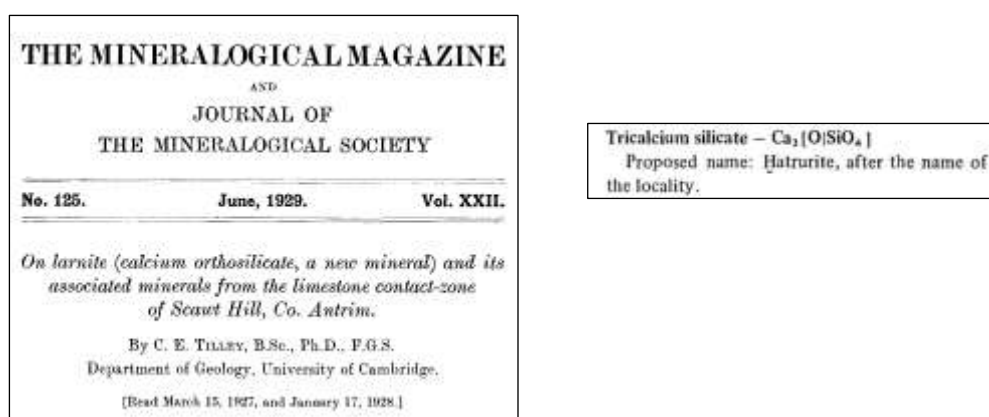
### 6.3.2 *Anhydrous high temperature minerals similar to clinker*

Clinker, in the sense of cement-based materials, designates the rocky product formed during the combustion of a raw meal:

- Clay and limestone for Portland clinker,
- Limestone and bauxite for calcium-aluminate cements,
- Limestone, bauxite and gypsum for calcium sulfoaluminate cements.

We have briefly seen in §6.3.1 that ultra-high temperature metamorphism is frequently linked to sedimentary rocks, either in the case of coal seams combustion or ignition of mud discharge. Chemically, sedimentary rocks are generally carbonated and may also be rich in Al and Si, which means that they have a composition range ideal to produce cementitious phases if they are heated enough.

The two calcium silicates which are typical for Portland cement clinker, namely  $C_2S$  (dicalcium silicate) and  $C_3S$  (tricalcium silicate) have been discovered as natural minerals, larnite and hatrurite, respectively (Figure 31). The very complex crystallographic features of dicalcium silicate (Yamnova et al., 2011), expressed as so-called “striation” by cement chemists, is also present in natural larnite (Sokol et al., 2014).



**Figure 31** : original publications describing the natural analogues of  $C_2S$ , larnite (Tilley, 1929), and  $C_3S$ , hatrurite (Gross, 1977)

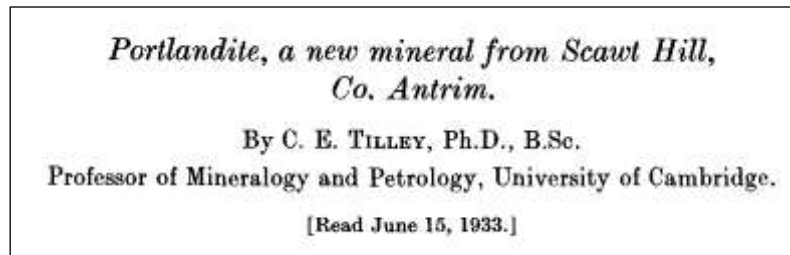
Calcium aluminate phases, some of them being common to both Portland and calcium aluminate cements, can be present in such contexts, such as for example brownmillerite, which have been described in xenoliths from lavas of the Eifel volcanic area (Hentschel, 1964). It is interesting to note that it was described very near to the ettringite type locality. A complete review of calcium aluminate phases present in calcium aluminate cements and in nature can be found in Pöllmann (2012).

### 6.3.3 Analogues of cement hydrates

The study of such minerals is a bit tricky since the formation of cement hydrates is complex and scalable. As noted by Scrivener and Nonat (2011), “Hydration is absolutely central to cementitious materials. It is the, almost magical, process by which a fluid suspension is transformed into a rigid solid, at room temperature, without the need for heat or other external processing agents and with minimal bulk volume change. We take it for granted, but just think if we had no previous experience of hydration and someone invented it how sensational that would be!”

We have seen that synthetic substances are not considered as minerals (§ 6.2); however, and fortunately, some minerals form during cement hydration and have also been described in nature. Generally, they occur as secondary phases as a result of interaction with atmosphere. As an

example, the very famous portlandite  $\text{Ca}(\text{OH})_2$  occurs as a natural mineral (Figure 32) described at Scawt Hill (§6.3.1.1). Its name recalls, without any surprise, Portland cement.



**Figure 32 :** original publication describing portlandite ( $\text{Ca}(\text{OH})_2$ ) in a natural context (Tilley, 1933)

A complete description and discussion of cement hydrates would take a whole manuscript. Reviews about the so-called calcium silicate hydrates, termed C-S-H, document such minerals both in nature and cement media (Richardson, 2008, 2000). Not surprisingly, most (if not all) of those hydrates (which can also be carbonates) have been described in the very specific geological context described above.

For example, jennite,  $\text{Ca}_9\text{Si}_6\text{O}_{16}(\text{OH})_{10}\cdot 6\text{H}_2\text{O}$  and tobermorite  $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2\cdot n\text{H}_2\text{O}$ , which are model structures for the C-S-H phase (Richardson, 2008; Grangeon et al., 2013, 2016; Bonaccorsi et al., 2004), have been described respectively in metamorphosed rocks from a contact aureole (Carpenter et al., 1966) and as void infill in lava flows (Heddle, 1880).

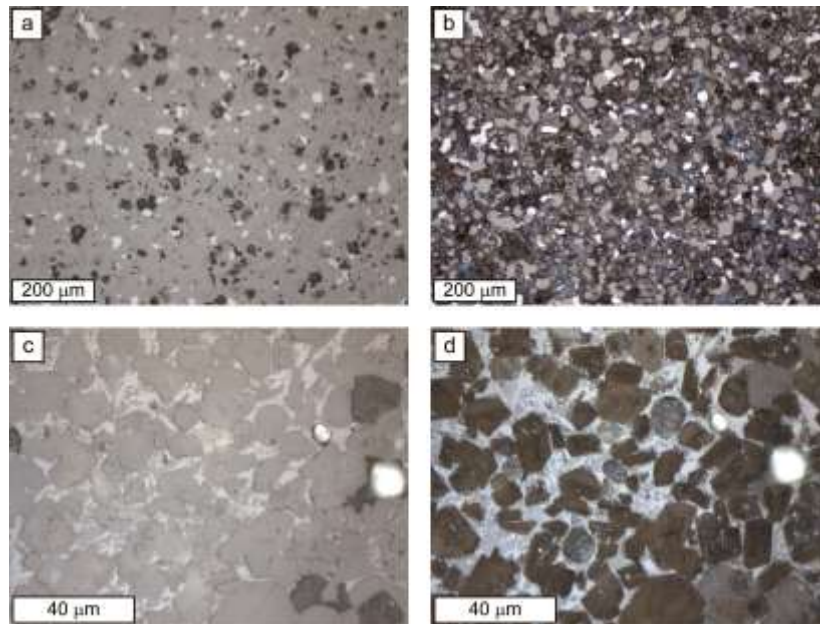
#### 6.3.4 Laboratory study of hydration of analogues

The aforementioned minerals within their geological context have only been described. An interesting question, both of fundamental and applied interest, is “*What happens if we try to hydrate those cement-like rocks as we would do with commercial cement?*”

I have presented some elements of answer at the 37<sup>th</sup> International Cement Microscopy Association (ICMA) meeting (Thiéry et al., 2014).

Larnite-bearing rocks from the Hatrurim basin (Sokol et al., 2014) have been investigated as if they were a regular Portland cement. A polished section has been etched with nital (1 % nitric acid in ethanol), which is commonly used in clinker microscopy to enhance the contrast between the phases (ref).

The results (Figure 33) are similar to what is obtained on Portland clinker. Larnite behaves as its industrial analogue (larnite) and becomes blue.



**Figure 33 a&b from Thiéry et al. ICMA 2014 oral presentation, c&d from Thiéry (2013).** Comparison of nital etching of a larnite-bearing rock (a/b, before/after) and a Portland cement clinker (c/d, before/after).

A crushed sample has been studied using calorimetry as if it was cement. The heat flux is weak and the rock is less reactive than cement but some hydration happens as revealed by XRD.

The hydration has been characterized using XRD as a comparison between unhydrated and hydrated powders (Figure 34). In the hydrated powder, larnite peaks are less intense (ca.  $37^\circ$ ,  $38^\circ$  and  $52^\circ$  in  $2\theta$ ). Broad, poorly defined peaks at  $13^\circ$  and in the  $16-17^\circ$  range ( $2\theta$ ) appears during hydration, consisting probably of AFm phases as well as amorphous  $AH_3$  gel. Mayenite main peaks at ca.  $21^\circ$  and  $35^\circ$  ( $2\theta$ ) almost disappeared. The gehlenite hydrate (strätlingite,  $C_2ASH_8$ ) main peak at  $7^\circ$  ( $2\theta$ ) is well marked in the hydrated sample but quite broad, revealing is poor crystallinity. Finally, katoite (hydrogrossular,  $C_3AH_6$ ) is also formed as revealed by the appearance of a broad peak at  $23.5^\circ$  ( $2\theta$ ) as well as with the broadening of the peak at  $20.2^\circ$  ( $2\theta$ ), for which there is an overlap with a secondary peak of gehlenite. Finally, a slight decrease in intensity of the brownmillerite peaks ( $13$  and  $39.5^\circ$   $2\theta$ ) is observed.

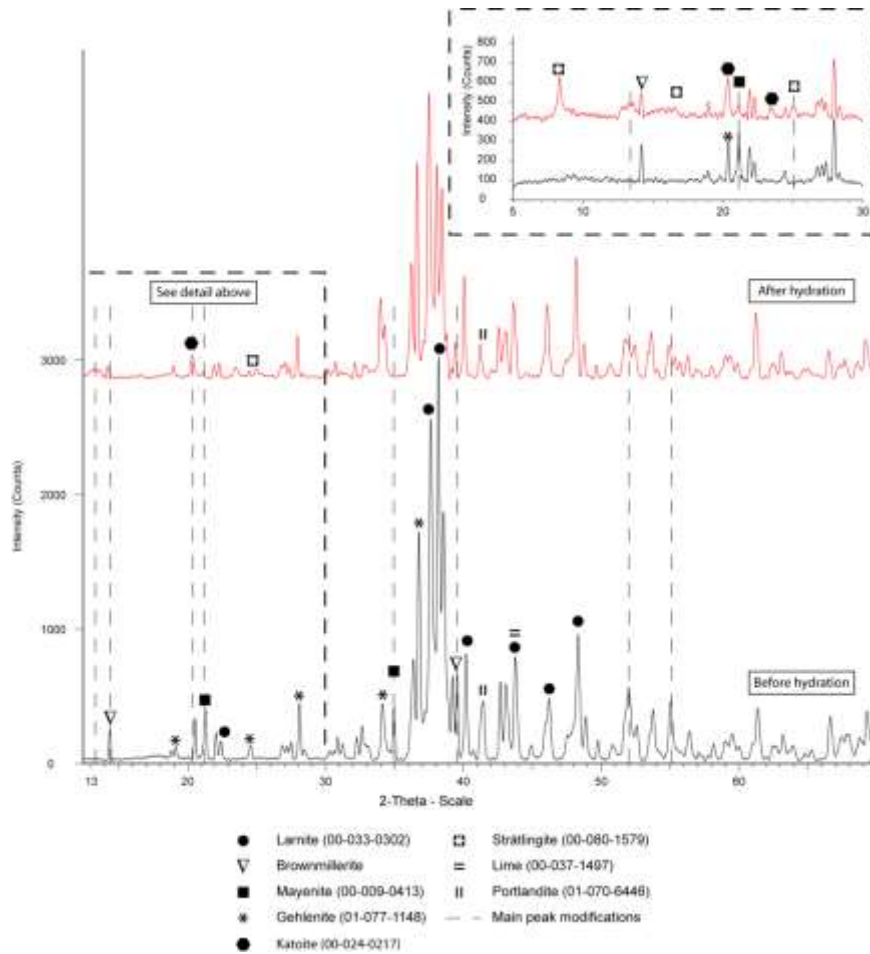


Figure 34 from Thiéry et al. (2014): XRD comparison before and after hydration of a larnite-bearing rock

#### 6.4 Ettringite: natural mineral, useful analogue (*part of this section has been submitted to the "Journal of Microscopy"*)

*Complete reference:* Thiéry, V., Trincal, V., Davy, C., *The elusive ettringite under the high-vacuum SEM – a reflection based on natural samples, the use of Monte-Carlo modeling of EDS analyses, and an extension to the ettringite group minerals*

##### 6.4.1 General considerations

This mineral, of prime interest in cement and concrete science, is also known in natural rocks. Ettringite was first recognized in the Eifel region in Germany (Lehmann, 1874) in xenoliths but the most famous occurrence of this mineral is located in South Africa, N'Chwaning mines, Kalahari manganese field (Pohwat, 2012; Gutzmer & Beukes, 1996). It forms elongated hexagonal prisms; generally yellow (Figure 35), up to 15 cm long.



Figure 35 : ettringite crystals from the N'Chwaning Mine

Ettringite is also known as a secondary product on slags from a former Pb-Cu mine (Chollet & Devouard, 2013) as well as in the weathering products of municipal waste incinerator bottom ash deposits (Johnson & Schweizer, 1998).

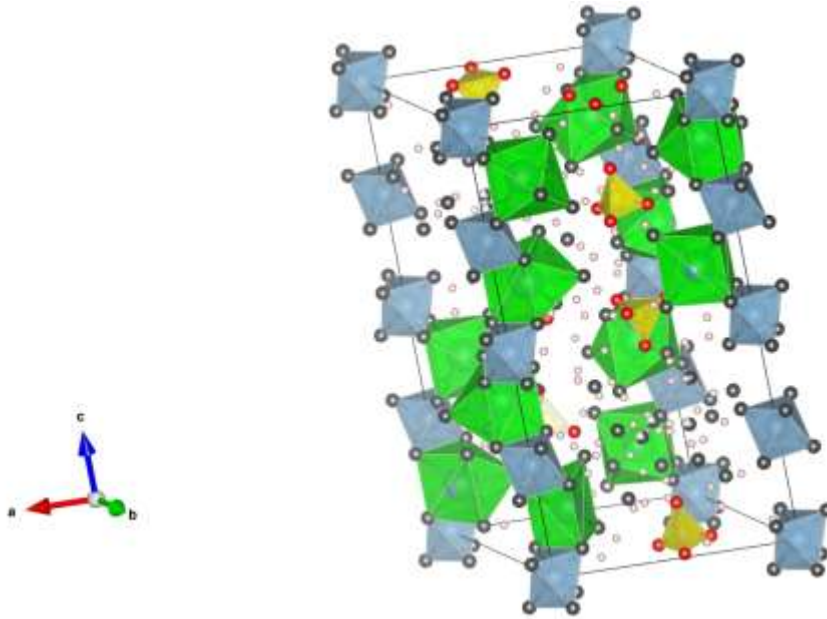
In cement and concrete science, three different ways can be considered for the presence of ettringite:

- This is the first mineral to form during Portland cement hydration, according to the following reaction (Mehta, 1986):  $[\text{AlO}_4]^- + 3 [\text{SO}_4]^{2-} + 6[\text{Ca}^{2+}] + \text{water} \rightarrow \text{C}_6\bar{\text{A}}\bar{\text{S}}_3\text{H}_{32}$ ,
- It is associated with a major concrete pathology, namely DEF - *Delayed Ettringite Formation* (Taylor et al., 2001), in which ettringite is not formed during the first steps of hydration but later, leading to an increase in concrete volume and the typical filling of voids surrounding aggregates by acicular ettringite crystals. It is worth noting that the processes of DEF are still partly unclear (Diamond, 1996),
- This is the main phase formed during the hydration of calcium sulfoaluminate cements according to, for example, the following reaction :  $\text{C}_4\bar{\text{A}}_3\bar{\text{S}} + 2 \text{C}\bar{\text{S}} + 38\text{H} \rightarrow \text{C}_6\bar{\text{A}}\bar{\text{S}}_3\text{H}_{32} + 2\text{AH}_3$  (Gastaldi et al., 2009).

In environmental sciences, ettringite is also widely studied because its structure can accommodate foreign ions; the ettringite group minerals, forming solid solutions, cover a wide spectrum of elements, such as for example Cr, As, Sb... (Gougar et al., 1996; Drebushchak et al., 2013)

The crystal structure of ettringite is complex (Figure 36) and has been refined through time (Courtois et al., 1968; Moore & Taylor, 1968; Goetz-Neunhoeffler & Neubauer, 2006). It is based on  $[\text{Al}(\text{OH})_6]^{3-}$  octahedral at the corner of the unit cell, linked through groups of three  $\text{Ca}^{2+}$  ions. The very high water content expressed in the structural formula is revealed in the structure by four  $\text{H}_2\text{O}$  molecules and four  $\text{OH}^-$  ions coordinated to each  $\text{Ca}^{2+}$ .





**Figure 36:** crystal structure of ettringite ; data from (Goetz-Neunhoeffer & Neubauer, 2006) drawn using VESTA software (Momma & Izumi, 2011)

#### 6.4.2 *Ettringite in cement media: considerations about its microscopy and microanalysis*

Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS) for microanalysis is nowadays routinely used in cement and concrete research (Stutzman, 2004; Scrivener, 2004). Based on electron-matter interactions (Reimer, 1998), it allows high magnification imaging of fractures as well as Z-contrast (Lloyd, 1987) between phases of different density.

EDS is a fast way to gain local semi-quantitative to quantitative (Newbury & Ritchie, 2015) chemical analysis and chemical mapping as well as linescans of minerals and materials. However, as outlined by Wong and Buenfeld (2006), the interaction volume resulting from the incident electron beam can be significantly larger than the probe size. More specifically, in complex microstructures such as cement pastes where phases develop a 3D porous network from the nanometric to the micrometric range (Yio et al., 2015; Skibsted & Hall, 2008), it is important to understand what volume is analyzed.

EDS analysis can be simulated by Monte Carlo modeling (Gauvin, 2005), especially by using user-friendly softwares (Drouin et al., 2007); this has yielded interesting results on cement-based materials (Wong & Buenfeld, 2006). The goal of such modeling is to gain insights of the interaction volume between the incident electrons and the sample.

#### 6.4.3 *The ettringite group minerals*

Ettringite belongs to the ettringite group minerals (Table 7) and thus solid solutions between pure end-members or intermediate compositions may occur (Barnett et al., 2002; Macphee & Barnett, 2004; Carpenter, 1963; Möschner et al., 2009) as well as intergrowths. For example, bentorite (Cr-ettringite) has been described in the hydration products of Cr-bearing wastes mixed with cement (Trezza & Ferraiuelo, 2003); charlesite (B-bearing ettringite) may be used to

immobilize boron in radioactive wastes (Atabek et al., 1992) whereas thaumasite is well known in some cases of sulfate attack (Menéndez et al., 2013).

Name	Structural formula	Density	Reference
Bentorite	$\text{Ca}_6(\text{Cr}^{3+}, \text{Al})_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$	2.021 (meas.)	(Gross, 1980)
Buryatite	$\text{Ca}_3(\text{Si}, \text{Fe}, \text{Al})(\text{SO}_4)[\text{B}(\text{OH})_4]\text{O}(\text{OH})_5 \cdot 12\text{H}_2\text{O}$	1.895 (calc.)	(Malinko et al., 2001)
Carraraite	$\text{Ca}_3(\text{SO}_4)[\text{Ge}(\text{OH})_6](\text{CO}_3) \cdot 12\text{H}_2\text{O}$	1.979 (calc.)	(Merlino & Orlandi, 2001)
Charlesite	$\text{Ca}_6(\text{Al}, \text{Si})_2(\text{SO}_4)_2[\text{B}(\text{OH})_4](\text{OH}, \text{O})_{12} \cdot 26\text{H}_2\text{O}$	1,77 (meas.)	(Dunn et al., 1983)
Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$	1.77 (meas.)	(Bannister et al., 1936)
Hielscherite	$\text{Ca}_3\text{Si}(\text{SO}_4)(\text{SO}_3)(\text{OH})_6 \cdot 11\text{H}_2\text{O}$	1,82 (meas.)	(Pekov et al., 2012)
Imayoshiite	$\text{Ca}_3\text{Al}(\text{CO}_3)[\text{B}(\text{OH})_4](\text{OH})_6 \cdot 12\text{H}_2\text{O}$	1,79 (calc.)	(Nishio-Hamane et al., 2015)
Jouravskite	$\text{Ca}_3\text{Mn}^{++}(\text{SO}_4)(\text{CO}_3)(\text{OH})_6 \cdot 12\text{H}_2\text{O}$	1.95 (meas.)	(Gaudefroy & Permingeat, 1965)
Kottenheimite	$\text{Ca}_3\text{Si}(\text{SO}_4)_2(\text{OH})_6 \cdot 12\text{H}_2\text{O}$	1.92 (meas.)	(Chukanov et al., 2012)
Micheelsenite	$(\text{Ca}, \text{Y})_3\text{Al}(\text{HPO}_4, \text{CO}_3)(\text{CO}_3)(\text{OH})_6 \cdot 12\text{H}_2\text{O}$	2.83 (meas.)	(McDonald et al., 2001)
Sturmanite	$\text{Ca}_6(\text{Fe}^{3+}, \text{Al}, \text{Mn}^{3+})_2(\text{SO}_4)_2[\text{B}(\text{OH})_4](\text{OH})_{12} \cdot 25\text{H}_2\text{O}$	1.847 (meas.)	(Peacor et al., 1983)
Tatarinovite	$\text{Ca}_3\text{Al}(\text{SO}_4)[\text{B}(\text{OH})_4](\text{OH})_6 \cdot 12\text{H}_2\text{O}$		(Chukanov et al., 2015)
Thaumasite	$\text{Ca}_3(\text{SO}_4)[\text{Si}(\text{OH})_6](\text{CO}_3) \cdot 12\text{H}_2\text{O}$	1.877 (meas.)	(Anthony et al., n.d.)

**Table 7 :** *the ettringite group minerals (EGM)*

#### 6.4.4 Crystal chemistry

A pluri-millimetric crystal was impregnated in epoxy resin and a cross section was done perpendicularly to its elongation axis. EDS chemical maps were acquired at 15kV (Figure 37). Three domains can be characterized. The innermost (number 3 on Figure 37) is homogeneous in composition and corresponds to an area in which BSE mode reveals an intense cracking. Its chemistry (Ca, Al, S, O) corresponds to ettringite s.s., as outlined by EDS spectra (figure 4). An intermediate domain (number 2 on Figure 37) of homogeneous composition is characterized by a dramatic drop in Al content and the apparition of Mn, Fe and Si. This domain shows less cracking. The outermost domain (number 1 on Figure 37) shows regular banding with variations in Al, Ca, S and Si content as well as a lesser amount in Mn than the intermediate domain

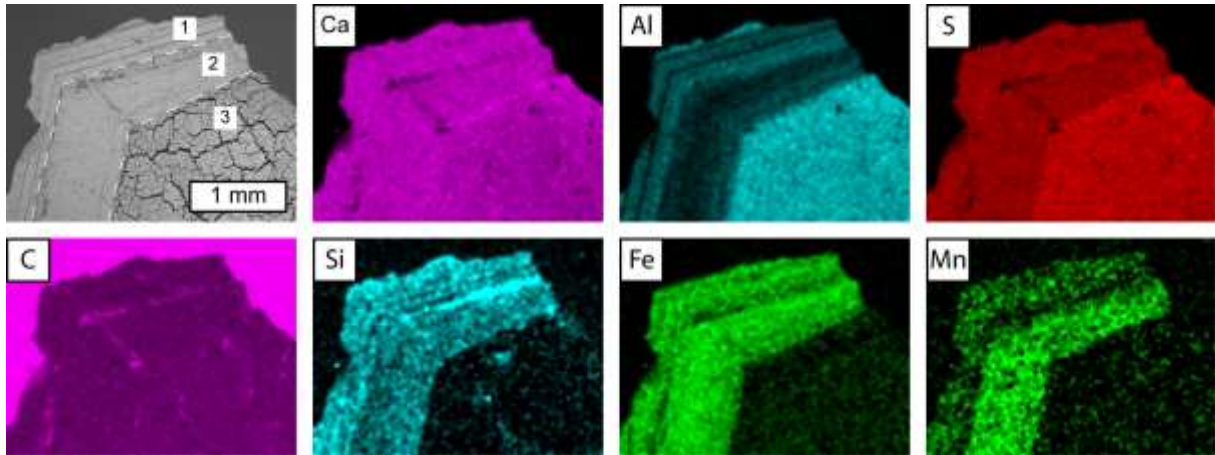


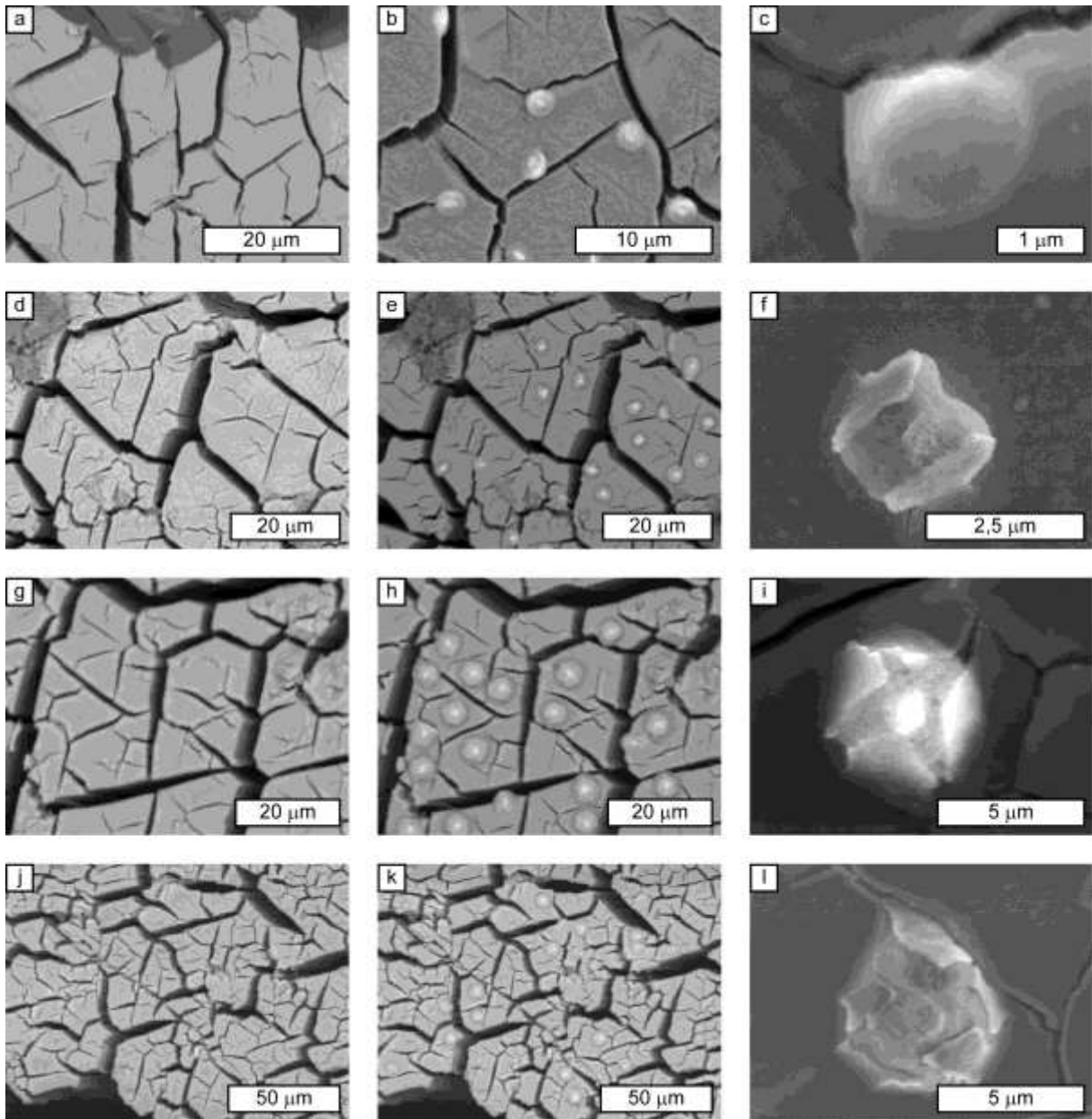
Figure 37 from Thiéry et al., submitted to “Journal of Microscopy”): EDS maps of ettringite crystals from the N’Chwaning mine, showing variations in composition. The core of the crystal is composed of almost pure ettringite

(Ca, Al, S) while the rims show variations towards other end-members with more complex chemistry (sturmanite  $\text{Ca}_6(\text{Fe}^{3+}, \text{Al}, \text{Mn}^{3+})_2(\text{SO}_4)_2[\text{B}(\text{OH})_4](\text{OH})_{12} \cdot 25\text{H}_2\text{O}$  or charlesite  $\text{Ca}_6(\text{Al}, \text{Si})_2(\text{SO}_4)_2[\text{B}(\text{OH})_4](\text{OH}, \text{O})_{12} \cdot 26\text{H}_2\text{O}$ )

#### 6.4.5 Beam damage

Ettringite crystals, even when embedded in resin, develop a very typical dehydration cracking pattern similar to what can be observed when mud dries; this pattern has already been illustrated in the literature as for example on ettringite in sulfoaluminate cement pastes (Chen et al., 2012; Ambroise et al., 2009) or on natural kottenheimite (Chukanov et al., 2012). However, as seen in Figure 37, this pattern seems to be dependent on the crystal chemistry. Indeed, the pattern which develops in more siliceous domains is smaller than in pure ettringite.

The interaction between the electron beam and the sample during analysis results in heating. The analysis spots (Figure 38) are characterized by surface bursting; the size of the damaged zone is larger when the voltage increases.



**Figure 38:** Triplets of images showing an area before and after analysis and a close-up view of the resulting beam damage. a, b, c: 7kV; d, e, f: 10 kV; g, h, i: 15 kV; j, k, l: 20 kV. Counting time 60s.

## 6.5 Anthropogenic analogues of natural phenomena: burnt colliery spoil and mineralogy of burnt coal heaps

This point of interest arose thanks to my integration at the École des Mines de Douai, located in a former coal mining area. Several actively burning dumps are present, as well as former ones, being exploited as aggregate source.

Coal heaps are typical features of coal-producing areas and are thus widely known throughout the world. However, not only coal heaps do exist and various mining leftovers have been left as heaps (tailings are not considered here), namely slag residues from Pb-Zn ore processing (Atanassova & Kerestedjian, 2009), retorted oil shales (Gatel et al., 2015)...

As presented in § 1.1.1, the materials present in such a context are truly civil engineering materials (Rainbow, 1987; Skarżyńska, 1995a).

### 6.5.1 Coal heaps

In the collective imagination, coal heaps are made of coal since they are usually very dark (almost black). However, coal heaps are leftovers from coal mining activities, thus they are mainly made up of everything else than coal. Older heaps may still contain large amounts of coal since the separation process were less efficient in the past (Heynen et al., 1994) but usually, coal heaps contain rocks that are associated with coal seams (Skarżyńska, 1995b, 1995a). They were also filled with various wastes associated with the coal industry such as railway tracks and sleepers, demolition wastes, fine particles from the cleaning of coals (Figure 39).



**Figure 39** : diversity in the filling of coal heaps: fine particles from the cleaning of coal, demolition wastes...

### 6.5.2 The coal heap burning phenomenon

This phenomenon has been documented throughout the world (Kruszewski, 2013; Fabiańska et al., 2013; Gentzis & Goodarzi, 1989; Dias et al., 2014). Indeed, burning coal heaps are typical features from coal-mining areas, e.g. the Silesian coal basin of Poland (Ciesielczuk, 2015; Fabiańska et al., 2013; Kruszewski, 2013), the North coal basin from France (Masalehdani et al., 2009), Czech republic (Žáček & Skála, 2015), Brazil (Dias et al., 2014) or the Tchelyabinsk coal basin in Russia (Sokol, 2005), within others. Even if the exact causes for ignition are not exactly known and may be the result of several phenomena such as lightning strikes or accidental causes (Misz-Kennan & Fabiańska, 2011; Nichol & Tovey, 1998), an active burning heap is a hazardous site (Figure 40) which deserves monitoring (Carpentier et al., 2005; Nyssen & Vermeersch, 2010). Catastrophic landslides and explosions have occurred in the past (Masalehdani & Paquette, 2013; Zio & Aven, 2013).

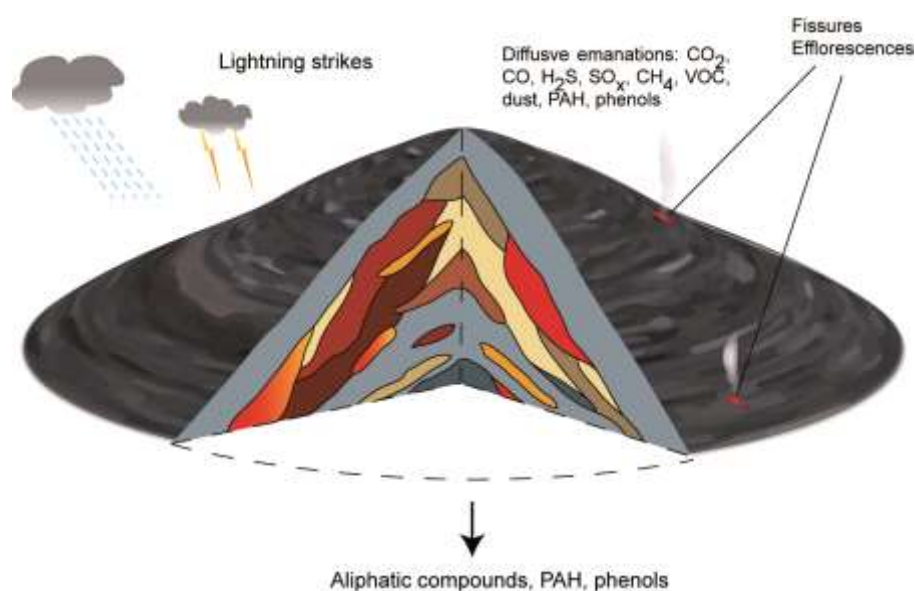


Figure 40 from Thiéry et al. (2013): synthetic cross-section through a burning coal heap

Complex petrographical and mineralogical transformations occur inside a burning heap ('anthropogenic pyrometamorphism', R. Grapes, 2011), due to an extreme heterogeneity of the material (shales, sandstones, coal dust, demolition wastes, rails from mining activities...) and also due to the fact that those phenomena occur at almost ambient pressure.

The extreme temperatures reached inside a burning heap results both in unmelted, annealed rocks termed "clinkers" (Grapes et al., 2011; Quintero et al., 2009) as well as partly to totally melted ones termed "paralavas" (Gawęda et al., 2013, 2011; Masalehdani et al., 2007).

## 6.6 The burning coal heap of La Ricamarie (work in progress)

### Complete references:

Thiéry, V., Guy, B., Kruszenski, Ł – *The burning coal heap of La Ricamarie chapter in prep. (due august 2017) for vol. 5 of the book series “Coal and Peat Fires: a Global Perspective”, edited by Stracher, Sokol & Prakash*

Guy, B., Thiéry, V., Garcia, D., Bascou, J., *Discovery of columnar structures in paralavas – la Ricamarie burning coal heap, Loire, France, in revision, International Journal of Coal Geology*

### 6.6.1 Geographical & geological context

The burning heap of la Ricamarie, so-called « Terril Saint-Pierre » (Saint-Pierre heap), is located within the Loire coal basin near the city of Saint-Étienne. This is the type-locality for the Stephanian age.

### 6.6.2 Historical coal fires in the Stephanian coal seams

It is worth mentioning the historical coal fires which have been described in the coal seams of the coal basin. They have strongly impressed the inhabitants and they were known for having burnt since “at least 300 years” (de Bournon, 1785). It is of interest to mention that some coal seams have been coined “*brûlante*” (burning) (Grüner, 1882). There is still nowadays in this city a place called “*le brûlé*” (the burnt).

The famous paralavas described worldwide associated with various coal fires (Sharygin et al., 2014; Grapes et al., 2009) have been termed likewise because of their similarities with natural lavas: they can be seen as an analogue. In the Loire coal basin, such analogies have been proposed since the first half of the 19<sup>th</sup> century (Girardin, 1831) in the following terms (direct translation from French): “*schistous clays [...] take the aspect of scoria almost similar to volcanic ones*”.

Porcellanites have also been described early in this basin (Jannettaz, 1874), but the most remarkable description of the effects of coal fires on associated rocks is due to the famous French mineralogist Jacques Louis de Bournon (1751-1825, in honour of whom the mineral bournonite has been named). In a seminal book (de Bournon, 1785) he describes thoroughly, although with an ancient vocabulary, a huge variety of baked shales, sandstones, argillites...

Several types of mineralogical efflorescence are thus known within this coal basin since more than 150 years (Table 8).





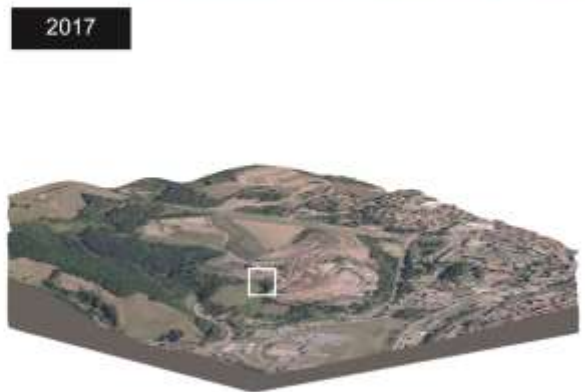


Figure 41: the evolution of the Ricamarie burning coal heap through time

Mineral	Formula	Reference
Native bismuth	Bi	(Daubrée, 1887) §40, p. 134
Epsomite	MgSO <sub>4</sub> · 7H <sub>2</sub> O	(Landrin, 1856) p. XLI
Salammoniac (ammonium chlorhydrate)	NH <sub>4</sub> Cl	(Drian, 1849), p.73 (ammonium chlorhydrate) Damour : contains also I and Br (Damour, 1884)
Vivianite	Fe <sub>3</sub> <sup>2+</sup> (PO <sub>4</sub> ) <sub>2</sub> · 8H <sub>2</sub> O	(Drian, 1849) (phosphated iron)

**Table 8 : historical descriptions of mineral efflorescences associated to coal seams fires in the Loire coal basin**

Stephanian coal basins are present in various places in France ; it has been demonstrated that their content has been deposited under high altitude (at least 4500 meters above sea level), mountainous conditions (Becq-Giraudon et al., 1996).

### 6.6.3 The Ricamarie heap – history

Since coal crops out in the Loire basin, its presence was probably noticed since immemorial times. Its exploitation is attested since at least the 13<sup>th</sup> century (Perrin, 1930). The mining activity has definitely ceased in 1983 but some remnants are still present such as coal heaps and mine shafts (one of them being a museum).

However, the present study documents a recent phenomenon which can be seen as recent in the history of the mining of the basin. It concerns a coal heap whose edification had begun in the 1940's.

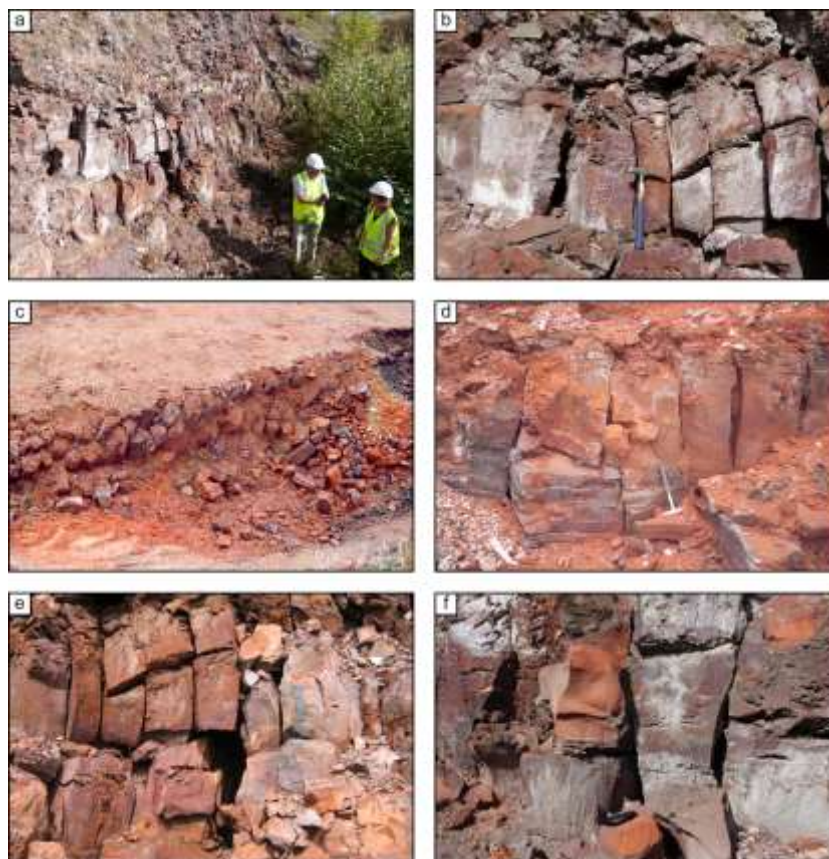
A survey based on aerial pictures from the French geographical institute (IGN, Institut Géographique National) allows a close monitoring of the successive steps of edification of the heap (Figure 41). In 1942, small (no more than 80 m in diameter) heaps were present very close to buildings in a wide, open-space area corresponding to a former quarry. From 1942 until 1967, screes marking the cutting face of the former quarry can be seen at the northern boundary between the fields and the future place of the heap.

From 1967 to 1989, although the dumping keeps on the heap, its definitive shape is more or less acquired. It looks from the above like an elongated peer of ca. 600 meters long by 300 meters wide.

During the 1990's, the quarrying operations have little by little revealed the interior of the heap. The exploitation has begun on the southwestern side. Nowadays, the entire heap is concerned by quarrying operations.

#### 6.6.4 Prismatic of paralavas – first worldwide occurrence?

At the core of the heap, the quarrying operations have revealed a “sill” of paralava within other clinker and related melted and/or annealed materials (Figure 42). This sill is approximately 20 meters long and 2 to 4 meters high. Its lower and lateral extensions within the heap are unknown.



**Figure 42 from Guy et al (in revision) :** (a) General view of the columnar “sill” from the burning heap. (b) Another general view of the columnar zone showing the part of the heap overlying the columns. This part is made of blocks sintered together because of burning and partial melting of the primary material. The length of the columns is about two to four meters. Condensate minerals are responsible for the white color on the surface of some of the rocks. (c) General view of the columnar zone seen from above, as revealed by digging of the heap. The polygonal sections of the columns can be seen. The diameter of the prisms is around 30 to 50 cm. The visible length of the columns is approximately 2 meters here. Picture taken in 2011. (d) Partial view of the base of the columns: paralavas are

found, showing horizontal layering (hammer gives the scale); this “layered” strata may show vertical fractures in continuity with the upper lying columns. The underlying part of the column is not visible at the moment. Picture taken in 2011. (e) Close-up view of the columnar structures. Some columns are interrupted by horizontal or nearly horizontal fractures that may make large voids appear. Some columns may also be separated from adjacent ones by vertical voids, see also Fig. 4f. (f) Close-up view of the columns. Some vertical voids may be seen between adjacent columns; the contours of one column may not fit with that of the neighboring one. The internal part of the columns is red, whereas the rim is grey-black. All pictures were taken in November 2014 unless specified.

The columnar structures are less regular than those that can be observed in some basaltic flows and are frequently fractured across their length. Their section is also irregular in shape but they typically display polygonal boundaries (the cross-sectional diameter of the prisms is about thirty to fifty centimeters). Some features are quite different from those typically found in basalt columns, such as the inward concavity of the column faces, the non-matching of adjacent columns and rock pustules found on the faces in the open spaces between the columns.

## 6.7 Summary

This chapter has presented highly contrasted materials, such as cement hydrates, coal heaps, and semi-anthropogenic phenomena on burning coal heaps.

This is not a hold all, although it may seem so. The discussion of ancient mud volcanoes flame eruptions has shed new light on the origin of unusual high temperature parageneses from the Hatrurim basin. Those cement-like rocks behave as anthropogenic cement; although the cement-like phases are less reactive (we must keep in mind that they are several millions years old).

In burning coal heaps, ultrahigh temperature affects a variety of rocks and waste, yielding interesting analogues of volcanic phenomena such as efflorescence and columnar structures.

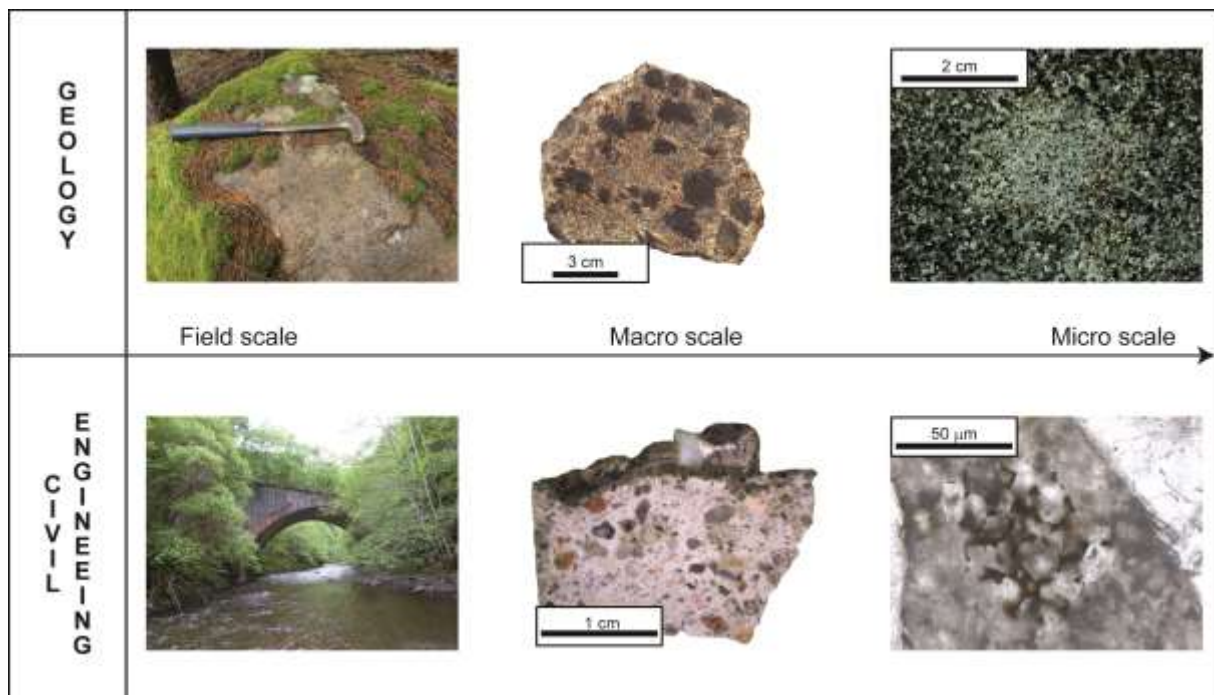
Minerals which are analogues of cement phases are also of great interest to understand microscopy and microanalysis of actual cement pastes. The specific case of ettringite has been presented based on the study of natural crystals. Beam damage seems to be different depending on the chemistry of ettringite.

## 7 CONCLUSIONS AND RESEARCH PERSPECTIVES

### 7.1 What have I done so far

Having discussed several points in a wide range of domains, it is now time to summarize the previous chapters.

Having switched from metamorphism to the durability of concrete buildings, the boundary between the 2 domains may seem impassable. However, in the present manuscript, both materials (rocks and concrete or civil engineering materials in the wide sense) have been considered with the same methodology: from the macro scale to the microscale (Figure 43).



**Figure 43** : from the field scale to the microscopic scale – similarity in the methodology of study for rocks and civil engineering materials

The present manuscript has summarized observations on various materials: ores, rocks, concrete; each material has also been studied at various scales and has revealed heterogeneous regarding its mineralogy, its microstructure...

**Some analogies between those materials** have been presented; some of them can even be puzzling. Who would have thought that nature makes cement?

## 7.2 Current work and perspectives

### 7.2.1 *Stabilization of antimony in cementitious phases*

Currently, I am working on a 2-years project dealing with the stabilization of antimony mining wastes using various binders. I have described in chapter 3.2.1 such mining wastes and leftovers from a geological and mineralogical point of view.

Some attempts of stabilization will be done likewise:

- Synthesis of Sb-AFm phase based on the reaction between pure  $C_3A$  and a S & Sb-bearing compound (Cornelis et al., 2012), using wastes from former mining sites as described earlier,
- Incorporation of various quantities of Sb-bearing wastes in the raw feed of the kiln (Kakali et al., 2003, 2005)

### 7.2.2 *Alkali-activation of mine tailings*

I have had the opportunity to go to Bulgaria and to visit several active mines in 2012: Elatsite (Cu-Au), Asarel (Cu-Mo) and Erma Reka (Pb-Zn) as well as a smelter near Plovdiv. Indeed, Bulgaria is a country in which mining is still active, since the Thracian times (Vassileva et al., 2009).

Mineral processing leads to a huge amount of tailings depositions (Figure 44). In the present case, they consist mainly of quartz and feldspar, i.e. they are rich in Si, Al, Na-Ca-K depending on the nature of the feldspar. Thus they are good candidates to make geopolymers (or alkali-activated materials); this kind of perspective for such materials has already been proposed (Komnitsas & Zaharaki, 2007); interesting results have been obtained on tungsten mine tailings (Pacheco-Torgal, J P Castro-Gomes, et al., 2008; Pacheco-Torgal, João Castro-Gomes, et al., 2008).



**Figure 44** : tailing from the Asarel mine in Bulgaria, july 2012.

### 7.2.3 *Diamond pollution in garnet during polishing: fact or fiction?*

I have presented in § 3.1.1 a case study of diamond inclusions in garnet, concerning which some doubt has arisen due to the possibility of diamond pollution during the sample preparation steps (sawing, polishing).

Even if the lapping and polishing mechanisms are extremely complex and still partly poorly understood (Schuelke & Grotjohn, 2013; Evans et al., 2003), polishing is a fundamental preparation method in materials science, especially when microanalysis is involved (Rémond et al., 2006; Newbury & Ritchie, 2015). Both flat, polished cross-sections and polished thin sections are routinely produced in laboratories dealing with geomaterials such as rocks, soils, concrete... (Kjellsen et al., 2003; Woodbury & Vogel, 1970; Camuti & McGuire, 1999; Marusin, 1995).

However, concerning specifically garnet and diamond polishing products, there is a constant doubt about the possibility that microdiamond may enter garnet during the preparation steps of coring, sawing and polishing (Nasdala et al., 2016; Perraki et al., 2009).

I am currently investigating garnet-quartz assemblages from the French Massif Central, namely centimetric garnet porphyroblasts which have already been well characterized (Gébelin et al., 2009). Based on samples impregnated under vacuum with fluorescent epoxy resin, a confocal laser scanning microscopy study may reveal that porosity is present only at quartz/garnet interfaces. Thus, in the case of diamond pollution by smushing of diamond-based abrasives (Nasdala et al., 2016), it can occur only at interfaces.

### 7.2.4 *Summary and perspectives about the devices used*

All along the present manuscript, most of the pictures correspond to hand sample photographs or to micrographs, either optical or electronic. This is not a surprise, I mainly work on a polarizing microscope (transmitted, reflected and UV light) as well as on a scanning electron microscope (SE, BSE and EDS).

It has not been presented here but I have also used (very basically and under supervision) TEM on burnt oil shale to investigate its microstructure and chemistry at the microscale (see the reprint at the end of the manuscript). Also, I often work on crushed samples to investigate their mineralogical composition by XRD (see also the reprint of the article about burnt oil shale).

I am currently training myself on confocal laser scanning microscopy (CLSM). This type of microscopy, of wide use in life science research (Pawley, 2006), has also some applications in geomaterials, such as for example the study of porosity in marbles (Mauko et al., 2009) or cement paste (Head & Buenfeld, 2006; Yio et al., 2015). Since I work on those two types of materials and that I need some information at the microscale, with 3D representation when possible, I have decided to learn how to use such a microscope.

For future research projects I would also like to develop skills on the aforementioned devices:

- Progress in quantitative estimation (or at least semi-quantitative) of the amount of phases in a sample by Rietveld analysis. I have already tried the Profex software (Doebelin & Kleeberg, 2015) but I need to improve my skills in crystallography to *really* understand what I do,

- Gain independence on TEM using various imaging modes depending on my needs on the studied sample.

### 7.2.5 *Perspectives in the study of mimetite*

Following the previous section, an interesting perspective of study of the fibrous mimetite (§ 3.2.2) lies in its study under the TEM. As a fibrous mineral, it falls within minerals of concern towards lung diseases (Osinubi et al., 2000). However, its scarcity (this fibrous variety of mimetite is the almost unique worldwide occurrence) does not imply that it may be particularly a dangerous one. However, it is worth characterizing it at this scale to understand the conditions which have led to this peculiar morphology. A good reference for this study would be the description of a fibrous variety of cuprite ( $\text{Cu}_2\text{O}$ ) under the TEM by Veblen & Post (Veblen & Post, 1983).

### 7.2.6 *A new occurrence of katoptrite $(\text{Mn}^{2+};\text{Mg})_{13}(\text{Al};\text{Fe}^{3+})_4\text{Sb}^{5+}_2\text{Si}_2\text{O}_{28}$*

Katoptrite is a rare mineral (Moore et al., 1976), known only in Långban type deposits, which are carbonate-hosted Fe-Mn-(Ba-Pb-As-Sb) deposits occurring within a supracrustal rock sequence dominated by felsic metavolcanics of Svecofennian (ca. 1,9 Ga) age. They are believed to be metamorphosed oceanic sedimentary exhalative deposits (Holtstam et al., 1998).

While studying some samples from a poorly characterized deposit of the Chavanon sequence (see § about my work in mapping), I have been puzzled by a strange EDS peak on an orange-red, acicular mineral with prominent cleavage perpendicular to the elongation. After a bit of research, I have identified this mineral as katoptrite.

The interest is that the deposit is unlikely a Långban type one, but most probably a Sb mineralization spatially associated to a dolerite intrusion. However, the metamorphic context of the Chavanon sequence, in which metacarbonates are present, may potentially reveal metamorphosed deposits. Currently, I am investigating the samples to describe their mineralogy, Raman spectra will be obtained on katoptrite since they have never been published.

### 7.2.7 *General geology, ore geology*

Even if this is not my main topic of research at the moment, I still have a strong interest on my former PhD field area. I have begun the writing of a book on the topic; which will popularize (or at least try to) my work and give a new sight on the area.

I am also very interested in mining geology and ore deposits; I also keep an eye on everything that can be done in areas that I know well.



### 7.3 General conclusion: “What can a hardrock geologist bring to a civil & environmental engineering laboratory in geomaterials characterization (and vice-versa)?”

#### 7.3.1 *Fundamental & applied thermometry*

Throughout the manuscript, microstructural studies on both natural and anthropogenic geomaterials have been carried out in order to understand the history of the material, either in a geological context (§ cordierite) or in an industrial device (§ ciment historique). In both cases, the presence of symptomatic phases and their textural relationships has allowed some geothermometric estimations.

Thus, a geological approach (geothermometry is a common tool in metamorphic petrology) can be applied to cementitious materials. More precisely, recent developments in thermodynamic modelling (Meyer et al., 2016) have many similitude with tools such as PERPLEX (Connolly & Petriani, 2002) which I have used during my PhD thesis.

#### 7.3.2 *Microscopy and microanalysis*

Contrarily to the cement paste of concrete, most rocks are coarse grained and microanalysis (EDS, WDS...) is not problematic in those cases – it’s not a problem to have an interaction zone of several cubic micrometers in a centimetric feldspar, whereas a cement paste, which is heterogeneous at the micrometric scale, one must keep in mind that several mineral/phases may be analysed simultaneously.

This is something that I have learned from my work on cementitious materials and I always keep this in mind when I analyze natural geomaterials – for example, as discussed in the § about katoptrite, I have been puzzled by the EDS spectra of this mineral and my first impression was that there was a matrix effect from the surrounding quartz, even if the size of the mineral was not coherent with an oversized electron/matter interaction zone. In the present case I must say that being part of a civil & environmental laboratory has greatly helped me to progress in this area of expertise.

#### 7.3.3 *Durability of construction and building materials as seen through natural analogues*

In the present case, in my opinion, both approaches have benefited from each other. Indeed, the mineralogy of cementitious materials is very specific. Before beginning my work on the topic of analogues, I was not aware that such mineralogy existed, either natural or industrial. So from this point of view, being engaged in this applied field of research has opened me the gates of ultra-high temperature mineralogy. But I have appropriated this field to my research through the eyes of a geologist and I have studied rocks as natural analogues, which are useful to understand their anthropogenic counterpart. So in the present case the two approaches are complimentary.

## REFERENCES

- ALEXANDER, M. & THOMAS, M. (2015). *Service life prediction and performance testing - Current developments and practical applications*.
- AMBROISE, J., GEORGIN, J. F., PEYSSON, S. & PÉRA, J. (2009). Influence of polyether polyol on the hydration and engineering properties of calcium sulfoaluminate cement. *Cement and Concrete Composites* **31**, 474–482.
- ANNEREL, E. & TAERWE, L. (2009). Revealing the temperature history in concrete after fire exposure by microscopic analysis. *Cement and Concrete Research* **39**, 1239–1249.
- ANTHONY, J. W., BIDEAUX, R. A., BLADH, K. W. & NICHOLS, M. C. (n.d.). *Handbook of Mineralogy*, Mineralogical Society of America, Chantilly, VA 20151-1110, USA. <http://www.handbookofmineralogy.org/>.
- ATABEK, R., BOUNIOL, P., VITORGE, P., LE BESCOP, P. & HOORELBEKE, J. M. M. (1992). Cement use for radioactive waste embedding and disposal purposes. *Cement and Concrete Research* **22**, 419–429.
- ATANASSOVA, R. & KERESTEDJIAN, T. (2009). Efflorescent minerals from the metallurgical waste heaps of the KCM non-ferrous metal smelter, Plovdiv, Bulgaria. *Geochemistry, Mineralogy and Petrology* **47**, 51–63.
- BAJDA, T. (2010). Solubility of mimetite  $Pb_5(AsO_4)_3Cl$  at 5–55°C. *Environmental Chemistry* **7**, 268–278.
- BAJDA, T., MOZGAWA, W., MANECKI, M. & FLIS, J. (2011). Vibrational spectroscopic study of mimetite-pyromorphite solid solutions. *Polyhedron* **30**, 2479–2485.
- BANNISTER, F. A., HEY, M. H. & BERNAL, J. (1936). Ettringite from Scawt Hill, Co. Antrim. *Mineralogical Magazine* **24**, 324–329.
- BARNETT, S. J., MACPHEE, D. E., LACHOWSKI, E. E. & CRAMMOND, N. J. (2002). XRD, EDX and IR analysis of solid solutions between thaumasite and ettringite. *Cement and Concrete Research* **32**, 719–730.
- BECC-GIRAUDON, J.-F., MONTENAT, C. & VAN DEN DRIESSCHE, J. (1996). Hercynian high-altitude phenomena in the French Massif Central: tectonic implications. *Palaeogeography, Palaeoclimatology, Palaeoecology* **122**, 227.
- BERGER, J. (2016). Discovery of metamorphic microdiamonds from the parautochthonous units of the Variscan French Massif Central: Comment. *Gondwana Research*.
- BETZ, V. (2005). Micromineral photography with multifocus processing. *The Mineralogical Record* **36**, 365–369.
- BITRI, A., TRUFFERT, C., BELLOT, J.-P., BOUCHOT, V., LEDRU, P., MILÉSI, J.-P. & ROIG, J.-Y. (1999). Imagerie des paléochamps hydrothermaux As-Au-Sb d'échelle crustale et des pièges associés dans la chaîne varisque: sismique réflexion verticale (GéoFrance3D: Massif central français). *Comptes Rendus de l'Académie des Sciences - Series IIA - Earth and Planetary Science* **329**, 771–777.
- BONACCORSI, E., MERLINO, S. & TAYLOR, H. F. W. (2004). The crystal structure of jennite,  $Ca_9Si_6O_{18}(OH)_6 \cdot 8H_2O$ . *Cement and Concrete Research* **34**, 1481–1488.
- BOUCHOT, V., LEDRU, P., LEROUGE, C., LESCUYER, J.-L. & MILESI, J. P. (2005). 5: Late Variscan mineralizing systems related to orogenic processes: the French Massif Central. *Ore Geology Reviews* **27**, 169–197.
- BOURDOT, A., THIÉRY, V., BULTEEL, D. & HAMMERSCHLAG, J. G. (2016). Effect of burnt oil shale on ASR expansions: A petrographic study of concretes based on reactive aggregates. *Construction and Building Materials* **112**, 556–569.
- DE BOURNON, J. L. (1785). *Essai sur la lithologie des environs de Saint-Etienne-En-Forez, et sur l'origine de ses charbons de pierre : Avec des observations sur les silex, pétro-silex, jaspes et granits*.
- BRGM (2007). *L'après-mine en France*.
- BROEKMANS, M. A. T. M. (2012). Deleterious Reactions of Aggregate With Alkalis in Concrete. *Reviews in Mineralogy and Geochemistry* **74**, 279–364.
- CAMUTI, K. S. & MCGUIRE, P. T. (1999). Preparation of polished thin sections from poorly consolidated regolith and sediment materials. *Sedimentary Geology* **128**, 171–178.
- CARPENTER, A. B. (1963). Oriented overgrowths of thaumasite on ettringite. *American Mineralogist* **48**, 1394–1396.
- CARPENTER, A. B., CHALMERS, R. A., GARD, J. A., SPEAKMAN, K. & TAYLOR, H. F. W. (1966). Jennite, a new mineral. *American Mineralogist* **51**, 56–74.
- CARPENTIER, O., DEFER, D., ANTCZAK, E. & DUTHOIT, B. (2005). The use of infrared thermographic and GPS topographic surveys to monitor spontaneous combustion of coal tips. *Applied Thermal Engineering* **25**, 2677–2686.
- CARROUÉ, J. P. (1964). *Les filons de stibine et de mispickel des Combrailles et de la partie orientale de la Marche. Description, étude géologique et métallogénique. Mémoire soutenu le 23 janvier 1964 devant la faculté de Clermont pour l'obtention du diplôme d'études supérieures*.
- CARTANNAZ, C. (2006). 'Magmatismes et déformations polyphasés : exemples des massifs de Guéret et de Millevaches (Massif Central Français). Origine des magmas et contexte de mise en place. Thèse, Université de Franche-Comté, Besançon'.
- CARTANNAZ, C., SONNET, R., ÉMONIN, Y., JUILLERAT, M., DEPRez, J., THIÉRY, V., MONTAZ, N., ROT, J. & BINETRUY, J. C. (2008). Carte géol. France (1/50 000), feuille Aubusson (667). Orléans : BRGM. Notice explicative par Cartannaz C., Rolin, P., Cocherie, A., Henry, P., Rossy M. (2008), 106p.
- LE CHATELIER, H. (1882). Recherches expérimentales sur la constitution des ciments et la théorie de leur prise. *Comptes Rendus Hebdomadaires de l'Académie des Sciences* **94**, 867–869.
- (1887). Recherches expérimentales sur la constitution des mortiers hydrauliques. *Annales des Mines Huitième S*, 345–465.
- CHATTERJI, S. & JEFFERY, J. W. (1966). Three-dimensional arrangement of hydration products in set cement paste. *Nature* **209**, 1233–1234.
- CHEN, I. A., HARGIS, C. W. & JUENGER, M. C. G. (2012). Understanding expansion in calcium sulfoaluminate-belite cements. *Cement and Concrete Research* **42**, 51–60.
- CHINNER, G. A. (1974). Memorial of Cecil Edgar Tilley May 14, 1894-January 24, 1973. *American Mineralogist* **59**, 427–437.
- CHOLLET, P. & DEVOUARD, B. (2013). La mine de cuivre et plomb des Rats, le Crozet (Loire). *Le règne minéral* **109**, 6–46.
- CHUKANOV, N. V., BRITVIN, S. N., VAN, K. V., MÖCKEL, S. & ZADOV, A. E. (2012). Kottenheimite,  $Ca_3Si(OH)_6(SO_4)_2 \cdot 12H_2O$ , a new member of the ettringite group from the Eifel area, Germany. *The Canadian Mineralogist* **50**, 55–63.
- CHUKANOV, N. V., KASATKIN, A. V., ZUBKOVA, N. V., BRITVIN, S. N., PAUTOV, L. A., PEKOV, I. V., VARLAMOV, D. A., BYCHKOVA, Y. V., LOSKUTOV, A. B. & NOVGORODOVA, E. A. (2015). Tatarinovite, IMA2015-055. CNMNC Newsletter No. 27, October 2015, page 1227. *Mineralogical Magazine* **79**, 1223–1230.
- CIESIELCZUK, J. (2015). Chapter 16 - Coal Mining and Combustion in the Coal Waste Dumps of Poland. In *Coal and Peat Fires: a Global Perspective*, Stracher, G. B., Sokol, E. & Prakash, A. (Eds.), pp. 463–473. Boston: Elsevier.
- COLLINS, C. L., IDEKER, J. H. & KURTIS, K. E. (2004). Laser scanning

- confocal microscopy for in situ monitoring of alkali-silica reaction. *Journal of Microscopy* **213**, 149–157.
- CONNOLLY, J. A. D. & PETRINI, K. (2002). An automated strategy for calculation of phase diagram sections and retrieval of rock properties as a function of physical conditions. *Journal of Metamorphic Geology* **23**, 771–991.
- CORNELIS, G., ETSCHMANN, B., VAN GERVEN, T. & VANDECASTEELE, C. (2012). Mechanisms and modelling of antimonate leaching in hydrated cement paste suspensions. *Cement and Concrete Research* **42**, 1307–1316.
- COSCA, M. A., ESSENE, E. J., GEISSMAN, J. W., SIMMONS, W. B. & COATES, D. A. (1989). Pyrometamorphic rocks associated with naturally burned coal beds, Powder River Basin, Wyoming. *American Mineralogist* **74**, 85–100.
- COSCA, M. A. & PEACOR, D. R. (1987). Chemistry and structure of esseneite (CaFe<sub>3</sub>+AlSiO<sub>6</sub>), a new pyroxene produced by pyrometamorphism. *American Mineralogist* **72**, 148–156.
- COURTIN-NOMADE, A., RAKOTOARISOA, O., BRIL, H., GRYBOS, M., FORESTIER, L., FOUCHER, F. & KUNZ, M. (2012). Weathering of Sb-rich mining and smelting residues: Insight in solid speciation and soil bacteria toxicity. *Chemie der Erde - Geochemistry* **72**, 29–39.
- COURTOIS, A., DUSAUSOY, Y., LAFFAILLE, A. & PROTAS, A. (1968). Étude préliminaire de la structure cristalline de l'ettringite. *Comptes rendus de l'académie des Sciences* **266**, 1911–1913.
- DAMOUR, A. (1884). Note sur un sel ammoniac iodifère. *Bulletin de la Société Minéralogique de France* **7**, 347–348.
- DARIZ, P., NEUBAUER, J., GOETZ-NEUNHOEFFER, F. & SCHMID, T. (2017). Calcium aluminates in clinker remnants as marker phases for various types of 19th-century cement studied by Raman microspectroscopy. *European Journal of Mineralogy* **28**, 907 LP-914.
- DAUBRÉE, A. (1887). *Les eaux souterraines à l'époque actuelle : leur régime, leur température, leur composition, au point de vue du rôle qui leur revient dans l'économie de l'écorce terrestre (tome 2)*.
- DE, I., CHANDA, B. & CHATTOPADHYAY, B. (2006). Enhancing effective depth-of-field by image fusion using mathematical morphology. *Image and Vision Computing* **24**, 1278–1287.
- DIAMOND, S. (1975). A review of alkali-silica reaction and expansion mechanisms 1. Alkalies in cements and in concrete pore solutions. *Cement and Concrete Research* **5**, 329–345.
- (1976). A review of alkali-silica reaction and expansion mechanisms. 2. Reactive aggregates. *Cement and Concrete Research* **6**, 549–560.
- DIAMOND, S. (1996). Delayed ettringite formation - Processes and problems. *Cement and Concrete Composites* **18**, 205–215.
- DIAS, C. L., OLIVEIRA, M. L. S., HOWER, J. C., TAFFAREL, S. R., KAUTZMANN, R. M. & SILVA, L. F. O. (2014). Nanominerals and ultrafine particles from coal fires from Santa Catarina, South Brazil. *International Journal of Coal Geology* **122**, 50–60.
- DOBRZHINETSKAYA, L. F. (2012). Microdiamonds — Frontier of ultrahigh-pressure metamorphism: A review. *Gondwana Research* **21**, 207–223.
- DOBRZHINETSKAYA, L., WIRTH, R. & GREEN, H. (2014). Diamonds in Earth's oldest zircons from Jack Hills conglomerate, Australia, are contamination. *Earth and Planetary Science Letters* **387**, 212–218.
- DOEBELIN, N. & KLEEBERG, R. (2015). Profex: A graphical user interface for the Rietveld refinement program BGMN. *Journal of Applied Crystallography* **48**, 1573–1580.
- DREBUSCHAK, V. A., SERVOTKIN, Y. V., KOKH, S. N. & SOKOL, E. V. (2013). Natural specimen of triple solid solution ettringite-thaumasite-chromate- ettringite. *Journal of Thermal Analysis and Calorimetry* **114**, 777–783.
- DRIAN, A. (1849). *Minéralogie et pétrologie des environs de Lyon disposées suivant l'ordre alphabétique*.
- DROUIN, D., RÉAL COUTURE, A., JOLY, D., TASTET, X., AIMEZ, V. & GAUVIN, R. (2007). CASINO V2.42—A Fast and Easy-to-use Modeling Tool for Scanning Electron Microscopy and Microanalysis Users. *Scanning* **29**, 92–101.
- DUÉE, C., BOURGEL, C., VÉRON, E., ALLIX, M., FAYON, F., BODÉMAN, F. & POIRIER, J. (2015). Phosphorus speciation in dicalcium silicate phases: Application to the basic oxygen furnace (BOF) slag. *Cement and Concrete Research* **73**, 207–214.
- DUNN, P. J., PEACOR, D. R., LEAVENS, P. B. & BAUM, J. L. (1983). Charlesite, a new mineral of the ettringite group, from Franklin, New Jersey. *American Mineralogist* **68**, 1033–1037.
- DYNI, J. R. (2005). *Geology and resources of some world oil-shale deposits*. U.S. Geological Survey Scientific Investigations Report 2005–5294.
- ELAQRA, H., GODIN, N., PEIX, G., R'MILI, M. & FANTOZZI, G. (2007). Damage evolution analysis in mortar, during compressive loading using acoustic emission and X-ray tomography: Effects of the sand/cement ratio. *Cement and Concrete Research* **37**, 703–713.
- ELSEN, J. (2006). Microscopy of historic mortars-a review. *Cement and Concrete Research* **36**, 1416–1424.
- EVANS, C. J., PAUL, E., DORNFIELD, D., LUCCA, D. A., BYRNE, G., TRICARD, M., KLOCKE, F., DAMBON, O. & MULLANY, B. A. (2003). Material Removal Mechanisms in Lapping and Polishing. *CIRP Annals - Manufacturing Technology* **52**, 611–633.
- FABIANSKA, M. J., CIESIELCZUK, J., KRUSZEWSKI, Ł., MISZ-KENNAN, M., BLAKE, D. R., STRACHER, G. & MOSZUMAŃSKA, I. (2013). Gaseous compounds and efflorescences generated in self-heating coal-waste dumps - A case study from the Upper and Lower Silesian Coal Basins (Poland). *International Journal of Coal Geology* **116–117**, 247–261.
- FAMY, C., SCRIVENER, K. L. & CRUMBIE, A. K. (2002). What causes differences of C-S-H gel grey levels in backscattered electron images? *Cement and Concrete Research* **32**, 1465–1471.
- FERNANDES, I., BROEKMANS, M. T. M. A. T. M. & NORONHA, F. (2009). Petrography and Geochemical Analysis for the Forensic Assessment of Concrete Damage. In *Criminal and Environmental Soil Forensics*, Ritz, K., Dawson, L. & Miller, D. (Eds.), pp. 163–180. Springer Netherlands.
- FIGUEIREDO, E., SILVA, R. J. C., ARAÚJO, M. F. & FERNANDES, F. M. B. (2013). Multifocus Optical Microscopy Applied to the Study of Archaeological Metals. *Microscopy and Microanalysis* **19**, 1248–1254.
- FLEISCHER, M. (1965). New mineral names. *American Mineralogist* **50**, 2096–2111.
- FLYNN, H. C., MEHARG, A. A., BOWYER, P. K. & PATON, G. I. (2003). Antimony bioavailability in mine soils. *Environmental Pollution* **124**, 93–100.
- FOOKES, P. G. (1991). Geomaterials. *Quarterly Journal of Engineering Geology and Hydrogeology* **24**, 3–15.
- FRENCH, W. J. (2005). Presidential address 2003: Why concrete cracks- geological factors in concrete failure. *Proceedings of the Geologists' Association* **116**, 89–105.
- FREZZOTTI, M. L., SELVERSTONE, J., SHARP, Z. D. & COMPAGNONI, R. (2011). Carbonate dissolution during subduction revealed by diamond-bearing rocks from the Alps. *Nature Geoscience* **3**, 703–706.
- GASCOYNE, M. (2002). Geological disposal of radioactive wastes and natural analogues. *Journal of Environmental Radioactivity* **61**, 241–243.
- GASTALDI, D., CANONICO, F. & BOCCALERI, E. (2009). Ettringite and calcium sulfoaluminate cement: Investigation of water content by near-infrared spectroscopy. *Journal of Materials Science* **44**, 5788–5794.
- GATEL, P., ŽÁČEK, V., KRUSZEWSKI, Ł., DEVOUARD, B., THIÉRY, V., EYTIER, C., EYTIER, J.-R., FAVREAU, G., VIGIER, J. & STRACHER,

- G. B. (2015). Combustion Mineralogy and Petrology of Oil-Shale Slags in Lapanouse, Sévérac-le-Château, Aveyron, France: Analogies with Hydrocarbon Fires. In *Coal and Peat Fires: a Global Perspective*, Stracher, G. B., Sokol, E. & Prakash, A. (Eds.), pp. 681–742. Boston: Elsevier.
- GAUDEFEY, C. & PERMINGEAT, F. (1965). La jouravskite, une nouvelle espèce minérale. *Bulletin de la Société Française de Minéralogie* **88**, 254–262.
- GAUVIN, R. (2005). X-ray microanalysis of real materials using Monte Carlo simulations. In *Surface and Interface Analysis* vol. 37, pp. 875–886.
- GAWĘDA, A., JANECZEK, J., KIEREPKA, M., KĄDZIOŁKO-GAWĘŁ, M. & KRZYKAWSKI, T. (2013). Indialite-rich paralava from a coalmine waste-dump, Sosnowiec, Poland. *Neues Jahrbuch für Mineralogie - Abhandlungen: Journal of Mineralogy and Geochemistry* **190**, 237–251.
- GAWĘDA, A., KIEREPKA, M., JANECZEK, J. & MAZUR-CUBER, A. (2011). Paralava from coal-dump combustion in Upper Silesia, Poland: melt separation leaving a cordierite-rich restite. In *10th International Congress for Applied Mineralogy*, pp. 221–227. Trondheim.
- GÉBELIN, A., ROGER, F. & BRUNEL, M. (2009). Syntectonic crustal melting and high-grade metamorphism in a transpressional regime, Variscan Massif Central, France. *Tectonophysics* **477**, 229–243.
- GENTZIS, T. & GOODARZI, F. (1989). Organic petrology of a self-burning coal wastepile from Coleman, Alberta, Canada. *International Journal of Coal Geology* **11**, 257–271.
- GHATAORA, G. S. & JARVIS, S. T. (1996). Use of colliery spoil for infilling mine workings. *Waste Management* **16**, 189–193.
- GHOUZI, D. (1982). The case of the French Nord/Pas-de-Calais coalfield. *Minerals and the Environment* **4**, 67–74.
- GIRARDIN, J. (1831). *Considérations générales sur les volcans, et examen critique des diverses théories qui ont été successivement proposées pour expliquer les phénomènes volcaniques*.
- GOETZ-NEUNHOEFFER, F. & NEUBAUER, J. (2006). Refined ettringite (Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)12·26H<sub>2</sub>O) structure for quantitative X-ray diffraction analysis. *Powder Diffraction* **21**, 4–11.
- GOSSELIN, C. & PINTÉR, F. (2016). Examples of early age Portland cements applied in historical masonries. In *4th Historical Mortars Conference*, pp. 211–219.
- GOUGAR, M. L. D., SCHEETZ, B. E. & ROY, D. M. (1996). Ettringite and C-S-H portland cement phases for waste ion immobilization: A review. *Waste Management* **16**, 295–303.
- GRANGEON, S., CLARET, F., LINARD, Y. & CHIABERGE, C. (2013). X-ray diffraction: A powerful tool to probe and understand the structure of nanocrystalline calcium silicate hydrates. *Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials* **69**, 465–473.
- GRANGEON, S., CLARET, F., ROOSZ, C., SATO, T., GABOREAU, S. & LINARD, Y. (2016). Structure of nanocrystalline calcium silicate hydrates: Insights from X-ray diffraction, synchrotron X-ray absorption and nuclear magnetic resonance. *Journal of Applied Crystallography* **49**, 771–783.
- GRAPES, R. (2011). *Pyrometamorphism*.
- GRAPES, R. (2011). Anthropogenic Pyrometamorphism. In *Pyrometamorphism*, pp. 235–288. Springer.
- GRAPES, R., KORZHOVA, S., SOKOL, E. & SERYOTKIN, Y. (2011). Paragenesis of unusual Fe-cordierite (sekaninaite)-bearing paralava and clinker from the Kuznetsk coal basin, Siberia, Russia. *Contributions to Mineralogy and Petrology* **162**, 253–273.
- GRAPES, R., ZHANG, K. & PENG, Z. LUN (2009). Paralava and clinker products of coal combustion, Yellow River, Shanxi Province, China. *Lithos* **113**, 831–843.
- GREEN, D. I. (2005). Digital combination photography: a technique for producing improved images of microscopic minerals. *Australian Journal of Mineralogy* **11**, 13–24.
- GREGEROVÁ, M. & VŠIANSKÝ, D. (2009). Identification of concrete deteriorating minerals by polarizing and scanning electron microscopy. *Materials Characterization* **60**, 680–685.
- GROSS, S. (1977). The mineralogy of the Hatrurim Formation, Israel. *Geological Survey of Israel Bulletin* **70**, 1–80.
- (1980). Bentorite. A new mineral from the Hatrurim area, west of the Dead Sea, Israel. *Israel Journal of Earth Sciences* **29**, 81–84.
- GROVES, G. W. (1981). Portland cement clinker viewed by transmission electron microscopy. *Journal of Materials Science* **16**, 1063–1070.
- GRÜNER, L. (1882). *Bassin houiller de la Loire. Première partie, Description générale du bassin*.
- GUTZMER, J. & BEUKES, N. J. (1996). Mineral paragenesis of the Kalahari manganese field, South Africa. *Ore Geology Reviews* **11**, 405–428.
- GUY, R., PIERRE, R., LUDOVIC, G., ROSSI, P., RAOUL, G. & GAVOIS, L. (2008). Utilisation des sous-produits industriels: Schistes houillers. *Techniques de l'ingénieur Génie civil - Terrassement et remblaiement base docum*.
- HALL, R. B. (1988). Hardrock versus softrock geology. In *Encyclopedia of Earth Science*, p. 331.
- HEAD, M. K. & BUENFELD, N. R. (2006). Confocal imaging of porosity in hardened concrete. *Cement and Concrete Research* **36**, 896–911.
- HEAD, M. K., WONG, H. S. & BUENFELD, N. R. (2006). Characterisation of 'Hadley' grains by confocal microscopy. *Cement and Concrete Research* **36**, 1483–1489.
- HEDDLE, M. F. (1880). Preliminary Notice of Substances Which May Prove to Be New Minerals. *Mineralogical Magazine* **4**, 117–123.
- HEFFERN, H. L., REINERS, P. W., NAESER, C. W. & COATES, D. A. (2007). Geochronology of clinker and implications for evolution of the Powder River Basin landscape, Wyoming and Montana. *Reviews in Engineering Geology* **18**, 155–175.
- HENCKENS, M. L. C. M., DRIESSEN, P. P. J. & WORRELL, E. (2016). How can we adapt to geological scarcity of antimony? Investigation of antimony's substitutability and of other measures to achieve a sustainable use. *Resources, Conservation and Recycling* **108**, 54–62.
- HENTSCHEL, G. (1964). Mayenit, 12CaO.7Al<sub>2</sub>O<sub>3</sub>, und Brownmillerit, 2CaO.(Al,Fe)2O<sub>3</sub>, zwei neue Minerale in den Kalksteineinschlüssen der Lava des Ettringer Bellerberges. *Neues Jahrbuch für Mineralogie Monatshefte* **1**, 22–29.
- HEYNEN, J. J. M., BOLK, H. N. J. A., SENDEN, G. J., TUMMERS, P. J. & J.J.J.M. GOUMANS, H. A. VAN DER S. AND T. G. A. (1994). Re-use of colliery spoils in construction materials using Fluidized Bed Combustion. In *Studies in Environmental Science* vol. 60, pp. 655–664. Elsevier.
- HOLTSTAM, D., NYSTEN, P. & GATEDAL, K. (1998). Parageneses and Compositional Variations of Sb Oxyminerals from Långban-type Deposits in Värmland, Sweden. *Mineralogical Magazine* **62**, 395–407.
- HUMPHRIES, D. W. (1992). *The preparation of thin sections of rocks, minerals, and ceramics*. Oxford University Press.
- IDORN, G. M. (2005). Innovation in concrete research - review and perspective. *Cement and Concrete Research* **35**, 3–10.
- INGHAM, J. P. (2009). Application of petrographic examination techniques to the assessment of fire-damaged concrete and masonry structures. *Materials Characterization* **60**, 700–709.
- INGHAM, J. P. (2011). *Geomaterials under the microscope*. Manson Publishing.

- JANA, D. (2005). Concrete petrography - Past, present and future. In *10th Euroseminar on Microscopy Applied to Building Materials*.
- (2006). Sample preparation techniques in petrographic examinations of construction materials: A state-of-the-art review. In *Proceeding of the 28th Conference on Cement Microscopy*, pp. 23–70.
- JANNETTAZ, E. (1874). *Les roches : description de leurs éléments : méthode de détermination : guide pratique à l'usage des ingénieurs, géologues, minéralogistes, agronomes, des élèves des écoles du gouvernement*.
- JOHNSON, C. A. & SCHWEIZER, C. (1998). Weathering processes in municipal solid waste incinerator bottom ash deposits. *Mineralogical Magazine* **62A**, 723–724.
- KADIROV, F. A & MUKHTAROV, A S. (2004). Geophysical fields, deep structure, and dynamics of the Lokbatan mud volcano. *Izvestiya Physics of the Solid Earth* **40**, 327–333.
- KAKALI, G., TSIVILIS, S., KOLOVOS, K., CHOUPA, K., PERRAKI, T., PERRAKI, M., STAMATAKIS, M. & VASILATOS (2003). Use of secondary mineralizing raw materials in cement production. The case study of a stibnite ore. *Materials Letters* **57**, 3117–3123.
- KAKALI, G., TSIVILIS, S., KOLOVOS, K., VOGLIS, N., AIVALIOTIS, J., PERRAKI, T., PASSIALAKOU, E. & STAMATAKIS, M. (2005). Use of secondary mineralizing raw materials in cement production. A case study of a wolframite–stibnite ore. *Cement and Concrete Composites* **27**, 155–161.
- KAMPF, A., MILLS, S. & PINCH, W. (2011). Plumboselite, Pb<sub>3</sub>O<sub>2</sub>(SeO<sub>3</sub>), a new oxidation-zone mineral from Tsumeb, Namibia. *Mineralogy and Petrology* **101**, 75–80.
- KELSEY, D. E. (2008). On ultrahigh-temperature crustal metamorphism. *Gondwana Research* **13**, 1–29.
- KETCHAM, R. A. & CARLSON, W. D. (2001). Acquisition, optimization and interpretation of X-ray computed tomographic imagery: applications to the geosciences. *Computers & Geosciences* **27**, 381–400.
- KJELSEN, K. O., MONSØY, A., ISACHSEN, K. & DETWILER, R. J. (2003). Preparation of flat-polished specimens for SEM-backscattered electron imaging and X-ray microanalysis- importance of epoxy impregnation. *Cement and Concrete Research* **33**, 611–616.
- KLESZCZEWSKA-ZEĘBALA, A., MANECKI, M., BAJDA, T., RAKOVAN, J. & BORKIEWICZ, O. J. (2016). Mimetite Formation from Goethite-Adsorbed Ions. *Microscopy and Microanalysis* **22**.
- KOLODNY, Y. (1979). Natural cement factory: a geological story. In *Cement Production and Use*, J. Skalny (Ed.), pp. 203–216.
- KOMNITSAS, K. & ZAHARAKI, D. (2007). Geopolymerisation: A review and prospects for the minerals industry. *Minerals Engineering* **20**, 1261–1277.
- KRUSZEWSKI, Ł. (2013). Supergene sulphate minerals from the burning coal mining dumps in the Upper Silesian Coal Basin, South Poland. *International Journal of Coal Geology* **105**, 91–109.
- KURTZ, J.-P. (2004). *Dictionary of Civil Engineering - English-French*. Springer.
- LACROIX, A. (1915). La silice fondue considérée comme minéral (lechatérierite). *Bulletin de la Société Française de Minéralogie* **38**, 182–186.
- LALINSKÁ-VOLEKOVÁ, B., MAJZLAN, J., KLIMKO, T., CHOVAN, M., KUČEROVÁ, G., MICHŇOVÁ, J., HOVORIČ, R., GÖTTLICHER, J. & STEININGER, R. (2012). Mineralogy of weathering products of Fe-As-Sb mine wastes and soils at several Sb deposits in Slovakia. *The Canadian Mineralogist* **50**, 481–500.
- LANDRIN, H. (1856). *Dictionnaire de minéralogie, de géologie et de métallurgie*.
- LARSEN, E. S. & DUNHAM, K. C. (1933). Tilleyite, a new mineral from the contact zone at Crestmore, California. *American Mineralogist* **18**, 469–473.
- LEHMANN, J. (1874). Über den ettringit, ein neues mineral, in Kalkeinschlüssen der Lava von Ettringen (Laacher Gebiet). *Neues Jahrbuch für Mineralogie, Geologie und Paläontologie* **273–275**.
- LESLIE, A. B. & HUGHES, J. J. (2004). High-temperature slag formation in historic Scottish mortars: Evidence for production dynamics in 18th-19th century lime production from Charlestown. In *Materials Characterization* vol. 53, pp. 181–186.
- LIMACHER, D. (1963). A propos de la formation de minéraux secondaires lors de la combustion des charbons. *Annales de la Société Géologique du Nord* **83**, 287–288.
- LINDGÅRD, J., ANDIÇ-ÇAKIR, Ö., FERNANDES, I., RØNNING, T. F. & THOMAS, M. D. A. (2012). Alkali-silica reactions (ASR): Literature review on parameters influencing laboratory performance testing. *Cement and Concrete Research* **42**, 223–243.
- LLOYD, G. E. (1987). Atomic number and crystallographic contrast images with the SEM: a review of backscattered electron techniques. *Mineralogical Magazine* **51**, 3–19.
- MACPHEE, D. E. & BARNETT, S. J. (2004). Solution properties of solids in the ettringite–thaumasite solid solution series. *Cement and Concrete Research* **34**, 1591–1598.
- MALINKO, S. V., CHUKANOV, N. V., DUBINCHUK, V. T., ZADOV, A. E. & KOPORULINA, E. V. (2001). Buryatite Ca<sub>3</sub>(Si, Fe<sup>3+</sup>, Al)[SO<sub>4</sub>][B(OH)<sub>4</sub>](OH)5O·12H<sub>2</sub>O, a new mineral. *Zapiski Vserossijskogo Mineralogicheskogo Obshchestva* **130**, 72–78.
- MARIGNAC, C. & CUNEY, M. (1999). Ore deposits of the French Massif Central : insight into the metallogenesis of the Variscan collision belt. *Mineralium Deposita* **34**, 472–504.
- MARUSIN, S. L. (1995). Sample preparation - the key to SEM studies of failed concrete. *Cement and Concrete Composites* **17**, 311–318.
- MASALEHDANI, M. N. N., BLACK, P. M. & KOBE, H. W. (2007). Mineralogy and petrography of iron-rich slags and paralavas formed by spontaneous coal combustion, Rotowaro coalfield, North Island, New Zealand. *Reviews in Engineering Geology* **28**, 117–131.
- MASALEHDANI, M. N. N., MEES, F., DUBOIS, M., COQUINOT, Y., POTDEVIN, J.-L., FIALIN, M. & BLANC-VALLERON, M.-M. (2009). Condensate minerals from a burning coal-waste heap in Avion, Northern France. *The Canadian Mineralogist* **47**, 573–591.
- MASALEHDANI, M. N. N. & PAQUETTE, Y. (2013). Chapter 8 - Coal Fires of Northern and Massif Central, France. In *Coal and Peat Fires: A Global Perspective*, pp. 121–136. Boston: Elsevier.
- MASSONNE, H. J., BERNHARDT, H.-J., DETTMAR, D., KESSLER, E., MEDENBACH, O. & WESTPHAL, T. (1998). Simple identification and quantification of microdiamonds in rock thin-sections. *European Journal of Mineralogy* **10**, 497–504.
- MATSCHKEI, T., LOTHENBACH, B. & GLASSER, F. P. (2007). The AFm phase in Portland cement. *Cement and Concrete Research* **37**, 118–130.
- MAUKO, A., MUCK, T., MIRTIC, B., MLADENOVIC, A. & KREFT, M. (2009). Use of confocal laser scanning microscopy (CLSM) for the characterization of porosity in marble. *Materials Characterization* **60**, 603–609.
- MCDONALD, A. M., PETERSON, O. V., GAULT, R. A., JOHNSEN, O., NIEDERMAYR, G., BRANDSTÄTTER, F. & GIESTER, G. (2001). Micheelsenite, (Ca,Y)3Al(PO3OH,CO3)(CO3)(OH)6·12H<sub>2</sub>O, a new mineral from Mont Saint-Hilaire, Quebec, Canada and the Nanna pegmatite, Narsaarsuup Qaava, South Greenland. *Neues Jahrbuch Fur Mineralogie-Monatshefte* **337–351**.
- MEHTA, P. K. (1986). *Concrete: structure, properties and materials*.
- MENÉNDEZ, E., MATSCHKEI, T. & GLASSER, F. (2013). Sulfate Attack of Concrete. In *Performance of Cement-Based Materials in*

- Aggressive Aqueous Environments* vol. 10, Alexander, M., Bertron, A. & De Belie, N. (Eds.), pp. 7–74. Springer Netherlands.
- MENNEKEN, M., NEMCHIN, A. A., GEISLER, T., PIDGEON, R. T. & WILDE, S. A. (2007). Hadean diamonds in zircon from Jack Hills, Western Australia. *Nature* **448**, 917–20.
- MERLINO, S. & ORLANDI, P. (2001). Carraraite and zaccagnaite, two new minerals from the Carrara marble quarries: their chemical compositions, physical properties, and structural features. *American Mineralogist* **86**, 1293–1301.
- MEYER, V., PISCH, A., PENTTILÄ, K. & KOUKKARI, P. (2016). Computation of steady state thermochemistry in rotary kilns: Application to the cement clinker manufacturing process. *Chemical Engineering Research and Design* **115**, 335–347.
- MIELENZ, R. C. (1962). Petrography applied to Portland-cement concrete. *Reviews in Engineering Geology* **1**, 1–38.
- MIŁODOWSKI, A. E., NANCARROW, P. H. A. & SPIRO, B. (1989). A mineralogical and stable isotope study of natural analogues of Ordinary Portland Cement (OPC) and CaO-SiO<sub>2</sub>-H<sub>2</sub>O (CSH) compounds. *United Kingdom Nirex Safety Studies Report, NSS/R240*.
- MIŁODOWSKI, A. E., ROCHELLE, C. A., LACINSKA, A. & WAGNER, D. (2011). A natural analogue study of CO<sub>2</sub>-cement interaction: Carbonation of calcium silicate hydrate-bearing rocks from Northern Ireland. *Energy Procedia* **4**, 5235–5242.
- MIRWALD, P. (1986). Ist cordierit ein geothermometer? *Fortschritte der Mineralogie* **64**, 119.
- MISZ-KENNAN, M. & FABIĄŃSKA, M. J. (2011). Application of organic petrology and geochemistry to coal waste studies. *International Journal of Coal Geology* **88**, 1–23.
- MOMMA, K. & IZUMI, F. (2011). VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography* **44**, 1272–1276.
- MOORE, A. & TAYLOR, H. F. W. (1968). Crystal structure of ettringite. *Nature* **218**, 1048–1049.
- MOORE, P. B., ARAKI, T. & BRUNTON, G. D. (1976). Moore P B, Araki T, Brunton Catoprite, (Mn<sub>52</sub>+Sb<sub>25</sub>+VI(Mn<sub>82</sub>+Al<sub>4</sub>Si<sub>2</sub>))IVO<sub>28</sub>, a novel close-packed oxide sheet structure. *Neues Jahrbuch für Mineralogie, Abhandlungen* **127**, 47–61.
- MÖSCHNER, G., LOTHENBACH, B., WINNEFELD, F., ULRICH, A., FIGI, R. & KRETZSCHMAR, R. (2009). Solid solution between Al-ettringite and Fe-ettringite (Ca<sub>6</sub>[Al<sub>1-x</sub>Fe<sub>x</sub>(OH)<sub>6</sub>](SO<sub>4</sub>)<sub>3</sub>·26H<sub>2</sub>O). *Cement and Concrete Research* **39**, 482–489.
- MUKHOPADHYAY, A. (2011). Next-Generation Nano-based Concrete Construction Products: A Review. In *Nanotechnology in Civil Infrastructure SE - 7*, Gopalakrishnan, K., Birgisson, B., Taylor, P. & Attoh-Okine, N. (Eds.), pp. 207–223. Springer Berlin Heidelberg.
- MUKHTAROV, A. S., KADIROV, F. A., GULIYEV, I. S., FEYZULLAYEV, A. & LERCHE, I. (2003). Temperature Evolution in the Lokbatan Mud Volcano Crater (Azerbaijan) after the Eruption of 25 October 2001. *Energy, Exploration & Exploitation* **21**, 187–207.
- MULTANI, R. S., FELDMANN, T. & DEMOPOULOS, G. P. (2016). Antimony in the metallurgical industry: A review of its chemistry and environmental stabilization options. *Hydrometallurgy* **164**, 141–153.
- NASDALA, L. & PEKOV, I. V. (1993). Ravatite, C<sub>14</sub>H<sub>10</sub>, a new organic mineral species from Ravat, Tazhikistan. *European Journal of Mineralogy* **5**, 699–705.
- NASDALA, L., STEGER, S. & REISSNER, C. (2016). Raman study of diamond-based abrasives, and possible artefacts in detecting UHP microdiamond. *Lithos*.
- NEWBURY, D. E. & RITCHIE, D. W. M. (2015). Performing elemental microanalysis with high accuracy and high precision by scanning electron microscopy/silicon drift detector energy-dispersive X-ray spectrometry (SEM/SDD-EDS). *Journal of Materials Science* **50**, 493–518.
- NICHOL, D. & TOVEY, N. P. (1998). Remediation and monitoring of a burning coal refuse bank affecting the Southsea Looproad at Brymbo, North Wales. *Engineering Geology* **50**, 309–318.
- NICKEL, E. H. (1995). The definition of a mineral. *The Canadian Mineralogist* **33**, 689–690.
- NICKEL, E. H. (1995). Mineral names applied to synthetic substances. *The Canadian Mineralogist* **33**, 1335.
- NIEDERÖST, M., NIEDERÖST, J. & SCUCKA, J. (2003). Shape From Focus: Fully Automated 3D Reconstruction and Visualization of Microscopic Objects. In *Proceedings of 6th International Conference on Optical 3-D Measurement Techniques*, pp. 4–11. Zurich, Switzerland.
- NIETO K.J.T. OBERTI, R., F. L. (ed.) (2013). *Minerals at the Nanoscale*. Mineralogical Society of Great Britain and Ireland.
- NISHIO-HAMANE, D., OHNISHI, M., MOMMA, K., SHIMOBAYASHI, N., MIYAWAKI, R., MINAKAWA, T. & INABA, S. (2015). Imayoshiite, Ca<sub>3</sub>Al(CO<sub>3</sub>)[B(OH)<sub>4</sub>](OH)<sub>6</sub>·12H<sub>2</sub>O, a new mineral of the ettringite group from Ise City, Mie Prefecture, Japan. *Mineralogical Magazine* **79**, 413–423.
- NYSSSEN, J. & VERMEERSCH, D. (2010). Slope aspect affects geomorphic dynamics of coal mining spoil heaps in Belgium. *Geomorphology* **123**, 109–121.
- OGASAWARA, Y. (2005). Microdiamonds in Ultrahigh-Pressure Metamorphic Rocks. *ELEMENTS* **1**, 91–96.
- OSINUBI, O. Y. O., GOCHFELD, M. & KIPEN, H. M. (2000). Health effects of asbestos and nonasbestos fibers. *Environmental Health Perspectives* **108**, 665–674.
- PACHECO-TORGAL, F., CASTRO-GOMES, J. & JALALI, S. (2008). Properties of tungsten mine waste geopolymeric binder. *Construction and Building Materials* **22**, 1201–1211.
- PACHECO-TORGAL, F., CASTRO-GOMES, J. P. & JALALI, S. (2008). Investigations of tungsten mine waste geopolymeric binder: Strength and microstructure. *Construction and Building Materials* **22**, 2212–2219.
- PASERO, M., KAMPF, A. R., FERRARIS, C., PEKOV, I. V., RAKOVAN, J. & WHITE, T. J. (2010). Nomenclature of the apatite supergroup minerals. *European Journal of Mineralogy* **22**, 163–179.
- PAWLEY, J. B. (2006). *Handbook Of Biological Confocal Microscopy*. Pawley, J. B. (Ed.). Springer.
- PEACOR, D. R., DUNN, P. J. & DUGGAN, M. (1983). Sturmanite, a ferric iron, boron analogue of ettringite. *The Canadian Mineralogist* **21**, 705–709.
- PEKOV, I. V., CHUKANOV, N. V., BRITVIN, S. N., KABALOV, Y. K., GÖTTLICHER, J., YAPASKURT, V. O., ZADOV, A. E., KRIVOVICHEV, S. V., SCHÜLLER, W. & TERNES, B. (2012). The sulfite anion in ettringite-group minerals: a new mineral species hielscherite, Ca<sub>3</sub>Si(OH)<sub>6</sub>(SO<sub>4</sub>)(SO<sub>3</sub>)·11H<sub>2</sub>O, and the thaumasite-hielscherite solid-solution series. *Mineralogical Magazine* **76**, 1133–1152.
- PERRAKI, M., KORSKOV, A. V., SMITH, D. C. & MPOSKOS, E. (2009). Raman spectroscopic and microscopic criteria for the distinction of microdiamonds in ultrahigh-pressure metamorphic rocks from diamonds in sample preparation materials. *American Mineralogist* **94**, 546–556.
- PERRIN, M. (1930). Le bassin houiller de la Loire. *Annales de Géographie* **39**, 359–375.
- PETERS, H. (1987). Exploitation of oil shale at Rohrbach cement plant. *World Cement* **18**, 320–322.
- PETFORD, N. & MILLER, J. A. (1990). SLM confocal microscopy: an improved way of viewing fission tracks. *Journal of the Geological Society* **147**, 217–218.
- PETFORD, N., MILLER, J. A. & RANKIN, A. H. (1995). Preliminary confocal scanning laser microscopy study of fluid inclusions in quartz. *Journal of Microscopy* **178**, 37–41.

- PLANKE, S., SVENSEN, H., HOVLAND, M., BANKS, D. A. & JAMTVEIT, B. (2003). Mud and fluid migration in active mud volcanoes in Azerbaijan. *Geo-Marine Letters* **23**, 258–268.
- DU PLESSIS, A., OLAWUYI, B., BOSHOFF, W. & LE ROUX, S. (2014). Simple and fast porosity analysis of concrete using X-ray computed tomography. *Materials and Structures* 1–10.
- POHWAT, P. W. (2012). Ettringite, N'Chwaning II Mine, Northern Cape Province, Republic of South Africa. *Rocks & Minerals* **87**, 430–435.
- PÖLLMANN, H. (2012). Calcium Aluminate Cements - Raw Materials, Differences, Hydration and Properties. *Reviews in Mineralogy and Geochemistry* **74**, 1–82.
- QUINTERO, J. A., CANDELA, S. A., RÍOS, C. A., MONTES, C. & URIBE, C. (2009). Spontaneous combustion of the Upper Paleocene Cerrejón Formation coal and generation of clinker in La Guajira Peninsula (Caribbean Region of Colombia). *International Journal of Coal Geology* **80**, 196–210.
- RAINBOW, A. K. M. (1987). Minestone and burnt minestone. *Ground Engineering* 9–13.
- RAOUL, G., ROSSI, P. & GAVOIS, L. (2008). Utilisation des sous-produits industriels Schistes houillers : chantier de Dourges. *Techniques de l'ingénieur Génie civil - Terrassement et remblaiement base docum.*
- RAYMENT, D. L. (1986). The electron microprobe analysis of the CSH phases in a 136 year old cement paste. *Cement and Concrete Research* **16**, 341–344.
- REIMER, L. (1998). *Scanning Electron Microscopy Physics of Image Formation and Microanalysis*. Springer.
- RÉMOND, G., NOCKOLDS, C., PHILLIPS, M. & ROQUES-CARMES, C. (2006). Implications of polishing techniques in quantitative X-ray microanalysis. *Journal of research of the National Institute of Standards and Technology* **107**, 639–662.
- RICHARDSON, I. G. (2000). The nature of the hydration products in hardened cement pastes. *Cement and Concrete Composites* **22**, 97–113.
- (2008). The calcium silicate hydrates. *Cement and Concrete Research* **38**, 137–158.
- RICHARDSON, I. G. & GROVES, G. W. (1993). Microstructure and microanalysis of hardened ordinary Portland cement pastes. *Journal of Materials Science* **28**, 265–277.
- RIEDHAMMER, M. (1985). The Rohrbach Process - the economical Alternative Method of Utilizing Oil Shale. *TIZ-Fachberichte* **109**, 941–944.
- ROCHELLE, C. A. & MIŁODOWSKI, A. E. (2013). Carbonation of borehole seals: Comparing evidence from short-term laboratory experiments and long-term natural analogues. *Applied Geochemistry* **30**, 161–177.
- ROLIN, P., THIÉRY, V., DUMONT, N., CHOLET, F. & MAVEL, J. (2008). *Carte géol. France (1/50.000), feuille de FELLETTIN (n°691). Orléans : BRGM. 157 p. Notice explicative par Rolin, P., Thiéry V., Cartannaz C., Cocherie, A., Rossy, M., Henry, P., Constant, J (2008).*
- RUNGUPHAN, T. & GUTHRIE, P. M. (2009). Investigation on the use of burnt colliery spoil as aggregate in low to normal strength concrete. In *Excellence in Concrete Construction through Innovation*, pp. 559–566. Boca Raton: Crc Press-Taylor & Francis Group.
- SCHUELKE, T. & GROTJOHN, T. A. (2013). Diamond polishing. *Diamond and Related Materials* **32**, 17–26.
- SCRIVENER, K. L. (2004). Backscattered electron imaging of cementitious microstructures: understanding and quantification. *Cement and Concrete Composites* **26**, 935–945.
- SCRIVENER, K. L. & NONAT, A. (2011). Hydration of cementitious materials, present and future. *Cement and Concrete Research* **41**, 651–665.
- SHARYGIN, V. V., SOKOL, E. V. & BELAKOVSKY, D. I. (2014). Mineralogy and Origin of Fayalite-Sekaninaite Paralava: Ravat Coal Fire, Central Tajikistan. In *Coal and Peat Fires: A Global Perspective* vol. 3, pp. 582–607.
- SHARYGIN, V. V., SOKOL, E. V. & BELAKOVSKII, D. I. (2009). Fayalite-sekaninaite paralava from the Ravat coal fire (central Tajikistan). *Russian Geology and Geophysics* **50**, 703–721.
- SKARŻYŃSKA, K. M. (1995a). Reuse of coal mining wastes in civil engineering-Part 2: Utilization of minestone. *Waste Management* **15**, 83–126.
- (1995b). Reuse of coal mining wastes in civil engineering - Part 1: Properties of minestone. *Waste Management* **15**, 3–42.
- SKIBSTED, J. & HALL, C. (2008). Characterization of cement minerals, cements and their reaction products at the atomic and nano scale. *Cement and Concrete Research* **38**, 205–225.
- SOKOL, E. (2005). *Combustion metamorphism (in Russian)*. Lepezin, G. G. (Ed.). Novosibirsk: Publishing house of the Siberian branch of Russian Academy of Science.
- SOKOL, E. V., KOKH, S. N., VAPNIK, Y., THIÉRY, V. & KORZHOVA, S. A. (2014). Natural analogues of belite sulfoaluminate cement clinkers from Negev desert, Israel. *American Mineralogist* **99**, 1471–1487.
- SOLIN, S. A. & RAMDAS, A. K. (1970). Raman spectrum of diamond. *Physical Review B* **1**, 1687–1698.
- ST JOHN, D. A., POOLE, A. W. & SIMS, I. (2016). *Concrete petrography - a handbook of investigative techniques (second edition)*. Arnold.
- STANTON, T. (1940). Expansion of concrete through reaction between cement and aggregate. In *Proceedings of American Society of Civil Engineers* **66**, pp. 1781–1811.
- ŠTUKOVNIK, P., PRINČIĆ, T., PEJOVNIK, R. & BOKAN BOSILJKOV, V. (2014). Alkali-carbonate reaction in concrete and its implications for a high rate of long-term compressive strength increase. *Construction and Building Materials* **50**, 699–709.
- STUTZMAN, P. (2004). Scanning electron microscopy imaging of hydraulic cement microstructure. *Cement and Concrete Composites* **26**, 957–966.
- (2012). Microscopy of clinker and hydraulic cements. *Reviews in Mineralogy and Geochemistry* **74**, 101–146.
- SUNDAR, S. & CHAKRAVARTY, J. (2010). Antimony toxicity. *International Journal of Environmental Research and Public Health* **7**, 4267–4277.
- TAYLOR, H. F. ., FAMY, C. & SCRIVENER, K. . (2001). Delayed ettringite formation. *Cement and Concrete Research* **31**, 683–693.
- THIÉRY, V. (2010). *Métamorphismes et déformations des séries cristallophylliennes du Chavanon, de la Sioule et d'Ussel (Massif Central français). Discussion du modèle de nappes du Massif Central. Ph.D. Dissertation, Université de Franche-Comté [in French]*. Besançon, France.
- THIÉRY, V. (2011a). Cumulative cordierite formation as a result of anatexis and melt expulsion. An example from the Chavanon sequence, Variscan French Massif Central. *Periodico di Mineralogia* **80**, 267–285.
- (2011b). Prospections minéralogiques alluvionnaires entre Auvergne et Limousin : les rivières de la région d'Eygurande (Corrèze). *Le cahier des micromonteurs* **112**, 30–35.
- THIÉRY, V. (2012). La série de la Sioule, 75 ans après les travaux de J. Richard (1938) - Historique des études géologiques et évolution des concepts. *Bulletin de la société d'histoire naturelle d'Auvergne* **76**, 73–91.
- (2013). Pétrographie appliquée à la caractérisation minéralogique et microstructurale des clinkers et ciments, pp 17-19. *Géochronique* **126**, 17–19.
- (2014a). Characterization of fibrous mimetite. *Microscopy and Microanalysis* **20**, 596–601.
- (2014b). Le district minier et les anciennes mines d'antimoine de Mérinchal (Creuse). *Le cahier des micromonteurs* **123**, 1–8.

- THIÉRY, V., BOURDOT, A. & BULTEEL, D. (2015). Characterization of raw and burnt oil shale from Dotternhausen : Petrographical and mineralogical evolution with temperature. *Materials Characterization* **106**, 442–451.
- THIÉRY, V. & CARTANNAZ, C. (2013). The Mérial district (French Massif Central). *Periodico di Mineralogia - Special issue: Mineral applications on Environments, Archaeometry and Cultural Heritage* **82**, 129–140.
- THIÉRY, V., DAMIDOT, D., SOKOL, E. & KOKH, S. N. (2014). Hydration properties of natural cementitious phases bearing rocks. In *36th meeting of the International Cement Microscopy Association*. Milano.
- THIÉRY, V. & GREEN, D. I. (2012). The multifocus imaging technique in petrology. *Computers & Geosciences* **45**, 131–138.
- THIÉRY, V. & GUY, B. (2015). Some aspects of petrography of burnt colliery spoil. In *Proceedings of the 15th Euroseminar on Microscopy Applied to Building Materials*, Çopuroğlu, O. (Ed.), pp. 71–76. Delft.
- THIÉRY, V., ROLIN, P., BARRAU, F., CATIMEL, F., CHOLET, F., EGLINGER, A., MOREAU, E., BELLE, P., BOUCLY, J., JUPPÉ, E., LAFAY, R., RAVIER, M. & REILÉ, B. (2010). *Carte géologique de la France, feuille Ussel (715). Orléans: BRGM. Notice explicative par Thiéry, V., Rolin, P., Cocherie, A.*
- THIÉRY, V., ROLIN, P., DUBOIS, M. & CAUMON, M.-C. (2015). Discovery of metamorphic microdiamonds from the parautochthonous units of the Variscan French Massif Central. *Gondwana Research* **28**, 954–960.
- THIÉRY, V., ROLIN, P., DUBOIS, M., CAUMON, M. C. & GONCALVES, P. (2016). Reply to J. Berger's comment on the article 'Discovery of metamorphic microdiamonds from the parautochthonous units of the Variscan French Massif' by Thiéry, V. et al., (2015), *Gondwana Research* **28**, 954–960. *Gondwana Research* **38**, 372–374.
- THIÉRY, V., SLOMIANNY, C. & SERRIS, É. (2016). From light and drawings to electrons and X-rays: a primer of Portland cement clinker microscopy. *Microscopy and Analysis* **26**, 17–21.
- THIÉRY, V., SOKOL, E. V., MASALEHDANI, M. N.-N. & GUY, B. (2013). La combustion des terrils. *Géochronique* **127**, 23–25.
- TILLEY, C. E. (1929). On larnite (calcium orthosilicate, a new mineral) and its associated minerals from the limestone contact-zone of Scawt Hill, Co. Antrim. *Mineralogical Magazine* **22**, 77–86.
- (1933). Portlandite, a new mineral from Scawt Hill, Co. Antrim. *Mineralogical Magazine* **23**, 419–420.
- TILLEY, C. E. & HARWOOD, H. F. (1931). The dolerite-chalk contact of Scawt Hill, Co. Antrim. The production of basic alkali-rocks by the assimilation of limestone by basaltic magma. *Mineralogical Magazine* **132**, 439–470.
- TILLEY, C. E. & HEY, M. H. (1930). Scawtite, a New Mineral from Scawt Hill, Co. Antrim. *Mineralogical Magazine* **22**, 222–224.
- TILLEY, C. E., MEGAW, H. D. & HEY, M. H. (1934). Hydrocalumite (4CaO·Al<sub>2</sub>O<sub>3</sub>·12H<sub>2</sub>O), a new mineral from Scawt Hill, Co. Antrim. *Mineralogical Magazine* **23**, 607–615.
- TILLEY, C. E. & VINCENT, H. C. G. (1948). The Occurrence of an Orthorhombic High-Temperature Form of Ca<sub>2</sub>SiO<sub>4</sub> (Bredigite) in the Scawt Hill Contact-Zone and as a Constituent of Slags. *Mineralogical Magazine* **28**, 255–271.
- VAN TITTELBOOM, K., DE BELIE, N. & HOOTON, R. D. (2013). Test Methods for Resistance of Concrete to Sulfate Attack -- A Critical Review. In *Performance of Cement-Based Materials in Aggressive Aqueous Environments: State-of-the-Art Report, RILEM TC 211 - PAE*, Alexander, M., Bertron, A. & De Belie, N. (Eds.), pp. 251–288. Dordrecht: Springer Netherlands.
- TREZZA, M. A. & FERRAIUELO, M. F. (2003). Hydration study of limestone blended cement in the presence of hazardous wastes containing Cr(VI). *Cement and Concrete Research* **33**, 1039–1045.
- VASSILEVA, R. D., ATANASSOVA, R. & BONEV, I. K. (2009). A review of the morphological varieties of ore bodies in the Madan Pb-Zn deposits, Central Rhodopes, Bulgaria. *Geochemistry, Mineralogy and Petrology* **47**, 31–49.
- VEBLEN, D. R. & POST, J. E. (1983). A TEM study of fibrous cuprite (chalcotrichite): microstructures and growth mechanisms. *American Mineralogist* **68**, 790–803.
- VILAIN, L. M. (1982). *Vapeur en montagne*. Tardy Lengellé.
- WARDANI, S. A. E. (1957). On the geochemistry of germanium. *Geochimica et Cosmochimica Acta* **13**, 5–19.
- WEISLEHNER, G. (1983). Verbrennung von Altreifen bei Rohrbach-Zement in Dotternhausen. *ZKG International* **36**, 454–457.
- WITZKE, T., DE WIT, F., KOLITSCH, U. & BLAB, G. (2015). Mineralogy of the Burning Anna 1 Coal Mine Dump, Alsdorf, Germany. In *Coal and Peat Fires: a Global Perspective. Volume 3: case studies-coal fires*, pp. 203–240.
- WONG, H. S. & BUENFELD, N. R. (2006). Monte Carlo simulation of electron-solid interactions in cement-based materials. *Cement and Concrete Research* **36**, 1076–1082.
- WOODBURY, J. & VOGEL, T. (1970). A Rapid, Economical Method for Polishing Thin Sections for Microprobe and Petrographic Analyses. *American Mineralogist* **55**, 2095–2102.
- WYHLIDAL, S., THÖNY, W. F. & TROPPER, P. (2007). New experimental constraints on the Na-in-cordierite thermometer and its application to high-grade rocks. In *Goldsmith conference abstract*.
- YAMNOVA, N. A., ZUBKOVA, N. V., EREMIN, N. N., ZADOV, A. E. & GAZEEV, V. M. (2011). Crystal structure of larnite b-Ca<sub>2</sub>SiO<sub>4</sub> and specific features of polymorphic transitions in dicalcium orthosilicate. *Crystallography Reports* **56**, 210–220.
- YIO, M. H. N., MAC, M. J., WONG, H. S. & BUENFELD, N. R. (2015). 3D imaging of cement-based materials at submicron resolution by combining laser scanning confocal microscopy with serial sectioning. *Journal of Microscopy* **258**, 151–169.
- ŽÁČEK, V. & SKÁLA, R. (2015). Mineralogy of Burning-Coal Waste Piles in Collieries of the Czech Republic. In *Coal and Peat Fires: a Global Perspective*, Stracher, G. B., Sokol, E. & Prakash, A. (Eds.), pp. 109–159. Boston: Elsevier.
- ZIO, E. & AVEN, T. (2013). Industrial disasters: Extreme events, extremely rare. Some reflections on the treatment of uncertainties in the assessment of the associated risks. *Process Safety and Environmental Protection* **91**, 31–45.



## 8 CURRICULUM VITAE

### 8.1 Background

2000-2002: General University Diploma in Earth and Universe Sciences, Joseph-Fourier University, Grenoble

2003-2005: Bachelor of Honour in applied geology, Franche-Comté University, Besançon

2005-2006: Master's degree in fundamental geology, Franche-Comté University, Besançon

2006-2010: PhD thesis, defended on the 30<sup>th</sup> of April 2010, entitled « Metamorphisms and deformations of the Chavanon, Sioule and Ussel metamorphic sequences (french Massif Central). Discussion on the nappe stacking model of the Massif Central. » (*Métamorphismes et déformations des séries cristallophylliennes du Chavanon, de la Sioule et d'Ussel (Massif Central français). Discussion du modèle de nappes du Massif Central.*)

### 8.2 Reviews of scientific papers

Applied Clay Science

Engineering Geology

Microscopy and Microanalysis

Periodico di Mineralogia

Journal of Sustainable Cement-based Materials

Journal of African Earth Sciences

Scanning

Materials

Member of the « international board of reviewers» for the 15<sup>th</sup> Euroseminar on Microscopy Applied to Building Materials (EMABM), 2015, Delft, the Netherlands.

Reviewer for the 38<sup>th</sup> International Cement Microscopy Association annual meeting, 2016, Lyon, France.

### 8.3 Teaching

General resource geology for civil engineers: 24 hours course since 2015.

Macroscopic mineralogy

Geological and topographic maps

Field geology

Short term projects of discovery of research for engineers

## 8.4 Supervision

- Bachelor of Honour of Marie Ravier, « Où sont les nappes dans la série métamorphique de la Sioule » (*Where are the so-called nappes in the Sioule metamorphic sequence*), 2008-2009
- PhD supervision of Alexandra Bourdot (dir.: Pr. David Bulteel), « Study of the influence of burnt oil shale on alkali-silica reaction towards the improvement of the use of reactive aggregates in concrete » (*Étude de l'influence des schistes calcinés sur la réaction Alkali-Silice pour une meilleure valorisation en bétons de granulats réactifs*), defended on the 12<sup>th</sup> of December 2013,
- PhD supervision of Angélique Rousselet (dir.: Pr. David Bulteel), « Inhibition of the alkali-silica reaction by lithium: efficiency in model reactors and mortars and understanding of the inhibition mechanisms » (*Inhibition de la réaction alkali-silice par le lithium: efficacité en milieu modèle et en matrice cimentaire et compréhension des mécanismes d'inhibition*), defended of the 13<sup>th</sup> of December 2016,
- PhD supervision of Houda Maimouni (in progress)

## 8.5 Professional or scientific society membership

French mineralogical society (SFMC)

French micro-mineralogical association (AFM)

French Mineral Industry Society (SIM)

## 8.6 Organization of conferences

- (RF)<sup>2</sup>B (Réseau Francophone de Recherche et de Formation sur le Béton – *French network on research and education about concrete*) 2014 (3-4 July), Douai, France. Member of the organization committee
- NoMaD (Nouveaux Matériaux et Durabilité – *New materials and durability*) 2015 (5-6 November), Douai, France. Member of the organization committee.
- International Cement Microscopy Association (ICMA) 38<sup>th</sup> annual meeting, Lyon, France, 17-21 april 2016. Responsible for the organization with Dr. Philippe Le Coustumer, Bordeaux University.

## 8.7 List of publications

### 8.7.1 International peer-reviewed journals

THIÉRY, V., ROLIN, P., DUBOIS, M., CAUMON, M.-C., GONCALVES, P. (2016), Reply to J. Berger's comment on the article 'Discovery of metamorphic microdiamonds from the parautochthonous units of the Variscan French Massif' by Thiéry, V. et al. (2015), *Gondwana Research* 28, 954–960 [Gondwana Research](#) 38, 372-374

BOURDOT, A., **THIÉRY, V.**, BULTEEL, D., HAMMERSCHLAG, J.-G., (2016), Effect of burnt oil shale on ASR expansions: A petrographic study of concretes based on reactive aggregates, Construction and Building Materials 112, 556-569

THIÉRY, V., ROLIN, P., DUBOIS, M., CAUMON, M.-C. (2015), Discovery of metamorphic microdiamonds from the parautochthonous units of the Variscan French Massif Central, Gondwana Research 28, 954-960

THIÉRY, V. BOURDOT, A., BULTEEL, D. (2015), Characterization of raw and burnt oil shale from Dotternhausen : Petrographical and mineralogical evolution with temperature, Materials Characterization 106, 442-451

SOKOL, E.V., KOKH, S.N., VAPNIK, Y., **THIÉRY, V.** & KORZHOVA, S.A. (2014), Natural analogues of belite sulfoaluminate cement clinkers from Negev desert, Israel, American Mineralogist 99 (7), 1471-1487

THIÉRY, V. (2014), Characterization of fibrous mimetite, Microscopy and Microanalysis 20 (2), 596-601

MOUNDOUNGOU, I., BULTEEL, D., GARCIA-DIAZ, É., **THIÉRY, V.**, DÉGRUGILLIERS, P., HAMMERSCHLAG, J.G. (2014), Reduction of ASR expansion in concretes based on reactive chert aggregates: Effect of alkali neutralization capacity, Construction and Building Materials, 54, 147-162.

THIÉRY, V., CARTANNAZ, C. (2013), The Mérinchal antimoniferous district (French Massif Central), Periodico di Mineralogia - Special issue: Mineral applications on Environments, Archaeometry and Cultural Heritage 82(1), 129-140

THIÉRY, V. (2013), External and internal features of garnet revealed by the multifocus imaging technique, Micron 44, 475-78

THIÉRY, V., GREEN, D.I. (2012), The multifocus imaging technique in petrology, Computers & Geosciences 45, 131-138

THIÉRY, V. (2011), Cumulative cordierite formation as a result of anatexis and melt expulsion. An example from the Chavanon sequence, Variscan French Massif Central, Periodico di Mineralogia 80(2), 267-285.

THIÉRY, V., ROLIN, P., MARQUER, D., COCHERIE, A., FANNING, C.M., ROSSI, P. (2009), Visean sinistral wrench faulting along the Sillon Houiller in the French Massif Central : Late Variscan Tectonic implications, Bulletin de la Société Géologique de France 180 (6), 513-528

ROLIN, P., MARQUER, D., COLCHEN, M., CARTANNAZ, C., COCHERIE, A., **THIÉRY, V.**, QUENARDEL, J.-M., ROSSI, P. (2009), Fameno-Carboniferous (370-320 Ma) strike slip tectonics monitored by syn-kinematic plutons in the French Variscan belt (Massif Armoricain and French Massif Central), Bulletin de la Société Géologique de France 180 (3), 231 - 246.

#### 8.7.2 *Geological maps and booklets*

THIÉRY, V., ROLIN, P., BARRAU, F., CATIMEL, F., CHOULET, F., MOREAU, EBELLE, P., BOUCLY, J., JUPPÉ, E., LAFAY, R., RAVIER, M., REILÉ, B., 2010. Carte géologique de la France, feuille Ussel. Notice explicative par **Thiéry, V.**, Rolin, P et Cocherie, A., 169p.

ROLIN, P., **THIÉRY, V.**, CHOULET, F., MAVEL, J. 2008. Carte géol. France (1/50.000), feuille de FELLETIN (n°691). Orléans : BRGM. Notice explicative par Rolin, P., **Thiéry V.**, Cartannaz C., Cocherie, A., Rossy, M., Henry, P., Constant, J (2008).

CARTANNAZ, C., SONNET, R., ÉMONIN, Y., JUILLERAT, M., DEPREZ, J., **THIÉRY, V.**, MONTAZ, N., ROT, J., BINETRUY, J.C. (2008). Carte géol. France (1/50 000), feuille Aubusson (667). Orléans : BRGM. Notice explicative par Cartannaz C., Rolin, P., Cocherie, A., Henry, P., Rossy M. (2008), 106p.

#### 8.7.3 *Edited book chapters*

GATEL, P., ŽÁČEK, V., KRUSZEWSKI, Ł., DEVOUARD, B., **THIÉRY, V.**, EYTIER, C., EYTIER, J.-R., FAVREAU, G., VIGIER, J., AND STRACHER, G.B. (2015) Chapter 28 - Combustion Mineralogy and Petrology of Oil-Shale Slags in Lapanouse, Sévérac-le-Château, Aveyron, France: Analogies with Hydrocarbon Fires. In G.B. Stracher, E. Sokol, and A. Prakash, Eds. Coal and Peat Fires: a Global Perspective Volume 3, p. 681-742. Elsevier, Boston.

#### 8.7.4 *Publications in French peer-reviewed journals*

THIÉRY, V. (2014), Les marbres de la Série du Chavanon (Massif central, France), Bulletin de la société d'histoire naturelle d'Auvergne 78, 17-34

THIÉRY, V., SOKOL, E.V., MASALEHDANI, M.N.N., GUY, B. (2013), La combustion des terrils, Géochronique 127, 23-25

THIÉRY, V. (2013), La série de la Sioule, 75 ans après les travaux de J. Richard (1938) - Historique des études géologiques et évolution des concepts, Bulletin de la société d'histoire naturelle d'Auvergne 76, 73-91

THIÉRY, V. (2013): editor of n°126 « Les Ciments», special issue of the journal « Geochronique» from the French geological survey/French geological society, and contributions to the following articles:

- THIÉRY, V., BULTEEL, D. Le ciment Portland et les ciments Portland composés : les additions minérales (supplementary cementitious materials ou SCM) – Notation et normalisation des produits, pp 15-16,
- THIÉRY, V. Pétrographie appliquée à la caractérisation minéralogique et microstructurale des clinkers et ciments, pp 17-19,
- THIÉRY, V., SOKOL, E.V., KOKH, S.N.,MASALEHDANI, N.M.N. Le métamorphisme naturel d’ultra-haute température (UHT) des roches à Ca-Si (Al,Fe) – Comparaison avec la minéralogie du clinker, pp 27-29,
- THIÉRY, V., ROCHELLE, C., MILODOWSKI, A. Aperçu des mécanismes d’hydratation du ciment et analogues naturels, pp 30-32

#### 8.7.5 *Conference proceedings*

THIÉRY, V., MEULENYZER, S., BOUICHOU, M., MARIE-VICTOIRE, E. (2016), Some historical points about cement and microscopy in France. International Cement Microscopy Association 38<sup>th</sup> annual meeting, Lyon, France, 17-21/04/2016

SONG, Y., DAVY, C.A., **THIÉRY, V.**, TROADEC, D., DAMIDOT, D., BOURBON, X., (2016), Multi-scale assessment of the 3D pore network of a high performance concrete. International Cement Microscopy Association 38<sup>th</sup> annual meeting, Lyon, France, 17-21/04/2016

KIRSANOVA, A., THIÉRY, V., KRAMAR, L. Ya, (2015) The Effect of Additives Including Metakaolin on the Freeze Resistance of Concrete , Materials Science Forum, 843, 263-268

ROUSSELET, A., **THIÉRY, V.**, BULTEEL, D. (2015), Inhibition de la réaction alcali-silice: mise en évidence d'un effet seuil à l'efficacité du lithium en milieu réactionnel modèle et matrice cimentaire, 16<sup>ème</sup> édition des journées scientifiques du regroupement francophone pour la recherche et la formation sur le béton , Lausanne, 9-10/07/2015

THIÉRY, V., GUY, B. (2015), Some aspects of petrography of burnt colliery spoil, in: O. Çopuroğlu (Ed.), Proceedings of the 15th Euroseminar on Microscopy Applied to Building Materials, Delft, 2015, 71-76

THIÉRY, V., DAMIDOT, D., SOKOL, E.V., KOKH, S.N. (2014), Hydration properties of natural cementitious phases bearing rocks, International Cement Microscopy Association 36<sup>th</sup> annual meeting, Milano, Italy, 14-17th April 2014

BOURDOT, A., **THIÉRY, V.**, BULTEEL, D. (2013), Effects of spent shales on reactive aggregates based concrete toward alkali-silica reaction, in “14th Euroseminar on microscopy applied to building materials, Helsingør, 2013/06/10-14 - Book of extended abstract”s, pp 21-24

#### 8.7.6 Conference without proceedings (abstracts only)

THIÉRY, V., ROLIN, P., DUBOIS, M., GONCALVES, P. (2015), New UHP evidences from the inner part of the Variscan belt: geology of the Chavanon sequence, French Massif Central. *The Variscan belt: correlations and plate dynamics. Special meeting of the French & Spanish Geological Societies*. Géologie de la France n°1, p. 137

THIÉRY, V., ROLIN, P. (2007), Ante upper Visean ductile shear of the Sillon Houiller (Massif Central, France) : new cartographic and radiometric datas. *Mechanics of Variscan Orogeny: a modern view on orogenic research. Special meeting of French and Czech Geological Societies. September 13 – 15, 2007, Orléans, France*. Géologie de la France n°2, p. 164.

ROLIN, P., CARTANNAZ, C., MARQUER, D., COLCHEN, D., COCHERIE, A., **THIÉRY, V.**, QUENARDEL, J.-M., ROSSI, P. (2007), Progressive shortenig axis rotation monitored by 370-320 Ma syn-kinematic granites in the French Variscan belt (Armorican and western French Massif Central massifs). *Mechanics of Variscan Orogeny: a modern view on orogenic research. Special meeting of French and Czech Geological Societies. September 13 – 15, 2007, Orléans, France*. Géologie de la France n°2, p. 152.

#### 8.7.7 Popular science

THIÉRY, V., BULTEEL, D., REMOND, S. (2016), La pétrographie appliquée aux granulats de béton recyclés. Durabilité des ouvrages futurs et réaction alcali-granulat, Recyclage & Valorisation, 54, 50-54

THIÉRY, V. (2015), Des diamants en Corrèze, Le règne minéral 125, 33-34

THIÉRY, V. (2015), Nouveaux éléments de caractérisation de la mimétite fibreuse des Molérats, Saint-Prix, Saône-et-Loire, Le règne minéral 123, 33-35

THIÉRY, V. (2014), Le district minier et les anciennes mines d'antimoine de Mérinchal (Creuse) , Le cahier des Micromonteurs 123, 1-2014, 23-30

THIÉRY, V. (2014), La tourmaline des Lartault et Naudiots, Marmagne (Saône et Loire), Le règne minéral, 115, 41-42

THIÉRY, V. (2013), Diversité des pratiques en laboratoires, Mines et Carrières, 206, 174-176

THIÉRY, V. (2011), Sur les pentes du Coupet (Haute-Loire), Le règne minéral, 98, 28.

THIÉRY V. (2011), Prospections minéralogiques alluvionnaires entre Auvergne et Limousin : les rivières de la région d'Eygurande (Corrèze) », Le cahier des Micromonteurs 112, 2-2011, 30-35

LEBOCEY, J., **THIÉRY, V.**, GRATIA, B. (2010), La concession minière de Meymac (Corrèze), Le règne minéral 91, 9-22.

THIÉRY V. (2007), Le microscope polarisant ou « Un autre œil sur la beauté du monde minéral », Minéraux et Fossiles 358, 54-57 et 359, 56-60

PASSAQUI, J.P., **THIÉRY, V.**, GOURAULT, C., DE ASCENÇÃO GUEDES, R. (2007), L'uranium du Morvan, Le règne minéral, Hors-Série n°13, « Les minéraux du Morvan », 21-30.

PASSAQUI, J.P., DEMAIZIÈRE, J.F., GOURAULT, C., SZULAK, L., **THIÉRY, V.**, PERRAUDIN, M., DE ASCENÇÃO GUEDES, R. (2007), Voltennes (Saône et Loire), Le règne minéral, Hors-Série n°13, « Les minéraux du Morvan », 41-56.

DEMAIZIÈRE, J.F., SZULAK, L., **THIÉRY, V.**, PERRAUDIN, M., GOURAULT, C. (2007), Les autres minéraux du Morvan, Le règne minéral, Hors-Série n°13, « Les minéraux du Morvan », 102-112.

THIÉRY, V. (2004), Les mines de fluorine de Voltennes, Minéraux et fossiles 329, juin 2004, pp 5 – 11

## 8.8 Selected reprints

In order to illustrate the scientific results obtained following the gait of the manuscript, I have chosen to include selected reprints of papers for which I am the first author or co-author.

To remain in agreement with the organization of the manuscript, they are presented following the order of the chapters.

The first paper, entitled “Discovery of metamorphic microdiamonds from the parautochthonous units of the Variscan French Massif Central”, has been published in 2015 in Gondwana Research (IF 2015 8,743, 5 years IF 7,953). The main aspects of the papers are described in § 3.1.1.

The second paper, entitled “Characterization of fibrous mimetite”, has been published in 2014 in Microscopy and Microanalysis (IF 2015 1,73, 5 years IF 2.026). Some aspects are presented in § 3.2.2.

Those two papers are directly linked to a fundamental approach in geosciences and illustrate my work in microscopy and analysis, using the following devices: optical microscopy, scanning electron microscopy with EDS analysis, Raman spectroscopy. This is also a good illustration of the need for a proper preparation of sample in the case of diamond inclusions.

To continue and to illustrate the shift in the materials on which I have worked, I have chosen to include a reprint of the paper entitled “Characterization of raw and burnt oil shale from Dotternhausen : Petrographical and mineralogical evolution with temperature”, published in 2015 in the journal Materials Characterization (IF 2015 2,383, 5 years IF 2,605). The petrographic approach is still there, but the paper also illustrates some work carried out using XRD and TEM.

The fourth and fifth papers are related to chapter 3 (aka “all about microscopy”). “The multifocus imaging technique in petrology», published in 2012 in Computers & Geosciences (IF 2.474, 5 years IF 2.540), along with “External and internal features of garnet revealed by the multifocus imaging technique”, published in 2013 in Micron (IF 1.838, 5 years IF 1.932), present both the multifocus imaging technique and some possibilities of application in earth sciences, as a complement to § 5.4.

Finally, “Natural analogues of belite sulfoaluminate cement clinkers from Negev desert, Israel”, published in 2014 in The American Mineralogist (IF 1.918, 5 years IF 2.196) is the perfect illustration of the analogies between natural and anthropogenic geomaterials. It documents rare rocks which are “natural cements”, illustrating § 6.3 of the manuscript.



## GEOGRAPHICAL LOCATION OF PLACES STUDIED

