GEOLOGICA BELGICA (2004) 8/3: 3-14.

THE "CALAMINE-TYPE ZINC-LEAD DEPOSITS IN BELGIUM AND WEST GERMANY: A PRODUCT OF MESOZOIC PALAEOWEATHERING PROCESSES

Léon DEJONGHE[1] & Maria BONI[2]

(2 figures, 2 plates)

1. Royal Belgian Institute of Natural Sciences, Geological Survey of Belgium, 13 Jenner street, B-1000 Brussels, Belgium, E-mail: Leon.Dejonghe@naturalsciences.be; also Free University of Brussels, 50 Av. F.D. Roosevelt, B-1050 Brussels, Belgium.
2. Università di Napoli, Dipartimento di Geofisica e Vulcanologia, Via Mezzocannone 8, I-80134 Napoli, Italy, E-mail: boni@unina.it; also Geologisch-Palaeontologisches Institut der Universität Heidelberg, Im Neuenheimer Feld 234, 69120 Heidelberg, Germany.

ABSTRACT. The word "calamine", designating non-sulphide Zn-ores of supergene origin in carbonate rocks, originates from the Belgian locality "La Calamine" where an ore deposit was exploited from the 14th century up to 1884. The genesis and age of La Calamine, described in the literature as a palaeokarstic type of deposit, have never been fully understood. Likewise, the age of the deep supergene alteration of Zn-Pb veins exploited in Belgian and German neighbouring mining districts has never been clearly determined. This paper aims at identifying the geological constraints responsible for the genesis of willemite-smithsonite-bearing La Calamine deposit, as well as of the deep-reaching gossans of the surrounding Zn-Pb veins. The kaolinised regolith remnants ranging from Uppermost Jurassic to Lower Cretaceous, which developed on the post-Variscan palaeosurface, could be one of the surface expressions of the weathering responsible for the genesis of non-sulphide Zn-ore deposits in Belgium and Germany. Locally, Upper Cretaceous sediments, whose deposition interrupted the weathering process, cover the regolith. Neither Cainozoic weathering, that was responsible in Belgium for halloysite accumulations at the bottom of giant cryptokarsts, nor Quaternary landscape modelling, should have played a major role in the formation of the economic "calamine-type" Zn-deposits.

KEYWORDS. calamine, zinc oxide, gossan, palaeoweathering, Mesozoic, Belgium, Germany

1. Introduction

Prior to the development of flotation and smelting processes for zinc sulphide ores at the beginning of the 20th century, the non-sulphide deposits were the principal source of zinc in the world. At present, notwithstanding the numerous occurrences of non-sulphide Zn mineralisation in several countries, there has been no significant exploitation or exploration of calamine ores in Europe (Boni & Large, 2003). However, with the development of solvent-extraction and electro-winning and the modernisation of the Wälz technology for the treatment of non-sulphide zinc ores, there has been a revival in commercial (and consequently scientific) interest for this style of mineralisation throughout the world (Large, 2001; Hitzman *et al*. 2003; Boni, 2003). The commercial exploitation of non-sulphide zinc ores, often known collectively as "zinc oxide" deposits, could again become an important source of metallic zinc.

Based on their geological characteristics, Large (2001) classified the non-sulphide zinc deposits into three main groups:
- "Calamine"-dominant deposits in Mississippi Valley Type and stratiform sulphide protores in carbonate rocks. Here, the non-sulphide mineralisation is related to the oxidation of primary sulphides and preservation in karst-cavity infilling and replacement aggregations;
- Willemite-dominant deposits in Late Proterozoic to Early Cambrian sedimentary rocks where the mineralisation occurs in marked fault zones. These deposits might be hydrothermal in origin, formed under specific low S- and high O-fugacities;
-"Gossan"-type deposits containing hydrated zinc silicates that were formed by residual surface oxidation of primary sulphides, and then preserved by a special set of circumstances (tectonic, climatic etc.).

Hitzman *et al*. (2003) have produced a more articulated classification, in which a first broad distinction between supergene and hypogene deposits has been contemplated. The supergene deposits, corresponding to types 1. and 3. in Large (2001), form primarily from the oxidation of sulphide-bearing deposits and can be subdivided in three main subtypes:
- Direct-replacement deposits (essentially the equivalent of Zn-rich gossans);
- Wallrock-replacement deposits (derived by buffering reactions between acidic groundwater containing zinc and carbonate host rocks deeper down the water table);
- Residual and karst-fill deposits (resulting from accumulation of secondary zinc minerals in a network of karst cavities).

Most of the European examples of non-sulphide zinc mineralisation are considered to be supergene. They belong to Group 1 ("Calamine") as well as to Group 3

("Gossan") deposits of Large (2001), mainly hosted by carbonate rocks. After Hitzman *et al*. (2003), they can be classified as simply "supergene". Their prevailing mineralogy consists of smithsonite-hemimorphite-hydrozincite, with the local occurrence of Pb-carbonates and sulphates. However, the ore in the historically important "La Calamine" deposit in Belgium, hosted by Upper Palaeozoic carbonates, contained up to 40% willemite (Dejonghe & Jans, 1983).

The non-sulphide zinc mineralisation in Europe is thought to record distinct periods of uplift, oxidation, and subsequent fossilisation of the weathering profile that occurred repeatedly in the past (paleoweathering). Therefore, many of the factors governing the formation of supergene non-sulphide mineralisation may be common to many of the different deposit types. The main aim of this paper is to demonstrate that most of the Belgian and part of the German non-sulphide zinc-deposits, are also products of palaeoweathering processes.

2. Geological setting

2.1. East Belgium

Sedimentary rocks dominate the geology of Belgium. Igneous rocks are very rare and of small areal extent. Three main geological units may be distinguished (Fig. 1):

- A basement, made up of Cambrian, Ordovician and Silurian rocks (mainly slates and quartzites). The basement outcrops in the Stavelot, Rocroi, Givonne, Serpont, Brabant Massifs and in the Condroz Ridge (also named Sambre-et-Meuse Ridge);

- An older cover, made up of Devonian and Carboniferous rocks (alternating sandstones, shales and carbonates). This unit outcrops in the Namur, Dinant, Verviers and Neufchâteau-Eifel Synclinoria as well as in the Ardenne Anticlinorium.

- A younger cover, consisting of rocks spanning in age from Permian to Recent (mainly sands and clays). This post-Variscan cover outcrops in the northern part of the country (approximately to the north of the line joining Mons, Namur and Liège) and the southern extremity (Belgian Lorraine). These two areas are interconnected

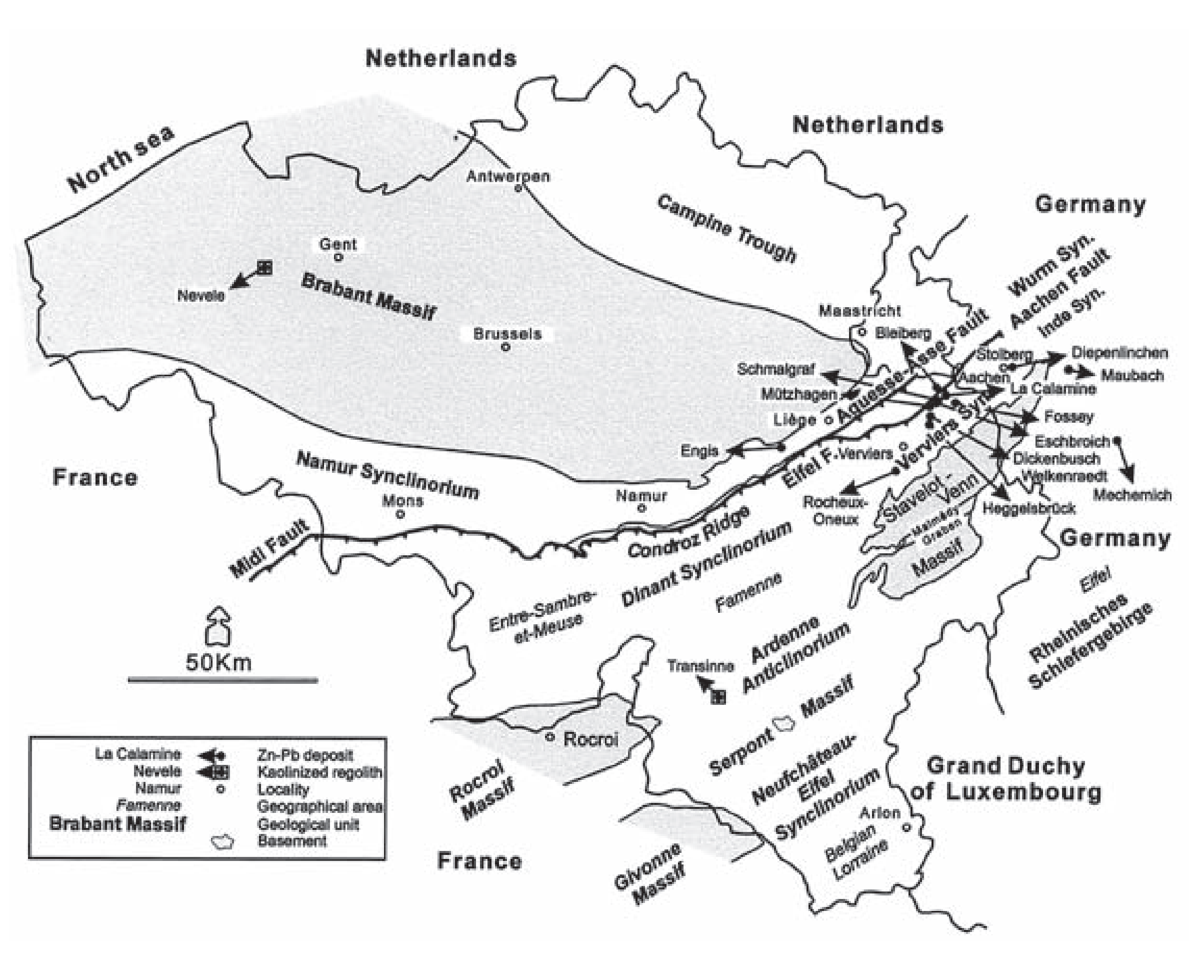

Figure 1. Location map of the main Palaeozoic structural units of Belgium and west Germany as well as of the Zn-Pb deposits, kaolinised regoliths and localities quoted in text.

through the North of France (northern extremity of the Paris Basin).

With exception of the Brabant Massif, the basement underwent a first deformation initially during the Caledonian and was deformed again during the Variscan orogeny, together with the post-Caledonian Palaeozoic cover.

The post-Variscan cover is tabular and sub-horizontal. It is generally admitted that, following the Variscan orogeny, Permian sediments in Belgium have been deposited and then removed by erosion. Possible relicts are preserved in the Malmédy Graben, although a Permian age of the conglomerates of the Malmédy Formation infilling the graben has never been confirmed nor rejected (Bultynck *et al.*, 2001). For what pertains to Triassic and Jurassic sediments, either they have been never deposited, or they could have been only deposited on the eastern side of the Brabant Massif. If it has been the case, they were also fully eroded following the Cimmerian uplift of the Brabant Massif during Jurassic. Vercautere & Van den Haute (1993) considered that ≅c. 3000 m of sediments, which covered the Brabant Massif, were removed after Middle Jurassic. In fact, the latter area was certainly emerged from 150 to 100 Myr ago, and perhaps even since 250 Ma.

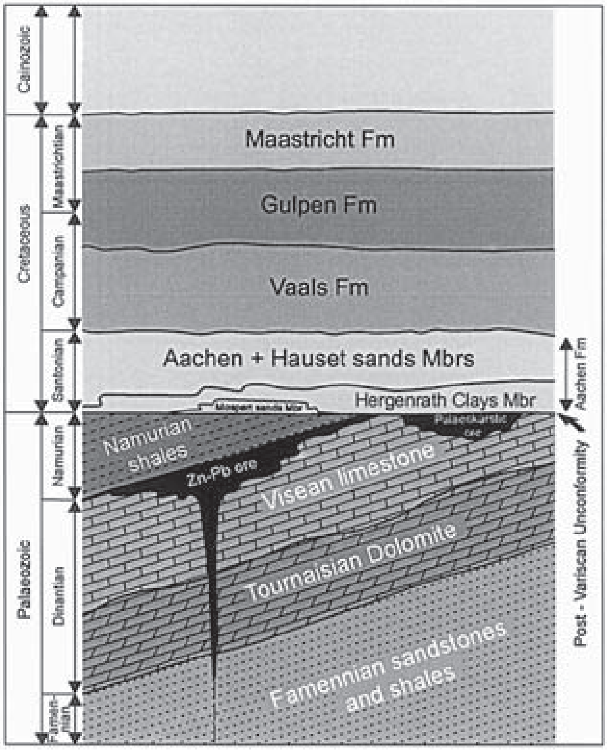

Figure 2. Chrono- and lithostratigraphical units of the Verviers Synclinorium with the setting of the veins, flats and palaeokarstic Zn-Pb ores. Abbreviations: Fm: Formation; mbr: Member.

Upper Mesozoic sediments (Fig. 2) unconformably cover the folded Palaeozoic rocks in the Verviers Synclinorium. This succession starts with the deposition of the Aachen Formation of Santonian age (Upper Cretaceous). The latter formation may reach a maximum thickness of 60 m that decreases to the West and to the North. The Hergenrath Clays Member, consisting of alternating layers of silty clays and argillaceous sands and silts, with abundant plants debris, marcasite and pyrite nodules, represents the basis of the Aachen Formation. Locally, a few meter of coarse-grained sands (the Mospert Sands Member) have been described to occur below the Hergenrath Clays Member. The Aachen Formation follows with the members of the Aachen- and Hauset Sands, both consisting of shallow-water to continental coarse- to fine-grained white sands, characterised by strong bioturbation, plant debris, channels, oblique- and cross-bedding etc. The Aachen Formation is overlain by the Vaals Formation of Campanian age. This consists mainly of up to about 150 m of sands, silts and clay layers with glauconite, the latter pointing to generalised water deepening. The Gulpen Formation (Upper Campanian to Mastrichtian), made up to about 175 m of chalk and calcarenites with chert nodules, overlay the Vaals Formation. The Maastricht Formation made up between 45 and 80 m of chalk tops the Cretaceous lithological units. Cainozoic sediments follow, consisting mainly of alternating sandy and clayey units.

Additional data on lithology, facies distribution and tectonics can be found in Robaszynski & Dupuis (1983) and Bultynck & Dejonghe (2001).

The uplift of the Ardenne Massif started in Upper Oligocene and continued during Neogene, up to the present. This deformation took the form of a broad bulging accompanied by block faulting along the same direction as the Rhine graben. Since Oligocene, the uplift reached around 500 m in the Baraque Michel area (Hautes Fagnes, NE Belgium), around 375 m in the Central Ardenne, more than 300 m in the Condroz and Famenne areas and between 150 and 175 m in the Rocroi area (Demoulin, 1995). In some places of the Ardenne, the result of this uplift and related erosion has been the complete stripping of nearly all the Cretaceous and Cainozoic cover. This was however not the case in most of the Verviers Synclinorium.

2.2. West Germany (North Eifel area)

The NE lateral equivalent of the Ardenne Allochthonous Unit in Germany is the Rhenohercynian Zone, which includes most of the Rheinisches Schiefergebirge (Rhenish Slate Mountains), the Werra Anticline and the Harz. The Rhenohercynian Zone is made up of Devonian and Carboniferous sediments, up to 8000 m thick, intensely folded during the Variscan orogeny. Of special interest is the Inde Syncline, the NE prolongation of the Verviers Synclinorium, where the Pb-Zn Aachen-Stolberg mining district is located (Walther, 1986).

3. Features of the Zn-Pb ore deposits in Belgium

3.1 The sulphides

Dejonghe *et al.* (1993) and Dejonghe (1998) have published syntheses about the Belgian Zn-Pb deposits, whose exploitation dates back to prehistoric times. Its apogee was between 1850 and 1870, but the last mine was closed in 1946. During the period 1837-1945, the tonnage of exploited metals reached about 1.5 Mio tons Pb + Zn with a Zn/Pb ratio of 8-9. The Belgian zinc-lead productive district was mainly concentrated within an area of about 400 km^2 in the eastern part of Belgium (Dejonghe & Jans, 1983).

Several base metal ore deposit types may be distinguished, including syndiagenetic bodies, epigenetic vein- and connected flats (or mantos, interlayered between Visean limestones and Namurian shales), and palaeokarstic mineralized infilling. The mineralogy of the deposits is generally simple: sphalerite (mainly in form of schalenblende), galena, pyrite/marcasite, and locally Ni- and Co-sulphides. Formerly economic Zn-Pb veins occur in Devonian and Carboniferous carbonate rocks along faults, which are transverse to the Variscan fold axes, though rare veins also occur in siliciclastic rocks of Lower Devonian age or older. Hydrothermal solutions, whose nature and origin were discussed among others by Heijlen *et al*. (2001), precipitated the metals in the veins at temperatures < 180°C (110°C in the Verviers Synclinorium) and pressures of 10^8 Pa (< $2x10^7$ Pa in the Verviers Synclinorium). Fluids salinities are in the range between 10 and 23 equiv. weight % NaCl.

As the mineralised lodes intersect the Palaeozoic rocks folded during the Variscan orogeny but do not cross the overlying Upper Cretaceous series (Aachen Formation of Santonian age), the timing of their emplacement is technically constrained between the end of the Variscan orogeny (± 295 Ma) and the beginning of the Upper Cretaceous (± 100 Ma). de Magnée (1967) proposed that the main hydrothermal mineralizing event might have occurred at the end of the Jurassic (around 150 Ma). It is interesting to quote that Rb-Sr dating of the sphalerite from the large, Triassic sandstone-hosted, stratabound Maubach-Mechernich deposit in west Germany, yielded an age of 170 ± 4 Ma (Schneider *et al*., 1999). A similar age could be assessed also for the veins and "flats" mineralisation in Belgium.

Post-Variscan karstic dissolution and landscape modelling was virtually present during the long lasting periods of continentality occurring at different moments from the Permian up to the present day. Karstic process of ore concentration related to the Palaeozoic-Mesozoic unconformity, and notably mechanical reworking of pre-existing vein type deposits in exokarsts was underlined by Dejonghe & Jans (1983), as having occurred in some Belgian ores including the La Calamine deposit.

The primary sulphide deposits in east Belgium and nearby areas have been truncated and unconformably covered by the sediments of the Aachen Formation (Santonian). Lespineux (1905) was the first one to observe that in the Mützhagen mine, the sphalerite orebody is covered by 25 to 30 m of sands of the Aachen Formation, which are not mineralised.

3.2. The non-sulphides

Gossan-type concentrations representing the oxidation products of Fe, Pb and Zn sulphides, were exploited on top of the primary ores (Lespineux, 1905; Timmerhans, 1905; Dejonghe *et al.,* 1993). The non sulphide-Zn products were called "Calamine" (from the famous "La Calamine" deposit), which is a mining expression to describe a common mixture of zinc-ores such as Zn-carbonate {smithsonite = $ZnCO_3$} and Zn-silicate {hemimorphite = $Zn_4(Si_2O_7)(OH)_2.H_2O$}, or the assemblage of hemimorphite, smithsonite, hydrozincite {$Zn_5(CO_3)_2 (OH)_6$} and willemite {$Zn_2 SiO_4$}. Calamines are grey, yellow or even black in colour and occur as massive rock masses or with concretionary, foliated or stalactitic shapes. They could be microcrystalline- (so-called "amorphous" in the old literature) or coarse-grained aggregates, brecciated or vuggy, with druses filled with small idiomorphic smithsonite and hemimorphite crystals.

Smithsonite-dominated bodies, formed preferentially at the Zn-sulphide ore/Visean limestone contact. Zn-silicates occurred when the country rock was prevailing dolomitic (very clear at Fossey, Heggelsbrück, La Calamine). Timmerhans (1905) also mentioned that Zn-silicates were never found near the ore/Namurian shale contact. Calamine bodies are always described as irregularly shaped, with the carbonate-silicate ore often mixed with- or covered by- sands and coloured (greenish, reddish, yellowish) clays. Blocks detached from the country rocks (limestone, dolomite and Namurian shales in various grades of alteration) were also observed in the ore deposits. Locally, willemite is replacing directly the schalenblende concretions (Plate 1, a_1, a_2). Lead content of the calamine is generally low.

The most important resources of calamine ores have been exploited until the first half of the 20th century in the upper parts of the Schmalgraf, Engis, Dickenbusch, Fossey, Rocheux-Oneux and other smaller deposits, all concentrated in the NE of the country (Fig. 1). Their mineralogy is very variable, bearing mostly a combination of Zn-carbonates and silicates, among which willemite is always a component, even if a minor one. In addition, Pb- and Fe-minerals also occur. The shape of the Zn-non sulphide concentrations ranges from bulk replacement bodies of host carbonates and/or sulphides through amorphous and microcrystalline aggregates, to the concretionary infilling of isolated cavities in the oxidation zone. In the latter, beautiful up to few cm-sized crystals are often observed, displaying several generations of willemite, smithsonite and hemimorphite. A large number of these specimens (Plate 1, c, d, e, f) are preserved in the collections of the Royal Belgian Institute of Natural Sciences as well as in the Geological Survey of Belgium, but significant examples can be also observed in several museums around the world.

The calamine bodies, which developed above the primary sulphides in the upper parts of the veins or in the connected flats, usually reached down from the surface to an average depth of 40 to 50 m, sometimes even more. For example, at Rocheux-Oneux, the calamines were traced down till a depth of 70 m. But calamine as well as cerussite pockets are also irregularly enclosed in the primary sulphide bodies down to 121 m in depth. At Engis (the Dos ore deposit), the exploited calamine body reached down till 35-40 m below the level of the river Meuse. Because the latter coincides with the present-day level of the water table in the region, the total depth reached by the calamine at Engis was appreciatively ± 100 m below the recent surface. Sporadic oxidation products of the sulphide ores might occur even deeper: for example, at Schmalgraf, limonite pockets are described down to 211 m.

La Calamine Zn-deposit, the largest base metal orebody in Belgium, is situated at ± 30 km ENE of Liège and ± 10 km SW of Aachen. Ladeuze *et al.* (1991) described the important historical role played in the past by this mine whose production exceeded 600,000 tons of zinc metal and reached perhaps 760,000 tons (the uncertainty is due to the lack of production statistics before 1825). When the mine was still in operation, the concentrates were essentially made up of non-sulphide ore with 33-47% Zn. The deposit produced only zinc, whereas all other Belgian deposits have yielded, besides zinc, variable amounts of lead and iron. Furthermore, its zinc production topped that of all other Belgian deposits.

The orebody was located in a narrow syncline, plunging at about 15° to the SW, made up of Famennian sandstones and shales overlain by Tournaisian dolomites and dolomitic shales (Dejonghe & Jans, 1983). It formed an enormous lenticular pocket, located in the nose of the above-mentioned syncline. These features are quite different from those of the weathered stratabound flats, capping the veins below the Namurian shales. The ore deposit had the shape of a sinkhole infill, extending for a length of 450 to 500 m and a width of 65 to 100 m, and reaching 110 m in its deepest part. Dejonghe *et al.* (1993) considered the La Calamine deposit to be a surficial infill of a paleokarst sinkhole that was developed along a Palaeozoic-Mesozoic unconformity. After Laloux *et al.* (2000), the orebody is also located on a thrust fault (the Schmalgraf Fault, at the front of the Donnerkaul tectonic unit), which can have facilitated the karstification process.

The economic concentrations were lying on Famennian siliciclastic sediments, not directly, but with an intermediate irregular layer of silicified dolomite of very variable thickness at the bottom. The ore was nearly completely oxidised up to a depth of 110 m below present surface, whereas in most other Belgian zinc-lead deposits, sulphides usually predominate already at a depth of few tens of meters. The sulphides (galena, sphalerite, pyrite, marcasite, greenockite) as well as native sulphur (Dejonghe *et al.,* 1983) are extremely rare and preferentially located near the walls of the old pit. The calamine ores occurred as irregular bodies hosted in mottled clays; they were essentially zinciferous, but also mixed with Fe-(hydr)oxydes and very subordinate Pb-minerals. The petrographic assemblage ranged from prevailing smithsonite in the most surficial layers, to a progressive mixture of carbonates and silicates with increasing depth, and to a whole silicates (willemite and Zn-clays) lithology below -80/85 m in depth.

The zinc silicate named "Willemite" was discovered for the first time in a sample of La Calamine orebody. This mineral was described in 1829 by M. Levy and named after Willem I of Orange-Nassau, King of Holland, who had appointed him as Professor at the University of Liège. For description and further mineralogical considerations on zinciferous minerals from Belgian calamines in the older literature, see for example: Levy (1843), Cesàro (1887, 1898, 1908), Servigne (1943) and Mélon *et al.* (1976).

Our preliminary observations have shown at least two distinct forms of willemite agglomerates: a) brownish massive concretions with minute botryoidal terminations (rhombohedric) in druses and radial concretions (Plate 1, c, e; Plate 2, a, b, c) and b) masses of clear, idiomorphic hexagonal, mm-sized crystals with prismatic terminations (Plate 2, d). Microcrystalline, massive willemite also cements a reddish-brown mottled breccia (Plate 1, b), showing evidence of mechanical reworking and chemical dissolution of a possible palaeokarstic infill. In many samples present at the Royal Belgian Institute of Natural Sciences, willemite agglomerates appear to be cut and locally replaced by idiomorphic rhombohedra of iron-rich smithsonite (Plate 1, g_1, g_2; Plate 2, e), while thin and/or platy hemimorphite crystals (Plate 1, f) and rare hydrozincites build the last generations of the non-sulphides assemblage. Globular concretions of smithsonite (Plate 2, f, g) as well as rare monheimite (Fe-smithsonite) (Plate 2, h) have been also recorded. Besides zinc oxidation minerals, also several types of (hydr)oxides occur at the mine site: limonite, goethite, hetaerolite, braunite, manganite, hematite and pyrolusite.

The sulphides (galena, sphalerite, pyrite, marcasite, greenockite) as well as native sulphur (Dejonghe *et al.,* 1993) are extremely rare and preferentially located near the walls of the old pit. From mineralogical interest are also: allophane, aragonite, barite, calcite, dolomite, gypsum, pyromorphite, hopeite, fraipontite, sauconite, kolbeckite, quartz, siderite, hydrozincite and kaolinite. Hopeite $\{Zn_3(PO_4)_2.4H_2O\}$ (Brewster, 1824; Levy, 1843) and fraipontite $\{(Zn,Al)_3(Si,Al)_2O_5(OH)_4\}$ (Cesàro, 1883, 1927; Fransolet & Bourguignon, 1975) were new minerals, also discovered for the first time in samples from La Calamine.

4. Features of the Zn-Pb non-sulphide deposits in Western Germany

Across the border to Germany, in the north Eifel, similar Zn-Pb deposits as those of Belgium (consisting of both primary sulphides and calamine) were exploited in the Aachen-Stolberg district, but their economic potential was much lower than in Belgium. 300,000 tons of Zn and 150,000 tons of Pb were produced until the closure of the last Zn-Pb mine in 1919. The Diepenlinchen Mine (Fig. 1), near Stolberg, with its 320,000 tons Pb+Zn, was the largest operation in the district (Walther, 1986). In a broad outline, the Zn-Pb deposits are located in the same type of stratigraphic and tectonic setting as the above described mineralisations in Belgium. In fact, most of the economic ore deposits were NW-SE veins, cutting both Devonian and Dinantian limestones.

Several deposits, exploited already from the first century A.D. in the Aachen district, carried thick calamine ores, extending from the surface to 60 - max 100 m in depth. Limonite and minor cerussite were known to occur near the Zn-carbonates and silicates. Additional information on the Aachen-Stolberg mining district can be found in Gussone (1964), Scheps & Keyssner (1988) and Walther (1986).

5. Palaeoweathering stages in Belgium and Western Germany and their metallogenetic implications

Dupuis (1992) and Alexandre & Thorez (1995) pointed out that Palaeozoic rocks in Belgium were affected by deep weathering during Permian and Mesozoic periods before the Cretaceous transgression, as well as by multiple weathering phases during Cainozoic. A synthesis on palaeoweathering and related palaeosurfaces from north and east France to Belgium and Luxembourg is also given by Quesnel (2003). Demoulin (2003) made a historical review of scientific research on palaeosurfaces in Ardenne-Eifel areas during Mesozoic and Cainozoic times, quoting up to seven distinct generations of palaeosurfaces. Three of them are of special interest for the aim of this paper: the post-Variscan, the pre-Triassic and the pre-Senonian palaeosurfaces.

As mentioned by Laloux *et al*. (2000), in the Verviers Synclinorium, the top of the Palaeozoic rocks is deeply weathered down from 5 to 30 m. The alterite consists of clays of various colors (white, red, mottled-grey or black) depending on the nature of the underlying rocks. According to Breddin *et al*. (1963), the residual clays were derived from the desaggregation of the post-Variscan palaeosurface, before the deposition of the Santonian sediments (pre-Senonian palaeosurface). However, it is very difficult to draw a clear boundary between the mentioned residual clays and the overlying Santonian clayey sediments (Hergenrath Member), deposited at the base of the Aachen Formation. These clays have been interpreted by Bless (1987) as local reworking of the alterite.

Felix-Henningsen (1990, 1994) mentions in the Rhenisches Schiefergebirge also the existence of distinct saprolite covers exceeding 100 m in depth, whose formation was related to several periods of strong uplift and tectonic dissection. The ages of the saprolites were determined indirectly: a first one has been related to the strong peneplanation which took place between Mesozoic and Early Tertiary and a second to a Late Tertiary weathering phase, proceeding synchronously with the uplift of the entire area since the Oligocene. A very strong episode of ferralitic weathering of Miocene basalts can be eventually related to a short "greenhouse effect" that took place at the end of Miocene.

Palaeoweathering events in Belgium have also economic implications. Typical examples are the Uppermost Jurassic-Lower Cretaceous kaolinised regoliths and the Miocene halloysitic cryptokarsts.

5.1. Uppermost Jurassic-Lower Cretaceous kaolinised regoliths

Studies on the thick kaolinised regolith remnants spanning in age from Uppermost Jurassic to Lower Cretaceous, have been performed throughout Belgium (Dupuis, 1992). The regolith is developed on the post-Variscan palaeosurface, in rocks of various ages and compositions (siliciclastic and carbonate rocks ranging from Cambrian to Silesian). Locally, it is covered by upper Cretaceous sediments (Aachen Formation), whose deposition interrupted the weathering process. In some places, such as Transinne, where kaolinite deposits (China clay) are presently exploited, the regolith may reach a thickness up to 70 m (Dupuis *et al.,* 1996). Dupuis (1992) pointed out that post-Variscan uplift, in combination with an annual rainfall of at least 500-1500 mm (necessary for monosiallitisation process) and the existence of abundant forests (Wealden flora), were a key factor in determining the evolution of the giant regolith.

At Transinne, the weathering process responsible of kaolinite formation has been dated by Yans (2003) with absolute geochronological methods on K-rich hollandite ($BaMn_8O_{16}$) and cryptomelane (KMn_8O_{16}). Two distinct weathering periods can be distinguished:

- Early Cretaceous. K-Ar data on two hollandites reveal apparent ages of 126 ± 10 Ma and 135 ± 15 Ma (from Berriasian to Barremian);
- Early Miocene. Ar-Ar and K-Ar data on cryptomelanes point to an age of 21.1 ± 0.4 Ma.

In the past, Legrand (1968) already mentioned the presence of a rubified zone locally developed on the Palaeozoic rocks of the Brabant Massif, below the cover of Mesozoic and Cainozoic sediments. In particular, in the West Flanders region (Nevele borehole), a thick reddish saprolite was developed on Lower Cambrian silicoclastic rocks (Devillian) and covered by Cretaceous chalk deposits. In the same area, Stoops (1992) and Mees & Stoops (1999) could record the in-situ weathering profile of the Devillian sericite-chlorite phyllite, comparable with those occurring in the present day tropical areas. The process started with the oxydation of pyrite and the kaolinisation of chlorite, followed by the alteration of sericite.

Breddin (1932), Calembert (1947), Schmidt & Wolters (1950) and Knapp (1978) among others have also mentioned deep weathering and red paleosoils on the post-Variscan palaeosurfaces in the Aachen area.

In addition to the formation of red soils on the post-Variscan palaeosurfaces, other kinds of palaeokarstic features related to the same weathering processes have been observed affecting the Palaeozoic carbonates. In the Maastricht area (The Netherlands), Batten *et al.* (1987) observed a paleokarst erosion surface developed at the top of Dinantian limestones. This erosion surface has been recorded in a few boreholes drilled some kilometres to the east of Maastricht, but also at Valkenburg and at s'Gravenvoeren, a Belgian locality SW of Maastricht. From the analyses of the s'Gravenvoeren borehole, Batten *et al*. (1987) could deduce that, at the time of deposition of the Cretaceous Hergenrath Clay Member, open karstic features deepened into the Dinantian limestone, at least until 250 m down below the present-day surface, and were locally infilled. They could observe also that the uppermost lithologies of the Dinantian limestones in south Limburg (The Netherlands) and at Les Fourons (Voeren) in Belgium, had been extensively exposed to strong weathering which caused deep karstification of the carbonate rocks, followed by their partial silicification. The authors assume that this deep karstification may date back to the Jurassic and/or Early Cretaceous, and that warm and wet conditions were responsible for the lateritic alteration of the Visean shales resulting in the formation of a kaolinitic paleosoil. An indirect evidence of this karstification age, is given by the analyses performed by Muchez *et al.* (1998) on calcite cements sampled in a palaeokarstic cavity along the river Meuse. In fact, the latter authors assume that calcite precipitated in the cavity after Mid-Jurassic (Cimmerian) uplift and subsequent erosion, but before Late Cretaceous strike-slip movement. This interpretation is based on the climatic change from semiarid to humid conditions, recorded by the variation in ^{13}C and ^{18}O isotopic ratios in the analysed cements.

Another evidence of a particular climate in this part of Europe during Cretaceous could be derived from the ferricrete occurrence denominated *"borne de fer"* in Lorraine, close to Luxembourg, dated to 120-130 Ma by Théveniaut *et al.* (2002) with paleomagnetic methods.

5.2. Miocene halloysitic cryptokarsts

Halloysite accumulations occur at the bottom of giant cryptokarsts (100 to 150 m deep), infilled by Oligocene marine sands and Neogene continental deposits in the Entre-Sambre-et-Meuse and Condroz areas (Dupuis, 1992; Dupuis *et al.*, 2003). These occurrences are known where a carbonate substratum, covered by a thin veneer of permeable rocks (e.g. marine sands) is in turn overlain by continental (fluviatile, palustrine and lacustrine) sediments rich in organic matter and pyrite, which might have released organic and/or moderate sulphuric acid solutions. During part of the Neogene (mainly Miocene) continental periods, karstic dissolution of the topmost limestone was induced below the permeable sands. As a result, deep sinkholes began to develop under the Cainozoic cover (= cryptokarst or cryptolapiaz). This phenomenon was facilitated by percolation of moderately acid fluids, which bleached and locally leached the Cainozoic permeable rocks, while producing kaolinite in near surface conditions and a temperate/warm climate. These solutions were buffered at the limestone contact, precipitating alumina gel from which massive halloysite and associated kaolinite crystallised (Ertus *et al.,* 1989). To carry out this process, favourable paleoclimatic conditions were required, allowing the development of an extensive vegetation cover.

However, although the presence of halloysite as an accessory mineral in several Zn-Pb ore deposit of the Verviers Synclinorium has been mentioned locally (Dejonghe & Jans, 1983), the palaeokarstic "calamine"-type deposits are broadly related to the post-Variscan erosional palaeosurface and do not seem to have been deposited in cryptokarsts. In fact, the calamine-filled cavities do not contain any detritus of collapsed Meso-Cainozoic sediments: most of these deposits predate the deposition of the Cretaceous as well as the Cainozoic cover.

Also in many parts of the Rhenisches Schiefergebirge in Germany, feldspar-rich rocks were intensively kaolinised during Cretaceous and Lower Tertiary (Lippert *et al.*, 1968), but the resulting residual deposits were almost completely eroded, and preserved only in tectonic depressions and under the protective cover of younger sediments. More in the south, the supergene kaolins from Bavaria have been dated by Gilg (2000) as belonging to two main weathering phases: the first one occurring during Early Cretaceous and the second dating from Late Oligocene to Mid-Miocene.

6. Discussion

The Jurassic to Early Cretaceous kaolinised regoliths that developed on the post-Variscan palaeosurface, could be a parallel expression of the strong weathering event, which produced the non-sulphide Zn-ore deposit from Belgium and north Eifel. One of the reasons why the palaeoweathering hypothesis can be advanced is the fact that the depth of oxidation reached in most primary sulphide veins and associated flats in east Belgium and adjacent areas, is substantially below the present-day water table. This is especially true for the huge La Calamine deposit, where non-sulphide mineralisation has been exploited until more than 100 m in depth from surface outcrops.

Most of the primary sulphide deposits in east Belgium and nearby areas have been truncated and unconformably covered by the sediments of the Aachen Formation (Santonian). This demonstrates not only that they were formed before the deposition of the Aachen Formation, but also that they might have undergone the same Uppermost Jurassic-Lower Cretaceous weathering processes, including deep karstification and development of oxidation-cementation profiles in the mineralised sections, which produced elsewhere in Western Europe the kaolinised regoliths on the siliciclastic lithotypes.

If a positive connection may be found in Belgium between Zn-gossans (as can be also considered the "calamine" ore) and Jurassic to Early Cretaceous kaolinised regoliths, there is however no evidence for such a connection between Zn-gossans and Miocene halloysitic cryptokarsts. Cainozoic weathering has probably not played a major role on the already weathered ore deposits, as they probably did not crop out during this period, at least in east Belgium. Indeed, up to 465 m of Cretaceous formations are intercalated between the Variscan palaeosurface and the Cainozoic beds. Thus, during the Cainozoic, the non-sulphide Zn deposits where covered, and hence protected from erosion, by several hundreds meters of sediments. In the Verviers Synclinorium the Cretaceous and Cainozoic cover was never completely eroded, as in other places of the Ardenne. The base of the Aachen Formation was never deformed and has never filled basement sinkholes, as it is the case for the Miocene cryptokarsts.

During the Quaternary (since ± 2 Ma), even if the Zn-gossans already formed during Jurassic-Lower Cretaceous were again outcropping, weathering and oxidation would have played a minor role as the climate in this part of Europe was cold to very cold, with only short periods of interglacial releases. Several glacial periods are indeed recorded in Europe from 400,000 to 10,000 years ago, but glaciers never reached Belgium.

About the genesis of the La Calamine giant orebody, Dejonghe & Jans (1983) considered this deposit as the infill of a paleokarst sinkhole, related to the Palaeozoic-Mesozoic unconformity. In this interpretation, however, the significant occurrence of willemite was not particularly taken into account.

In the recent literature (Brugger *et al.*, 2003; Groves *et al.,* 2003; Hitzman *et al.*, 2003) the willemite concentrations occurring in economic amounts in Proterozoic carbonates of southern hemisphere, have been often considered of hydrothermal origin. In fact, according to Brugger *et al*. (2003), it is uncertain whether carbonate-hosted willemite deposits could form by supergene or hypogene fluids. Additional data from Vazante (Brazil), Beltana (Australia), and Kabwe (Zambia) point to willemite formation at temperatures in excess of 150°C under oxidizing (hematite stable) conditions (Hitzman *et al.,* 2003). After the mentioned authors, in the absence of sulphide sulfur, willemite is predicted to form instead of sphalerite under more oxidizing (e.g. magnetite-hematite, sulfate predominant) or alkaline (high pH) conditions, especially at temperatures higher than approximately 150°C.

Preliminary fluid inclusion analyses (Plate 1, h, i) have been performed on few willemite specimens from La Calamine and from the Welkenraedt area (no measurable inclusions were found in smithsonite) (Boni *et al*., 2004a). 80% of the inclusions are monophase (L) and 20% liquid-rich two-phase (L+V). Albeit widespread necking-down and leakage phenomena have been observed, homogenization temperatures, ranging between 80 and 190°C, could be measured in two-phase inclusions; Tm data suggest salinities between 0 and 5 wt. % NaCl equiv. The homogenization interval does not differ from the temperature range measured in other willemite ores in the world considered of hydrothermal origin (Hitzman *et al*. 2003), whose salinities, however, are much higher than those encountered in our willemites.

The fluid inclusion data from the willemites, due to the brittle structure of this mineral, are in our opinion not yet conclusive for the genesis of the deposits. On the other hand, if real, these high temperatures would pose a problem to the traditional supergene interpretation of the Belgian calamines (Dejonghe, 1998). The supergene interpretation seems to be still valid for the smithsonite phase, considering its typical stable isotopic pattern recently established by Boni *et al*. (2004b). At this stage, there are only few likely explanations for the measured temperatures:

- to assume the existence of an anomalous temperature gradient, active during the segregation of willemite before the sedimentation of the Cretaceous Aachen Formation;
- to consider a post-willemite thermal rise in the whole district, that allowed a complete re-equilibration of the inclusions' temperature;
- to assume a stretching mechanism (mechanical deformation related to the reactivation of older tectonic lineaments, like the one oriented SW-NE trending Moresnet fault occurring at La Calamine).

7. Conclusions

Critical features for oxidation of primary sulphides and formation of secondary Zn-ores are tectonic uplift and brittle fracturing, paired with favorable climatic conditions (hot and humid), which could allow the development of extensive weathering profiles. Several periods of hot and humid climatic conditions typical of tropical weathering have been recorded in several European regions during Cretaceous and Early Tertiary, causing the deposition of bauxites and lateritic clays. These periods were also favorable to the development of extensive gossans on primary sulphides, especially if these were carbonate-hosted Mississippi Valley Type or Sedex-type mineralisation.

In Belgium, because the primary ores are possibly of Upper Jurassic age, the formation of the calamine ore reached its maximum in the Cretaceous, before the deposition of the Aachen Formation of Senonian (= Upper Cretaceous) age.

However, the presence of abundant willemite in the Belgian mineralization, especially at La Calamine is still enigmatic, and further work is required to determine if it is related to hydrothermal processes as in other deposits discussed in the recent literature (Brugger *et al*., 2003; Hitzman *et al*., 2003), or can be considered a rather exotic product of infra-Mesozoic weathering.

8. Acknowledgments

This is the second contribution to an EC-funded project (M.Boni & L.Dejonghe) on "The non-sulphide Zn-ores in Belgium: a new perspective" where have been used the facilities of Royal Belgian Institute of Natural Sciences (RBINS). The help of O. Retout and I. Van de Velde (international co-operation RBINS, management of the Access to Belgian Collections Programme) and M. Deliens (curator of the mineralogical collection at RBINS) is here warmly acknowledged. We want also to thank G. Balassone and V. Coppola of the University of Napoli for their help with the analytical work. Helpful reviews were provided by Ph. Muchez and an anonymous reviewer.

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Manuscript received on 7.05.2004 and
accepted for publication on 1.12.2004.

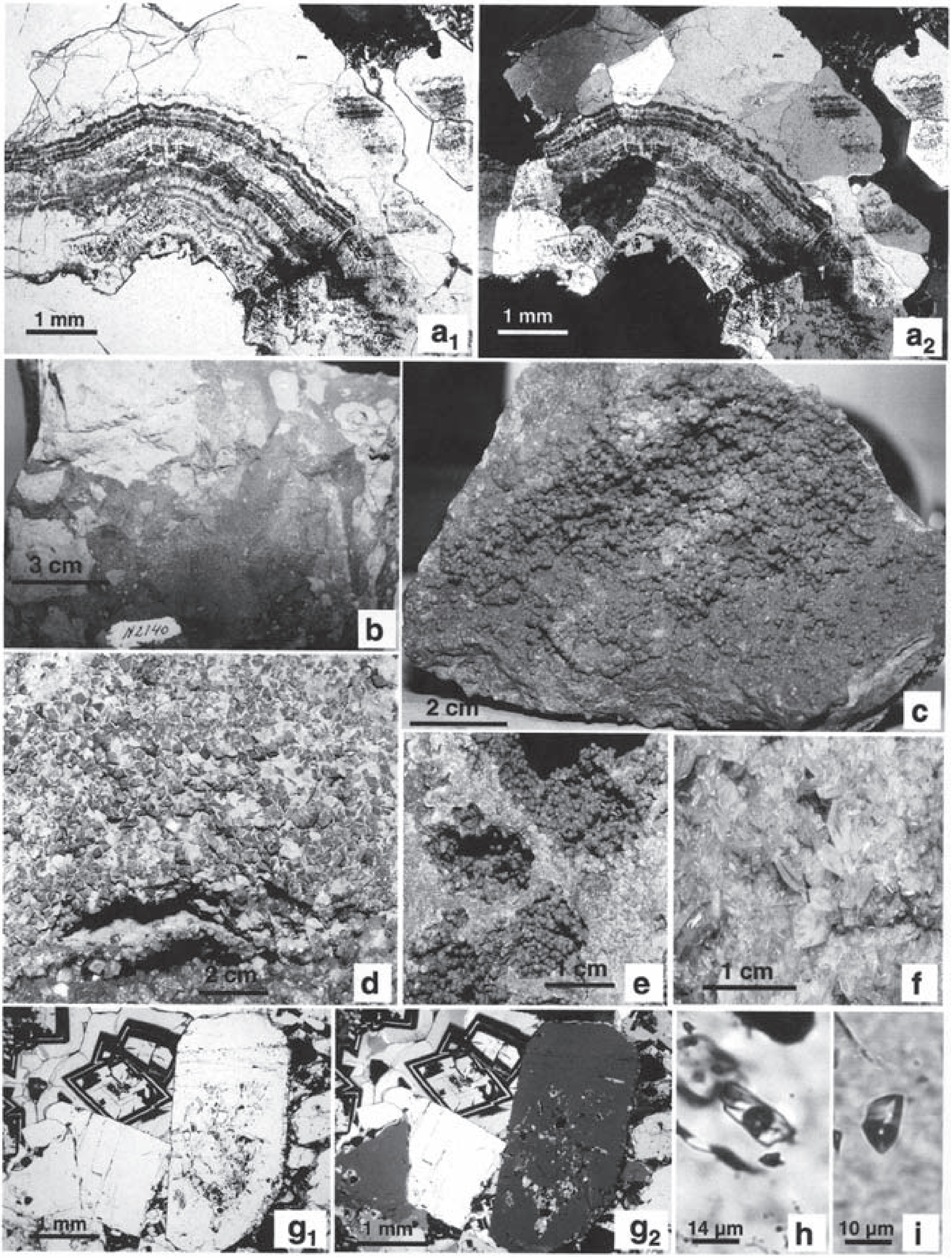

Plate 1. a1. RA5011. La Calamine: ghost of "schalenblende" structure replaced by willemite. a2. same, in N+; b. RN2140. La Calamine: dissolution breccia, cemented by microcrystalline willemite; c. RN3856. La Calamine: microglobules of reddish willemite; d. RN2005. La Calamine: idiomorphic crystals of smithsonite growing on willemite; e. RN2140. Willemite concretions (enlargment of b); f. RA4790. La Calamine: platy hemimorphite crystals; g1. RN2224. Welkenraedt: willemite laths replaced by zoned Fe-smithsonite; g2. same, in N+; h. RN2224. Welkenraedt: two-phase fluid inclusion in willemite; i. Museo Mineralogia Napoli. La Calamine: two-phase fluid inclusion in willemite. The numbers of the samples refer to the catalogue of the Royal Belgian Institute of Natural Sciences, with the exception of i.

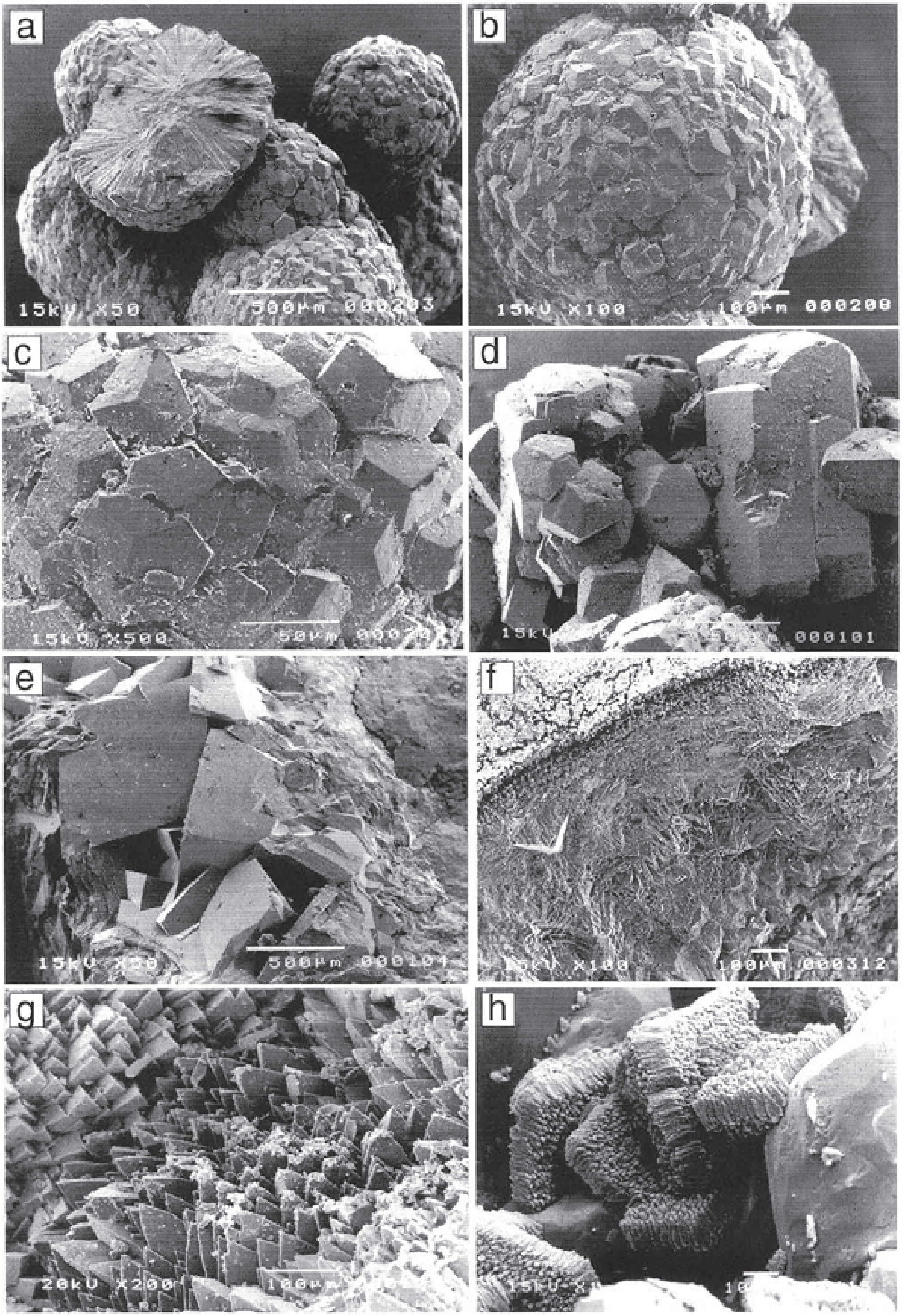

Plate 2. a-b-c. RN3856. La Calamine: SEM images of globular concretions of willemite, the terminations of the crystals are rhombohedral; d. Museo Mineralogia Napoli. La Calamine: willemite as idiomorphic hexagonal crystals; e. RN2224. Welkenraedt: smithsonite crystals growing on massive willemite and partly replacing it; f. RN4986. Welkenraedt: Zoned , globular smithsonite; g. enlargement of f.: rhombohedral terminations of globular smithsonite concretions; h. RN2298. Fossey: monheimite (Fe-smithsonite) aggregates. The numbers of the samples refer to the catalogue of the Royal Belgian Institute of Natural Sciences, with the exception of d.