

## STATE OF THE ART ON THE “CALAMINE”-TYPE ZINC DEPOSITS OF BELGIUM

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(3 figures)

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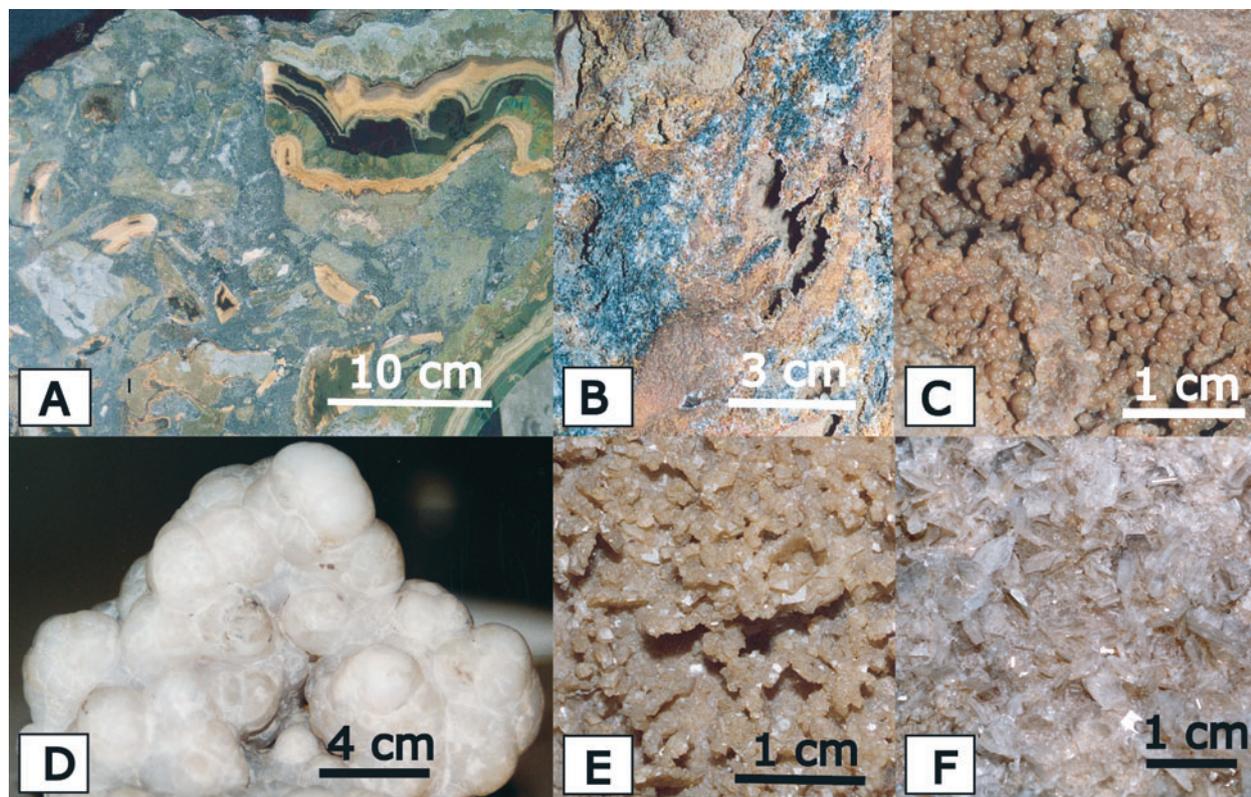
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### Introduction and geological setting

The Belgian “Calamine”-type nonsulphide Zn deposits, mainly located in the Verviers Synclinorium in the northeastern part of the country, represent the historical basis for zinc mining and smelting industry in Europe. The most important was the La Calamine orebody (more than 600,000 tons of Zn metal) that was continuously exploited for several centuries. Nonsulphide ores associated to sulphides, were also exploited at Schmalgraf, Engis,

Dickenbusch, Fossey, Rocheux-Oneux, Welkenraedt and other smaller deposits (Dejonghe, 1998). Across the border to Germany, in the north Eifel, similar Zn-Pb deposits as the Belgian ones (also consisting of both primary sulphides and calamines) were exploited in the past in the Aachen-Stolberg district, but their economic potential was much lower than in Belgium.

The primary Zn-Pb sulphide mineralization consists of post-Variscan hydrothermal veins and replacement- and breccia bodies (Fig. 1A), mostly occurring at the top of



**Figure 1:** A. La Calamine: primary sulphide breccia ore: zoned collomorph sphalerite fragments with minor galena are cemented by a microcrystalline sulfide assemblage; B. La Calamine: sphalerite bands (blue) partly replaced by microcrystalline willemite (red-brown); C. La Calamine: willemite as reddish microglobules; D. La Calamine: globular smithsonite concretion; E. La Calamine: crusts of scalenohedral smithsonite; F. La Calamine: hemimorphite crystals on the surface of a smithsonite sample. Collections of the Royal Belgian Institute of Natural Sciences, Brussels.

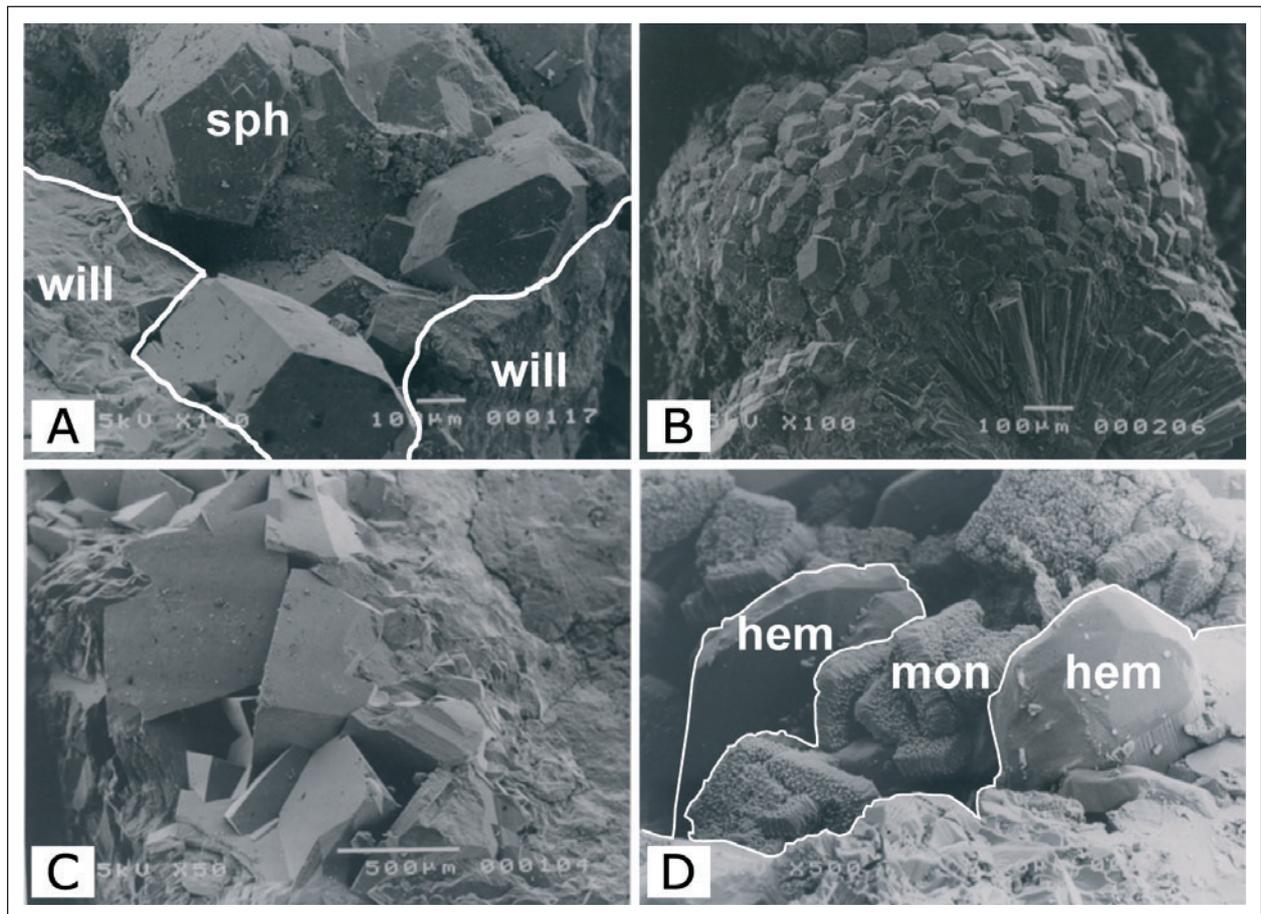
Dinantian (Visean) limestones. The sulphides, whose formation should date back to the end of Jurassic (Heijlen et al., 2001), intersect the Palaeozoic rocks and are truncated and unconformably covered by Late Cretaceous sediments (Santonian Aachen Fm). The same stratigraphic setting has been observed for the nonsulphide ores, thus suggestive of a pre-Late Cretaceous weathering (Lespineux, 1905; Dejonghe, 1998).

### Nonsulphide ores

The Belgian nonsulphide zinc ores consist of a mixture of Zn silicates [willemite =  $Zn_2SiO_4$ , hemimorphite =  $Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$  and Zn clays] (Fig. 1B, C & F; Fig. 2A-B) and Zn carbonates [smithsonite =  $ZnCO_3$  and hydrozincite =  $Zn_5(CO_3)_2(OH)_6$ ] (Fig. 1D & E; Fig. 2C & D). Limonite, minor cerussite and other, more exotic mineral species, have been recorded together with the Zn-carbonates and silicates (Dejonghe & Boni, 2005).

The extensive occurrence of willemite, that appears to be the first deposited nonsulphide mineral replacing

sphalerite (Fig. 1B; 2A), is a striking particularity of the Belgian calamines, which differentiates them from other nonsulphide Zn ores in Europe (Boni & Large, 2003). Fluid inclusions in willemite from La Calamine and Welkenraedt ore deposits were studied by Boni et al. (2005). Most fluid inclusions of willemite (80%) and all inclusions in smithsonite are monophasic (aqueous), pointing to a low temperature depositional environment. Homogenization temperatures of the more rare two-phase inclusions, occurring only in willemite, display a large variation between 80 and 190°, an interval matching the temperature ranges of other willemite ores throughout the world. Indeed, at the world scale, willemite is found in a wide variety of geological environments: it is a common accessory mineral formed during the low-temperature alteration of zinc-sulfide ores and it can also form from hydrothermal fluids with a range of temperatures from < 100°C to approximately 250°C (Brugger et al., 2003; Hitzman et al., 2003). Nevertheless, the Belgian willemites have always been considered as supergene oxidation products of primary sulphide ores (Dejonghe, 1998; Dejonghe & Boni, 2005), because both their structure and

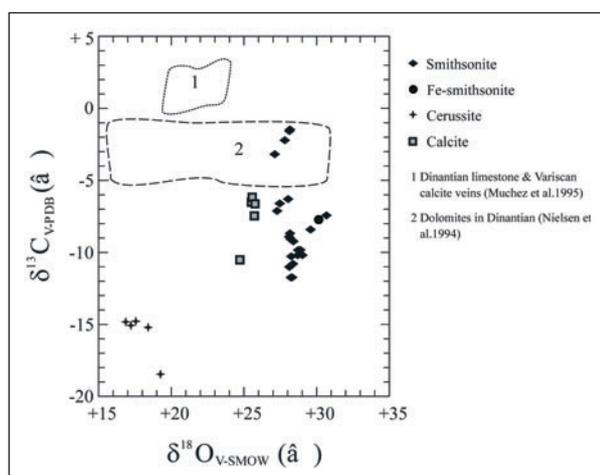


**Figure 2:** SEM micrographs of willemite and smithsonite samples. A. La Calamine: willemite (will) replaces sphalerite (sph) crystals; B. La Calamine: microcrystalline terminations of willemite spheroids in botryoidal aggregates; C. La Calamine: smithsonite (sph) filling a vein in willemite; D. Fossey: Fe-smithsonite (monheimite) among hemimorphite laths. Collections of the Royal Belgian Institute of Natural Sciences, Brussels.

mineralogical association argue against the deposition of this mineral from hot hydrothermal fluids. The locally high temperatures may have been caused either by post-entrapment tectonically induced deformation of the fluid inclusions (Boni et al., 2005), or by heterogeneous entrapment of air and water within the vadose zone.

The stable isotope range of Belgian smithsonites and cerussites (Coppola et al., in press) (Fig. 3) is very similar to the isotopic intervals measured in other supergene nonsulphide deposits in the world (Gilg & Boni, 2004). Calcites coeval with nonsulphide ores follow (with some difference) the isotopic behaviour of metal carbonates. Carbon isotopes in Zn-carbonates show a considerable range of values from -11.6 to -1.6‰ V-PDB, while Pb-carbonates range from -18.4 to -14.7‰. These broad ranges point to mixing processes between at least two different sources of carbon: a <sup>13</sup>C-depleted carbon (derived from the organic matter of C3 plants in the overlying soils) and a <sup>13</sup>C-enriched carbon, originated from dissolution of the carbonate host rocks. Smithsonites exhibit a limited interval of δ<sup>18</sup>O values from 27.1 to 30.6‰, averaging 28.4‰ ± 0.8‰ V-SMOW (Coppola et al., in press). Cerussites have oxygen isotope values ranging from 16.8 to 19.3‰, averaging 17.8 ± 1.0‰.

The relatively small variability of the oxygen isotope values for the carbonate minerals in the calamines (<1%, 1σ), suggests that both temperatures and oxygen isotope composition of the waters did not change much during oxidation. The calculated values of the waters precipitating the Zn, Pb and Ca-carbonates in the Belgian calamines are around -6.2‰ δ<sup>18</sup>O<sub>SMOW</sub>, while the present-day meteoric waters in NE Belgium have δ<sup>18</sup>O values ranging between -6.8 and -8.1‰ (Beyer, 1995).



**Figure 3:** Plot of δ<sup>13</sup>C vs. δ<sup>18</sup>O for smithsonite, cerussite and cogenetic calcite from Belgian nonsulphide ores (modified from Coppola et al., in press). Field 1 depicts the isotope compositions of Dinantian limestones and Variscan calcite veins throughout the mining district (Muechez et al., 1994). Field 2 comprises all the published values for several generations of Dinantian dolomites (Nielsen et al., 1994).

## Age of the nonsulphide deposits

The occurrence of truncated nonsulphide deposits below cover of the Aachen Formation (Timmerhans, 1905) demonstrates not only that the nonsulphide deposits were formed before the deposition of these Late Cretaceous sediments, but also that they might have undergone the same Early Cretaceous weathering processes, including deep karstification and development of oxidation-cementation profiles in the mineralized sections, that have produced elsewhere in Belgium and in other European areas a wide series of kaolinized regoliths (Dejonghe & Boni, 2005). On the base of absolute dating methods, Yans (2003) could individuate two distinct weathering periods responsible for the genesis of the Belgian kaolinite deposit of Transinne: early Cretaceous (126 ± 10 and 135 ± 15 Ma) and early Miocene (21.1 ± 0.4 Ma). The oxygen isotopes of the meteoric waters that should have precipitated the early Cretaceous kaolinites at Transinne, have a value (calculated by Yans, 2003) of -6.1‰ δ<sup>18</sup>O<sub>SMOW</sub>, which is in accord with the values of meteoric waters precipitating other European kaolinite deposits of similar age (Gilg, 2000). After our calculations, also the meteoric waters involved in the formation of the nonsulphide ores have values of -6.2‰ δ<sup>18</sup>O<sub>SMOW</sub>, perfectly comparable with the data of Yans (2003). Thus, an old (possibly Cretaceous) age of the weathering phase responsible for the formation of the Belgian calamines could be also confirmed by the oxygen isotopic data on the Zn-, Pb- and Ca-carbonates.

## Conclusions

The Zn-Pb sulphide deposits of Eastern Belgium have undergone a polyphase history, which started with a possibly Jurassic sulphide precipitation, followed by their oxidation under high silica activity (causing willemite precipitation) and then by frankly supergene weathering. At least the processes causing willemite deposition could have had a pre-Late Cretaceous timing, in common with other paleoweathering evidences in Western Europe. It is also possible that the deposition of the willemite concentrations could have been derived from low-temperature, localized hydrothermal processes operated by deeply reaching oxidizing fluids. Unfortunately, we were not able so far to carry out isotopic measurements on the Belgian willemites, which could help to unravel their genetic processes. Cerussite, hemimorphite and smithsonite, the latter often developed at the expenses of willemite, have all the characteristics of supergene oxidation products.

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