

Willemite in the Belgian non-sulfide zinc deposits: a fluid inclusion study

MARIA BONI¹*, VITO COPPOLA¹, LÉON DEJONGHE² and LUCA FEDELE¹¹ Dipartimento di Geofisica e Vulcanologia, Università di Napoli Federico II, Via Mezzocannone 8, 80134 Napoli, Italy² Geological Survey of Belgium, 13 Rue Jenner, B-1000 Brussels, Belgium

Submitted, June 2004 - Accepted, February 2005

ABSTRACT. — European non-sulfide Zn deposits, mainly hosted in carbonate rocks and considered so far of supergene origin, represent the historical basis for zinc mining and smelting industry. They were called «Calamine», from the famous Belgian locality where a mixture of Zn-carbonates {smithsonite = ZnCO_3 , hydrozincite = $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, Zn-silicates {hemimorphite = $\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})_2\cdot\text{H}_2\text{O}$, willemite Zn_2SiO_4 } and Zn-clays has been exploited for centuries. A fluid inclusion study has been carried out on Belgian willemite samples, in order to gain information on temperature and salinity of the fluids involved in the formation of the non-sulfide ore deposits. Among all (observed?) inclusions, 80% are monophasic (L) and 20% liquid-rich two-phase (L+V). Albeit widespread necking-down and leakage phenomena have affected most of the fluid inclusions trapped, a reliable set of homogenization temperatures, ranging between 80 and 190°C, has been collected from the two-phase inclusions. Tm data suggest salinities between 0 and 5 wt. % NaCl equiv. The detected Th intervals match temperature ranges measured in other willemite ores throughout the world, part of which are considered of hydrothermal origin. These fluid inclusion data pose many questions on the genesis and evolution of Belgium non-sulfide deposits.

RIASSUNTO. — I depositi a non-solfuri di zinco in Europa, generalmente considerati di origine supergenica, sono ospitati in rocce carbonatiche ed hanno rappresentato la base storica dell'industria estrattiva e della lavorazione dello zinco. Essi vengono denominati «Calamine», dal nome della famosa omonima località del Belgio: sono costituiti da una miscela di carbonati e silicati di zinco {smithsonite = ZnCO_3 , hydrozincite = $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, hemimorphite = $\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})_2\cdot\text{H}_2\text{O}$, willemite Zn_2SiO_4 ed argille zincifere}. Sono state effettuate misure termometriche sulle inclusioni fluide delle willemite belghe, allo scopo di determinare la temperatura e salinità dei fluidi che hanno contribuito alla formazione dei depositi a non-solfuri. Delle inclusioni osservate, l'80% sono monofase (L) ed il 20% bifase a liquido prevalente (L+V): è stato possibile misurare solo queste ultime. Nonostante la presenza di estesi fenomeni di *leakage* e *necking-down*, di queste ultime è stato possibile raccogliere una serie affidabile di misure di omogeneizzazione che sono distribuite in un campo tra 80 e 190 °C. I dati delle Tm suggeriscono basse salinità: tra 0 e 5 wt. % NaCl equiv. L'intervallo delle temperature di omogeneizzazione non differisce dagli intervalli di temperatura riscontrati in altri depositi a willemite nel mondo, alcuni dei quali sono considerati di origine idrotermale. I risultati analitici delle inclusioni fluide aprono una nuova problematica sulla genesi e l'evoluzione dei depositi a non-solfuri del Belgio.

* Corresponding author, E-mail: boni@unina.it

KEY WORDS: *Willemite, non-sulfides, Belgium, fluid inclusions*

INTRODUCTION

European non-sulfide zinc deposits represented the historical basis for zinc mining and smelting industry. Based on their geological characteristics, they have been assigned mainly to the «Calamine» group, genetically derived from supergene alteration of carbonate-hosted MVT and Sedex deposits (Large 2001, Boni & Large 2003).

The word «Calamine» originates from the Belgian locality La Calamine, where a non-sulfide zinc deposit was continuously exploited from the 14th century up to 1884, with a production of more than 600.000 tons of Zn metal. Since its discovery, «Calamine» became a mining expression to describe a mixture of zinc-oxidated minerals in earthy or crustified masses with iron (hydr)-oxides and clays. The morphology of the non-sulfide zinc concentrations observed in most mines throughout the world, ranges from bulk replacement bodies of host carbonates and/or sulfides in the deepest levels, through amorphous and microcrystalline aggregates, to the concretionary infilling of isolated druses and cavities in the upper zones (Boni *et al.* 2003). The non-sulfide zinc mineralization in Europe is thought to record distinct periods of uplift, oxidation, and subsequent fossilization of the weathering profiles from Permian onward. Therefore, many of the factors governing the formation and distribution of supergene non-sulfide mineralization, may be common to many deposits in several European countries (Boni & Large 2003).

Contrary to the usual mineral assemblage of known European non-sulfides where smithsonite and hemimorphite prevail, the major «La Calamine» deposit in Belgium, as well as other small mineral occurrences throughout the country, contains very high percentages of the Zn-silicate willemite (Zn_2SiO_4). A fluid inclusion study has been

carried out on willemite samples, in order to gain information on temperature and salinity of the fluids involved in its formation. Albeit when dealing with willemite fluid inclusions data, one has always to keep in mind the statement by Groves *et al.* (2003) that «...owing to brittle crystal structure, fluid inclusions in willemite are fragile and one must use caution when interpreting the results», this set of data poses many questions on the genesis and evolution of the non-sulfide deposits in Belgium.

GEOLOGICAL SETTING AND SULFIDE ORES

The non-sulfide zinc deposits are located in the structurally complex Verviers Synclinorium (Graulich *et al.* 1984), between Liège and Aachen (Fig. 1).

In Belgium the pre-Permian basement underwent a first deformation during the Caledonian and was deformed again during the Variscan orogeny, together with the post-Caledonian Paleozoic cover. The main Variscan tectonic phase commenced at the end of Westphalian (Asturian phase). The post-Variscan cover is tabular and sub-horizontal. It is generally accepted that, following the Variscan orogeny, Permian sediments in Belgium were deposited and then removed by erosion. Possible relicts are preserved in the Malmédy Graben, where red fluvio-lacustrine sediments could have been deposited under semi-arid climatic conditions (Bultynck *et al.* 2001). In the Verviers synclinorium Triassic and Jurassic sediments are unknown: they might have been completely eroded following a strong uplift during the Middle Jurassic (Vercoutere & Van Den Haute 1993). Upper Cretaceous sediments unconformably cover the folded Paleozoic rocks. This succession starts with the deposition of the Aachen Formation (Breddin 1932) of Santonian age, overlain by the Vaals Formation (Felder 1975) of Campanian age and then by the Gulpen Formation (Upper Campanian to Maastrichtian). Cenozoic sediments follow.



Fig. 1 – Sketch map of the Zn-Pb districts in Belgium, showing the location of the primary and secondary deposits (modified from Dejonghe, 1998).

The uplift of the whole area started in the Upper Oligocene and continued during Neogene, up to the present. Since the Oligocene, the uplift reached a maximum of 500 m locally. In some parts of Eastern Belgium, the result of this uplift and related erosion has been the complete stripping of nearly all the Cretaceous and Cenozoic cover. This was, however, not the case in most of the Verviers Synclinorium. After Demoulin (2003), the uplift may be tentatively linked with the lithospheric buckling induced along the front of the developing Alpine orogeny. Alternatively, it could also be related to the plume activity associated with the Eifel volcanism (Ritter *et al.* 2001).

With the exception of La Calamine, the non-sulfide deposits are overlying primary Zn-Pb sulfide orebodies, set in a post-Variscan extensional fault network parallel to the northern sector of the Rhine tectonic graben. The sulfide orebodies consist of hydrothermal veins, cutting the deformed carbonate successions of Carboniferous age, that are connected to stratabound «flats» or «mantos» branching off them. The age of their emplacement is constrained between the end of the Variscan orogeny (± 295 Ma) and the beginning of the Upper Cretaceous (± 100 Ma). It has been proposed to date the main hydrothermal mineralizing event at the end of the Jurassic (≈ 150 Ma) (de Magnée 1967, Heijlen *et al.* 2001).

THE «CALAMINES»

Characteristics of the ores

Gossan-type concentrations representing the oxidation products of Fe, Pb and Zn sulfides were exploited on top of the primary ores in the NE of the country (Fig. 1), which locally replace the carbonate country rocks (Dejonghe *et al.* 1993). The most important resources of Zn non-sulfide ores were exploited until the first half of the 20th century in the upper parts of Schmalgraf, Engis, Dickenbusch, Fossey, Rocheux-Oneux, Welkenraedt and other smaller deposits. The oxidized bodies usually extended down from the surface to an average of 40 to 50 m in depth, sometimes even more. Their mineralogy was very variable, consisting mostly of a combination of Zn-carbonates and silicates, among which willemite was always a substantial component. Pb- and Fe-minerals were also present, even if in variable amounts.

La Calamine deposit, located in easternmost Belgium, was one of the first non-sulfide zinc resources to be developed. The deposit is known by various names (e.g. Vieille Montagne, from the name of the exploiting company, Altenberg or Moresnet) and the denominations of the many samples from this deposit in museums and private collections are also highly variable. The ore deposit site has been rehabilitated and is no longer accessible for study. Dejonghe (1998) and Dejonghe *et al.* (1993) described the deposit as an enormous lenticular pocket located in the nose of a narrow syncline of Devonian-Carboniferous sedimentary rocks that plunges about 15° SW. The orebody overlies Famennian siliciclastic rocks and is overlain by Tournaisian (Lower Carboniferous) carbonates with a basal layer of silicified dolomite. La Calamine deposit is crossed by the Moresnet fault, an old Variscan longitudinal thrust fault, with a SW-NE direction (Ghysel *et al.* 2000). The dimensions of the deposit that was exploited to a depth of 110 m, were 450 to 500 m in length and 65 to 100 m in width. It consists entirely of non-sulfide zinc ore, whereas in all other Belgian

deposits, sulfides always predominated at depth.

The ore is essentially zinciferous with only traces of lead and is mixed with Fe and Mn (hydr)-oxides. It occurs as irregular bodies in collapse breccias and in mottled clays. It consists primarily of Zn-carbonates at the surface, progressively mixed with Zn-silicates with increasing depth, to a totally silicate assemblage dominated by willemite (often described as forming detrital blocks) below a depth of 80 m. Zn-clays (sauconite and fraipontite) occur locally from the surface to a depth of 50 m. Significant amounts of hemimorphite were recorded in the uppermost levels of the mine.

The Willemite

The zinc silicate named «Willemite» was discovered for the first time in a sample of La Calamine orebody and dedicated by B. Lévy to the King Willem of Orange. In fact, most of the famous specimens in many mineralogical museums around the world were sampled from this mine when still in operation. At least two distinct forms of willemite occur:

a) brownish massive agglomerates of roundish radial concretions with minute botryoidal terminations (rhombohedra). Microcrystalline, massive willemite also cements a reddish-brown mottled breccia, showing evidence of mechanical reworking and chemical dissolution of a possible paleokarstic infill;

b) masses of clear, idiomorphic hexagonal, mm-sized crystals with prismatic terminations (Fig. 2a).

In many samples from the Royal Belgian Institute of Natural Sciences at Brussels, willemite agglomerates appear to be cut and locally replaced by idiomorphic rhombohedra of several generations of smithsonite (Fig. 2b), whereas thin and/or platy hemimorphite crystals and very rare hydrozincite build the last generations of the non-sulfide assemblage (Dejonghe & Boni in press).

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 and Cambrian carbonates of southern hemisphere, have been often considered of hydrothermal origin. In fact, according to Brugger *et al.* (2003), it is uncertain whether supergene or hypogene fluids could have formed carbonate-hosted willemite deposits. 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). According to these authors, in the absence of sulfide sulfur, precipitation of willemite is preferred instead of sphalerite, especially at temperatures higher than 150°C, under more oxidizing or alkaline conditions.

METHODS OF STUDY AND MICROTHERMOMETRIC RESULTS

Microthermometric analytical measurements on fluid inclusions have been carried out at the Dipartimento di Geofisica e Vulcanologia of the University of Napoli Federico II, using a Linkam TH 600 stage. The stage was calibrated using synthetic fluid inclusions (Bodnar & Sterner 1987), precision is ± 1 °C in the temperature range of interest. More than 60 liquid-rich two-phase (L+V) inclusions, both primary and secondary in origin, were measured in willemite samples representative of a small number of mine localities (see Table 1).

Primary inclusions (about 60% of the total) occur isolated or in small clusters and do not relate to cleavage or fractures (Fig. 2c,d). Leakage was easily detected in many inclusions, which were avoided during microthermometry or discarded after measurement when an increase in bubble dimension was detected during or after the experiments. Occasionally, phenomena such as the disappearance of the bubble during freezing, made impossible to determine Th or Tm.

Inclusions are irregular in shape and range in length from 2µm to 30µm (Fig. 2d,e). Primary monophasic, liquid only, inclusions in willemite are rather frequent (80% of the total observed). Presence of liquid was detected by freezing and subsequent melting, however no bubble could be generated on freezing despite repeated efforts. This made impossible to attempt any reliable salinity measurement (i.e. Tm) on these inclusions by microthermometry.

Secondary monophasic inclusions are very common, albeit generally very small (few microns), lined along a network of small fractures crossing the contacts between crystals (Fig. 2f). Secondary two-phase inclusions are more rare and few of them were measured. Rare monophasic liquid-only inclusions could be observed, but not measured, also in smithsonite and post-willemite quartz crystals. The occurrence of monophasic liquid-only (primary but also secondary) inclusions in all minerals points to a prevailing low-temperature system (< 50°C) (Groves *et al.* 2003).

Due to the brittle behavior of willemite, samples have been handled very carefully during section preparation and microthermometric experiments. In order to minimize the risk of inducing stretching and/or leakage, inclusions were heated slowly while approaching homogenization temperature (< 5°C/min) to further slow down (< 1 °C/min) in the last phases of the experiment. However the possibility of experiment-induced stretching cannot be completely ruled out. Microthermometric results are reported in Table 1.

Homogenization temperatures (V + L → L) in two-phase primary inclusions, range between 80 and 190°C (Fig. 3). Few measured T_e values suggest that inclusions contain essentially a H₂O-NaCl, albeit we cannot exclude the presence of other components, both for the variability of the measured T_e (range -18 ÷ -29 °C), and the chemistry of the geologic environment. In lack of a better approximation, salinity has been calculated using the equation of Bodnar (1993), as revised by Goldstein & Reynolds (1994). Measured T_m range between

TABLE I
Primary and secondary two-phase (L+V) fluid inclusion data in willemite

Sample	Locality	Length (μm)	Th $^{\circ}\text{C}$	Te $^{\circ}\text{C}$	Tm-ice $^{\circ}\text{C}$	wt.% NaCl eq.	Note 1 $^{\circ}$ = prim. 2 $^{\circ}$ = sec.		
Museo Mineralogia Università, Napoli	(La Calamine?)	10	115.1	n.d.	-2	3.39	1 $^{\circ}$		
		7.5	110	n.d.	0.3	n.d.	2 $^{\circ}$		
		5	74.5	n.d.	0.4	n.d.	2 $^{\circ}$		
		5.5	158.4	-29	-3.2	5.26	1 $^{\circ}$		
		5	132.1	n.d.	n.d.	n.d.	stretching		
		20	56.6	n.d.	n.d.	n.d.	1 $^{\circ}$		
		12	84.1	n.d.	n.d.	n.d.	1 $^{\circ}$		
		10	n.d.	n.d.	0 $^{\circ}\text{C}$	n.d.	1 $^{\circ}$		
		40	n.d.	n.d.	-3.7+1.	6.01+2.24	1 $^{\circ}$		
		16	93.9	n.d.	n.d.	n.d.	stretching		
		10	99.8	n.d.	n.d.	n.d.	1 $^{\circ}$		
		10	164.5	n.d.	n.d.	n.d.	1 $^{\circ}$		
		Royal Belgian Institute of Natural Sciences, Brussels	RN2224 - (Welkenraedt)	20	n.d.	n.d.	4.7	n.d.	1 $^{\circ}$
				20	n.d.	-23.2	-1.2	2.07	1 $^{\circ}$
				15	127	n.d.	n.d.	n.d.	1 $^{\circ}$
				7	191	n.d.	0.1	n.d.	1 $^{\circ}$
				14	156.7	-22.3	-1.6	2.74	1 $^{\circ}$
7	139.5			n.d.	4.7	n.d.	1 $^{\circ}$		
14	n.d.			n.d.	-0.2	0.35	1 $^{\circ}$		
5	130.4			n.d.	4.4	n.d.	1 $^{\circ}$		
10	n.d.			n.d.	4.5	n.d.	1 $^{\circ}$		
8	n.d.			n.d.	0	0	1 $^{\circ}$		
12	145			-18.9	>0	n.d.	2 $^{\circ}$		
13	184			-22.9	-1.3	2.24	1 $^{\circ}$		
5	n.d.			n.d.	-1.6	2.74	1 $^{\circ}$		
4	n.d.			n.d.	0	0	2 $^{\circ}$		
6	150.8	n.d.	n.d.	n.d.	1 $^{\circ}$				
2	169	n.d.	-2.1	3.55	2 $^{\circ}$				
3	181.1	-26	-2.6	4.34	2 $^{\circ}$				
11	n.d.	-22	-2.2	3.71	2 $^{\circ}$				

Sample	Locality	Length (µm)	Th °C	Te °C	Tm-ice °C	wt.% NaCl eq.	Note
		13	n.d.	n.d.	0	0	2°
		18	167.7	n.d.	-2	3.39	1°
		6	134.3	n.d.	n.d.	n.d.	1°
		6	140	n.d.	n.d.	n.d.	1°
		20	180	n.d.	0	0	1°
		6	113.5	n.d.	n.d.	n.d.	1°
		12	182.3	n.d.	n.d.	n.d.	1°
		14	162.3	n.d.	n.d.	n.d.	1°
		40	217.9	n.d.	0	0	1°
		10	118.2	n.d.	n.d.	n.d.	1°
		10	225.9	n.d.	0	0	1°
		40	174.3	n.d.	n.d.	n.d.	necking stretching
		8	112.5	n.d.	0	0	1°
		12	151.2	n.d.	0	0	1°
		16	161.1	n.d.	0	0	1°
		10	91.3	n.d.	n.d.	n.d.	1°
		20	145.5	n.d.	n.d.	n.d.	1°
		20	78.1	n.d.	n.d.	n.d.	1°
		9	207.1	-18.0	-1.6	n.d.	2°
		25	181.5	-17.5	-1.6	2.74	1°
	RN5011						
	(Moresnet-La Calamine)	5	n.d.	n.d.	-0.3	0.53	2°
		11	n.d.	-20	-1.1	1.91	1°
		9	n.d.	-20	-1.4	2.41	2°
		11	168.6	n.d.	0	0	stretching stretching
		8	94	n.d.	0	0	stretching stretching
		13	150	-23.4	-2.1	3.55	2°
		13	113	-18.8	2.5	n.d.	2°
		20	250	n.d.	n.d.	n.d.	stretching stretching
		20	250	n.d.	n.d.	n.d.	stretching stretching
		8	108.5	n.d.	n.d.	n.d.	1°
		20	90.5	n.d.	n.d.	n.d.	1°
		34	113.6	n.d.	n.d.	n.d.	1°
	RN2008 (Moresnet)	10	165	n.d.	n.d.	n.d.	1°
		14	104.8	n.d.	n.d.	n.d.	1°

n.d. = not detected

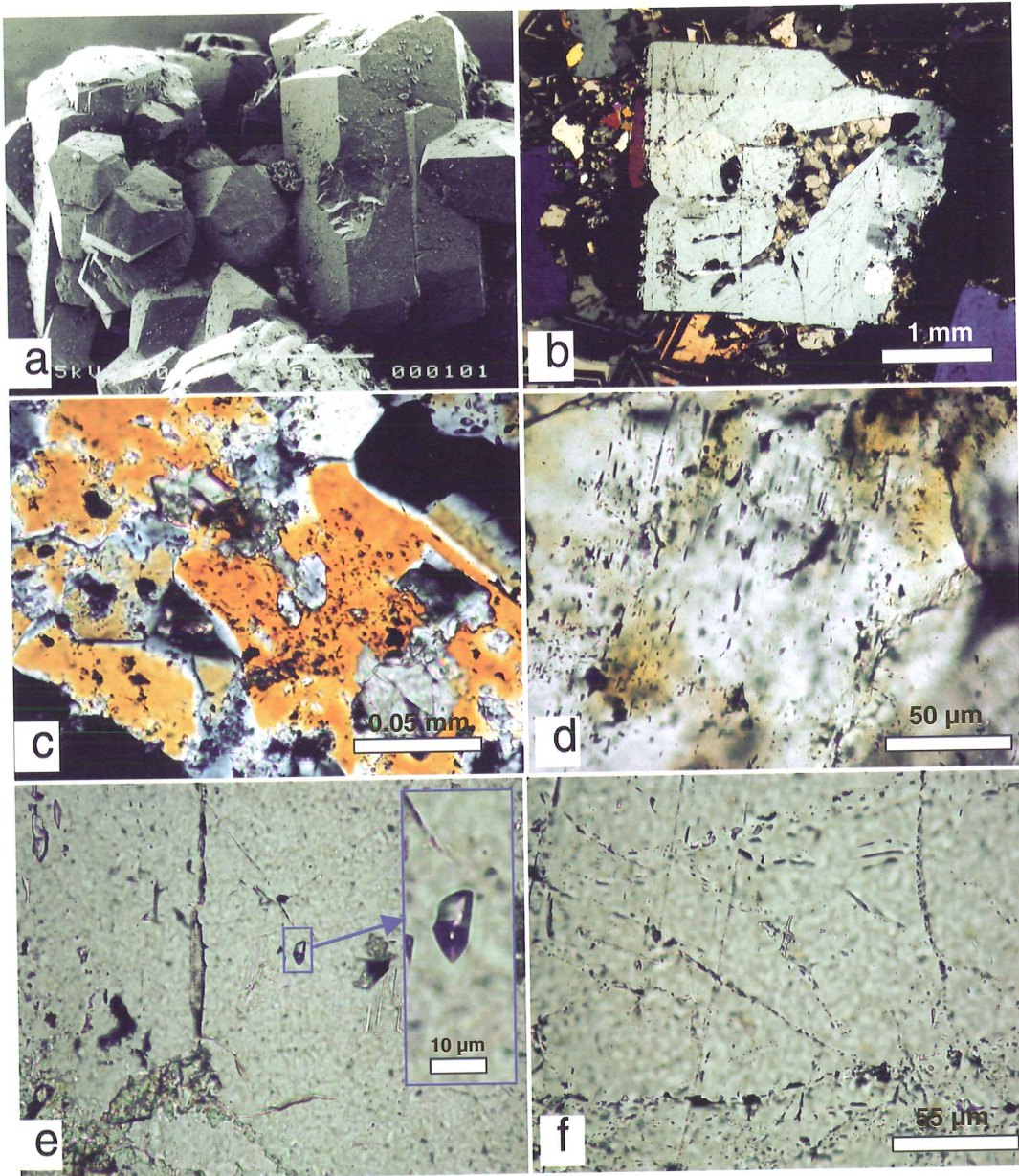


Fig. 2 – a. La Calamine: idiomorphic hexagonal crystals of willemite (Museo Mineralogia Università di Napoli); b. RN2224. Welkenraedt: willemite laths replaced by zoned Fe-Smithsonite (Royal Belgian Institute of Natural Sciences, Brussels); c. La Calamine: willemite lath with clusters of fluid inclusions (Museo Mineralogia Università di Napoli); d. La Calamine: primary monophase fluid inclusions in Willemite (Museo Mineralogia Università di Napoli); e. RN2224. Welkenraedt: primary two-phase fluid inclusion in Willemite (Royal Belgian Institute of Natural Sciences, Brussels); f. RN5011. La Calamine: secondary monophase inclusions in willemite (Royal Belgian Institute of Natural Sciences, Brussels).

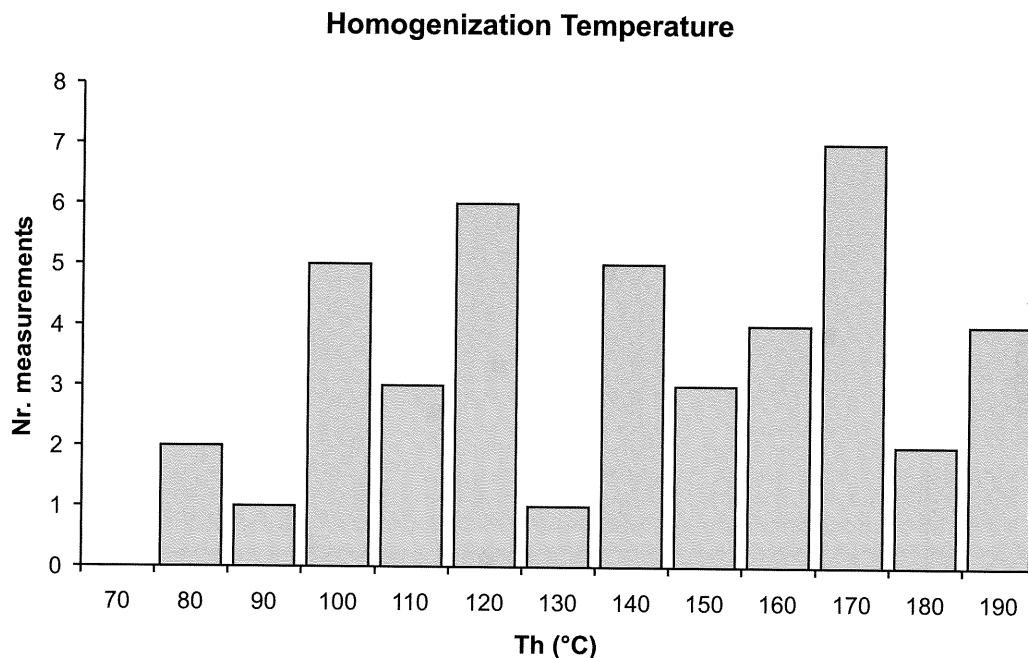


Fig. 3 – Histograms of homogenization temperatures (T_h) of primary two-phase inclusions in willemite

0 °C and -3.7 °C, corresponding to salinities between 0 and 6 % wt. NaCl eq. (Fig. 4). Salinities measured in few secondary inclusions (max length < 5 μ m) are always lower than 4% wt. NaCl eq. In the secondary two-phase inclusions, T_h (V + L \rightarrow L) data range between 80 and 200°C. Occasionally final melting was observed above 0 °C (up to 4,7 °C). In this case metastability could have been induced by the presence of components other than Na, or the melting phase could have been an hydrate compound (Na and Ca?). Unfortunately a final determination could not be done based only of microthermometry.

Homogenization temperatures from Belgian willemite fluid inclusions show a wide spread (in Fig. 3 we show only the two-phase set of data) which might have been caused by post entrapment phenomena (i.e. re-equilibration due to thermal gradients, stretching or leakage). Due to the brittle nature of willemite, mechanical stress or thermal gradients could have easily

affected the fluid inclusions homogenization temperature. Therefore, a discussion is in order to evaluate the reliability of the data.

Stretching or leakage (or both) can be caused either by geological phenomena (i.e. tectonics) or during sample preparation and heating experiments. Since sample preparation was conducted with extreme care in order to avoid stretching and leakage of the inclusions, and since these phenomena (if and when occurred) were easily detected during microthermometric experiments (and the corresponding inclusions discarded), we tend to rule out these as possible causes.

According to Vityk and Bodnar (1998), fluid inclusions re-equilibration (through stretching and leakage) leads to T_h data spread, and complexities in the related histograms shapes «[...] which reflect the sample's *P-T* history». In particular the authors conclude that:

1) plastically deformed fluid inclusions (high temperature/low strain rates) show essentially

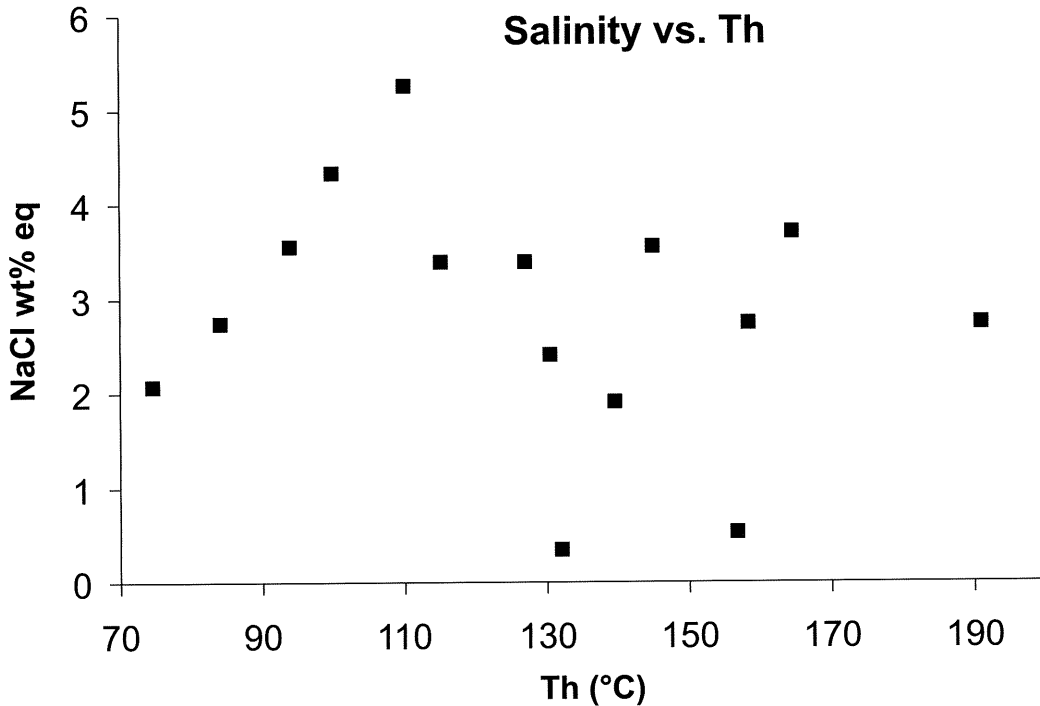


Fig. 4 – Diagram of homogenization temperatures (Th) vs. salinities (wt % NaCl equiv.) in primary and secondary inclusions in willemite.

no correlation between size and T_h , and generate unimodal skewed histograms, exhibiting high data spread,

2) brittle deformed fluid inclusions (low temperature/high strain rates) show a strong positive correlation between size and T_h and generate multimodal histograms, exhibiting high data spread.

It has to be pointed out that the finding of Vityk and Bodnar (1998) cannot be simply applied to our case, due to the differences in mechanical behavior between quartz and willemite and the different P-T range. However a plot of Th vs size of measured fluid inclusions (not shown), reveals that there is no apparent correlation between the size of these fluid inclusions and their homogenization temperatures, while the absence of a clear peak and the scattering of data in the histogram in

Fig. 3 point toward a post entrapment plastic modification of fluid inclusions in willemite, possibly due to a combination of T and low strain rates.

DISCUSSION

The range of homogenization temperatures in the Belgian willemites does not differ from those measured in other willemite ores in the world that are considered of hydrothermal origin, whose salinities, however, are much higher than those encountered in Belgium. However we have to consider the possibility that some additional components went undetected and the fact that salinities data in monophasic fluid inclusions are at the moment not available, due to the limitations of the

microthermometric techniques. Since the majority of the primary inclusions found in the Belgian willemites are monophasic (which points to a low temperature formation) or two-phase (V+L) which at least in part seem to have been affected by post entrapment phenomena, we cannot exclude that the ultimate origin of Belgian willemites was not hydrothermal. However, no fluid inclusion data have been reported so far from supergene non-sulfide Zn deposits. We will quote here a few examples taken from typical hypogene non-sulfide ores, as described by Hitzman *et al.* (2003).

Primary fluid inclusions in willemite from Beltana (Flinders Range, Australia) are all single phase and liquid-filled with salinities ranging from 4 to 14 % wt. NaCl eq. (Groves *et al.* 2003). Reliable homogenization temperatures could not be measured in Beltana, but data obtained from calcite crystals following and replacing the willemite generation have a temperature range between 70° and 130°C and relatively high salinities (20-22 wt % NaCl eq.; Hallam 2000). Dardenne & Freitas-Silva (1999) report homogenization temperatures between 65° and 180°C in the willemites from the Vazante mine (Brazil), suggesting fluid mixing processes but also partial leaking of some of the inclusions. Salinities cluster between 8 and 16 % wt. NaCl eq. In the willemites of Berg Aukas mine (Namibia), Ypma (1978) recorded homogenization temperatures between 220° to 240°C, while fluid salinities averaged 20 % wt. NaCl eq. Sweeney *et al.* (1991) were unable to locate two-phase fluid inclusions suitable to be measured, in the willemites from the Kabwe mine in Zambia. They could detect, however, homogenization temperatures between 150° to 250°C in two-phase fluid inclusions in willemite from the apparently related Star Zinc deposit (Zambia). These inclusions displayed two salinity maxima, one between 7 and 12 wt % NaCl eq. and another around 22 wt % NaCl eq. Late calcite veins, cutting and replacing willemite in the latter deposit, contain low-salinity fluid inclusions with homogenization temperatures averaging 120°C. Sweeney *et al.*

(1991) interpreted these data as indicating a mineralization process through mixing of a saline hydrothermal fluid with a meteoric fluid.

On the whole, the reported literature data suggest that willemite can form from fluids with a range of temperatures from < 65°C to approximately 250°C. Also the wide range of salinities measured in willemite, seems to confirm that fluid mixing may be involved. Mixing between a warm to hot, moderately to highly saline fluid with a cooler, less saline fluid, could have formed willemite concentrations. Late, low-salinity fluids have caused replacement of willemite by calcite in some of the ore deposits.

Fluid inclusion data from the Belgian willemites, due to the brittle structure of this mineral and its influence on the measured values, are in our opinion not yet conclusive for the genesis of the deposits, as it is the case for other willemite occurrence in the world, where their discussed hypogene or supergene genesis does not rely on the fluid inclusion temperatures only. However, in the Belgian deposits the limited high temperature set of data has been encountered only in willemite and not in smithsonite or hemimorphite.

On the other hand if these high temperatures and the encountered moderate salinity were confirmed by further study, this fact would pose a problem to the traditional supergene interpretation of the Belgian calamines, deposited from meteoric waters (Dejonghe 1998). The supergene interpretation seems to be valid in any case for the smithsonite phase, considering its typical stable isotopic pattern recently established by Boni *et al.* (2004).

At this stage, it is possible to suggest three explanations for the temperatures measured in the two-phase inclusions:

- 1) to assume the existence of an anomalous temperature gradient, active during the segregation of willemite before the sedimentation of the Cretaceous Aachen Formation, but NOT during (late?) smithsonite and hemimorphite deposition;

- 2) to consider a post-willemite thermal rise in the whole district, that allowed a re-

equilibration of the temperature in part of the inclusions;

3) to assume a stretching mechanism (mechanical deformation related to the reactivation of older tectonic lineaments, like the one oriented SW-NE occurring at La Calamine?).

In the first case, the genesis of willemite mineralization might have been related:

1a) to the waning effects of a late phase of the same hydrothermal activity that was responsible for the sulfide deposits in veins and *flats*. However, the salinity measured in the fluid inclusions does not fit with the high values recorded by the hydrothermal fluids of the sulfide veins (Hejlen *et al.* 2001), because the willemite forming fluid of the Belgian deposits has a much lower salinity, similar to a heated meteoric fluid that interacted only to a limited extent with the host rocks. Hitzman *et al.* (2003), while arguing that hydrothermal «willemite can form from fluids with a range of temperature from $< 100^{\circ}\text{C}$ to approximately 250°C » from a saline fluid, also mentioned that «Vadose-zone formation of willemite,.....should lead to inclusions with variable liquid-to-vapor ratios and low salinities».

1b) to the presence during Lower Cretaceous of an anomalous geothermal gradient in the mineralization area, so far not recorded in NE Belgium, but well known in the Lower Saxonian Basin in Germany (Littke *et al.* 2000): one of the Late Jurassic – Early Cretaceous rift basins in Central Europe, which became inverted during Late Cretaceous and Early Tertiary.

The re-equilibration of the fluid inclusions in the willemite under the effect of a later established higher thermal gradient (2) could also have multiple reasons. These should comprise the wide thermal influence of the Eifel volcanic plume and related geothermal activity between Late Tertiary and Quaternary (Ritter *et al.* 2001), or the tensional tectonic activity coupled with Eocene magmatism related to the opening of the north western branch of the Rhine graben (Fekiacova *et al.* 2003).

A mechanical deformation of willemite crystals (3) related to the reactivation of older tectonic lineaments, like the SW-NE trending Moresnet fault (which might have caused a general stretching of the inclusions), is another possibility to be taken into account. It is interesting to consider that along the older thrust lineaments also directed SW-NE, are positioned the thermo-mineral springs of Chaudfontaine (Eifel fault) and Aachen in Germany (Aachen and Burtscheid thrust faults) (Graulich 1983, Herch 2000). The temperature of the mineral waters reaches a maximum of 120°C in depth (Herch 2000), far below from the maximum temperatures measured in the willemites (190°C), but their salinities have also evidenced mixing processes between meteoric fresh waters and thermal fluids, which have been enriched in several elements through water-rock interaction, during a long residence period in the Paleozoic formations.

Only a study which goes beyond microthermometry and collects data on the compositions of the fluid inclusions by Raman or ICPMS (laser ablation), coupled with stable isotopic analyses of the oxidation minerals and a comparison with the isotopic ratios of the different waters in the region (mine waters, thermo-mineral waters etc.), could unravel the relationships between the calamine formation and their related fluids and eventually, together with a more detailed chronology of fluid inclusions formation, deliver some information about their possible timing.

ACKNOWLEDGMENTS

This is the second contribution to an EC-funded project (M. Boni & L. Dejonghe) on «The Non-Sulfide Zn-ores in Belgium: a new perspective», for which the facilities of the Royal Belgian Institute of Natural Sciences, Brussels (RBINS) and the Geological Survey of Belgium (GSB) have been used. The help of O. Retout and I. Van de Velde (International co-operation IRScNB, Management of the Access to Belgian Collections Program) and M. Deliens (former curator of the mineralogical collection at IRScNB) is here warmly acknowledged. We want also to thank G. Balassone of University of Napoli for her help with the

analytical work and R. Ghiara and C. Petti of the Museo di Mineralogia for allowing access to the mineral collections.

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