

Mineralogical and geochemical characterization of nonsulfide Zn–Pb mineralization at Silvermines and Galmoy (Irish Midlands)

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Abstract

The nonsulfide zinc–lead mineralization in the Irish Midlands represents an example of surface oxidation of primary sulfide mineralization, redeposition and preservation under glacial till. In this preliminary study, we report on the mineralogy and chemical composition of the nonsulfide zinc mineralization at Silvermines and Galmoy deposits. At Silvermines, the analyses were carried out on samples from two drill cores (drillholes 302/3 and 303/3) located in Knockanroe Townland, at the periphery of the main orebody. At Galmoy, the nonsulfides were sampled from the G-orebody between 77 and 93 m below the surface, in an area where oxidation is very strong. At both sites, the dominant mineral composition of oxidized ores is relatively simple with smithsonite–hemimorphite at Silvermines and smithsonite at Galmoy. Primary sulfides and secondary carbonates/silicates are generally associated at both localities. Whole rock chemical analysis, SEM and optical studies have revealed evidence for open space filling and replacement of both primary sulfides and Carboniferous dolomite host rock by nonsulfide minerals.

Smithsonite at Silvermines shows an evolution of different forms from early encrustations and botryoidal aggregates to late “rice grain” shaped crystals and a systematic decrease of Fe content with time in the paragenetic sequence. Early smithsonite replacing dolomite host rocks can be Fe- and Mn-rich. This evolution points to slightly more reducing conditions during deposition of the early Zn carbonates, compared to late smithsonites, which coexist with Mn and Fe (oxy)hydroxides. A complex association of at least three different, often intergrown types of smithsonite aggregates were observed at Galmoy, where replacement of sulfides and vug-infilling are predominant. Early globular or crustiform Pb- and Ca-rich smithsonite is followed by tiny rounded (Fe-poor) to one-dimensional (Fe-rich) clusters of smithsonite and again by late “rice grain” shaped smithsonite. Hemimorphite is virtually absent. Thin encrustations of sulfates, such as gypsum, boyleite, rozenite, copiapite and jarosite, often coat both sulfide and nonsulfide minerals and testify to recent and/or ongoing alteration. The lack of rhombohedral smithsonite, which characterizes the upper phreatic zone in Sardinia and in Belgium, indicates the relative immaturity of the weathering profiles in Ireland, the absence of a well-developed karstic network and, in consequence, the uneconomic character of nonsulfide concentrations.

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1. Introduction

Ireland is renowned for its sulfide zinc deposits and has the greatest zinc endowment of any country on an area basis (Singer, 1995). Since the late 1950's five deposits have been developed — Tynagh, Silvermines, Navan, Galmoy and Lisheen (the latter three being modern discoveries) (Table 1). Numerous sub-economic deposits have also been discovered. Collectively the deposits are known as the “Irish Orefield”, which also describes the geographic region in which the deposits occur (Fig. 1). Nonsulfide zinc has also been located in Ireland, generally associated with the sulfide zinc deposits. Descriptions have been published for nonsulfide zinc mineralization at both Tynagh and Silvermines (Morrissey and Whitehead, 1971; Clifford et al., 1986, on Tynagh; Boland et al., 1992 on Silvermines).

There has been a recent renewal of interest internationally in nonsulfide zinc deposits and several high profile discoveries have been made, including the deposits of Skorpion (Namibia) and Angouran (Iran). This has led a number of authors to attempt a classification of these deposits, which could serve also for exploration purposes: principal among these authors are Large (2001) and Hitzman et al. (2003). This paper is one of a series on nonsulfide Zn–Pb ores in Western Europe (Aversa et al., 2002; Boni et al., 2003; Boni and Large, 2003; Gilg and Boni, 2004; Dejonghe and Boni, 2005; Coppola et al., 2007—this volume; Strzelska-Smakowska, in press), in which the mineralogy, geochemistry and economic ore distribution of this kind of resource that was intensively exploited in the past have been reviewed. In this respect, this study on the Irish orefield is the first contribution where the nonsulfides have been actually sampled *in situ* and not from old ore dumps or mineral collections as in

other districts. This has allowed a more precise reconstruction of the nature of the secondary minerals and of the localization of the enrichment zones that could be used for further exploration in Ireland or elsewhere.

In our contribution, we report on detailed mineralogical, geochemical and petrographical studies carried out on nonsulfide zinc mineralization at Silvermines and Galmoy, in order to give indications about the supergene evolution of the ore deposit. A (semi)quantitative distribution of the different oxide minerals throughout the supergene ore is also provided. In the case of Silvermines, the samples were taken from two drillholes completed by the Geological Survey of Ireland in 2002, at the periphery of the main orebody. For Galmoy, the sampling was undertaken at the deposit underground by the senior author.

2. Regional geology

There are several excellent summaries of the regional geological setting of the Irish Orefield including Philips and Sevastopulo (1986), Andrew (1993) and Hitzman and Beaty (1996).

The geology of Ireland is dominated by Lower Palaeozoic rocks in the coastal regions with Upper Palaeozoic rocks occurring throughout the midlands of the country. Approximately half of the country is underlain by Carboniferous lithologies which are dominated by sedimentary sequences — limestones in the Early Carboniferous with terrestrial rocks including coal measures in the Middle and Upper Carboniferous. During Lower Carboniferous times, Ireland was positioned at low palaeolatitudes just south of the Equator and limestones of the Ballysteen Limestone and Waulsortian facies were deposited sequentially.

Table 1
The principal features of the Irish sulfide zinc orebodies

| Feature | Tynagh | Silvermines | Galmoy | Lisheen | Navan |
|------------------------------|---|---|------------------------------------|------------------------------------|------------------------------------|
| Age of host rocks | Courseyan | Courseyan | Courseyan | Courseyan | Courseyan |
| Host rock lithology | Waulsortian and Ballysteen | Waulsortian and Ballysteen | Waulsortian | Waulsortian | Navan Beds |
| Sulfide mineralogy | sph, py, ga | sph, py, ga | sph, py, ga | sph, py, ga | sph, py, ga |
| Age of mineralization | Courseyan to Arundian ^a | Courseyan to Arundian ^a | Courseyan to Arundian ^a | Courseyan to Arundian ^a | Courseyan to Arundian ^a |
| Presence of non-sulfide zinc | Yes | Yes | Yes | None reported | None reported |
| Form of non-sulfide zinc | Pockets of oxidized sulfides beneath glacial overburden | Pockets of oxidized sulfides beneath glacial overburden | Buried oxidized sulphides | None reported | None reported |
| Dominant sulfide textures | Replacement | Replacement | Replacement | Replacement | Replacement |

sph, sphalerite; py, pyrite; ga, galena.

^a There is some uncertainty on the precise age of mineralization. Most evidence supports a date somewhere in the range from Courseyan to Arundian. It should not be read that the mineralization event took place for the entire time between Courseyan and Arundian.

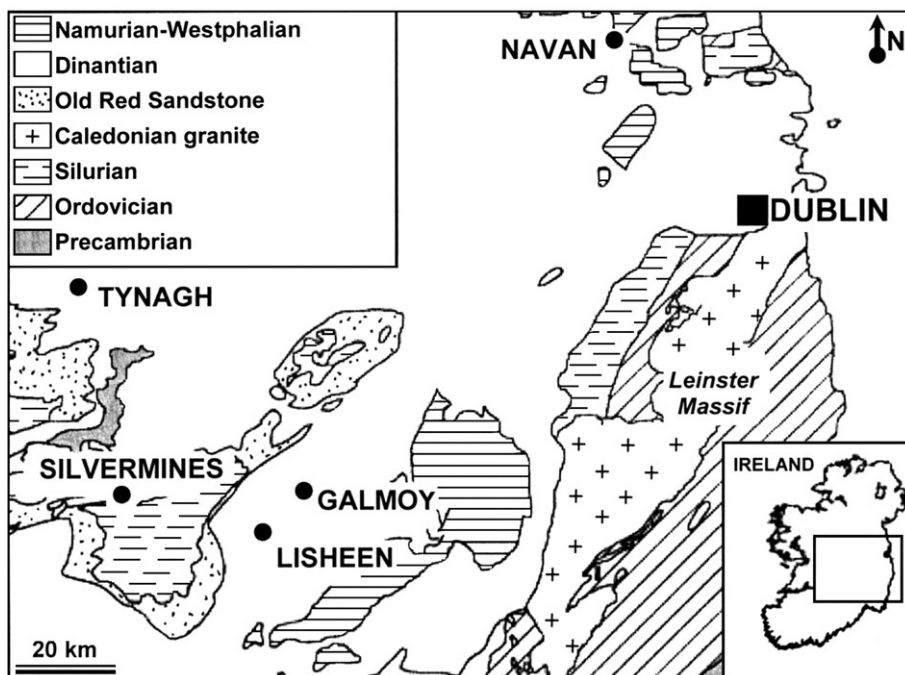


Fig. 1. Geological map of the Irish Midlands (modified after Wilkinson and Eyre, 2005).

The Ballysteen Limestones are a variable sequence of thin to medium bedded, generally dark blue–gray or gray clean bioclastic limestones or oolitic limestones, and limestones containing argillaceous material (“dirty” limestones). The overlying Waulsortian limestones are invariably massive, pale gray micritic limestones. Both rock units may be dolomitized but it is the cleaner parts of the Ballysteen (limestones) that are dolomitized while almost any part of the Waulsortian can be so altered. The timing of dolomitization is still a cause for debate and study (Somerville et al., 1997; Peace and Wallace, 2000; Wright et al., 2000, 2001; Gregg et al., 2001; Wilkinson, 2003).

The Lower Carboniferous represents a transgressive sequence from south to north with the Waulsortian forming in deeper waters (up to 300 m). Therefore the shallower water Ballysteen in the north part of the country can be the same age as the Waulsortian lithologies further south.

3. Overview of sulfide zinc metallogeny

The sulfide zinc deposits of Ireland occur in Courcayan (Lower Carboniferous) carbonate lithologies within the central midlands of Ireland. Five of these deposits have become operating mines (Tynagh, Silver-

mines, Galmoy, Lisheen and Navan), with three of them still active (Galmoy, Lisheen and Navan). All five mines share some common features but there are some subtle differences (see Table 1).

In terms of global classifications of mineral deposits, mineralization in the Irish Orefield shares some characteristics of both Mississippi Valley Type (MVT) deposits and Sedimentary Exhalative (Sedex) deposits. The features of the Irish deposits that are akin to MVT deposits are: they are hosted by carbonates, have epigenetic style textures, dolomitization is common, and the simple mineralogy. The features of the Irish deposits that are akin to Sedex type are: they occur close to major faults that have been demonstrated or interpreted to be the feeder channels for mineralization, they are formed from relatively hot (100 to 280 °C) hydrothermal solutions, and stratiform sulfide textures occur at a number of deposits. This duality has led to the adoption of the term ‘Irish-Type Deposits’ to classify this hybrid ore deposit type, which has features of both styles of deposit.

The genesis of the sulfide zinc deposits has been the matter of some debate in recent times. Two competing genetic models have been proposed — a deep convection model and a topographically driven fluid flow model. The former was presented initially by Russell (1978) and remains the preferred model for most workers

studying in the Irish Orefield, while the latter was proposed by Hitzman and Beatty (1996) and has a following among several North American workers. More recently Chapman and Hitzman (pers. comm.) have acknowledged that the source of metals for the Irish deposits was most probably the Lower Palaeozoic lithologies underlying them. However, they maintain that a topographically driven fluid from the south could have played a role in the formation of the deposits.

4. Nonsulfide zinc deposits

The only significant nonsulfide resource in Ireland, now mined out, occurred at Tynagh (Morrissey and Whitehead, 1971; Clifford et al., 1986). A zinc “oxide” deposit, sporadically exploited until 1953, was also known from the Silvermines area (Griffith, 1956; Boland et al., 1992). The secondary orebodies at both Tynagh and Silvermines, probably formed mainly during Tertiary or Quaternary weathering periods, were preserved below glacial till deposited during the Midlandian Cold stage by glaciers advancing southwards across Ireland (Boni and Large, 2003). The glacial overburden ranges in thickness from 6 to 10 m, and consists of clayey gravel underlain by silt to sandy clays.

4.1. Tynagh

The primary sulfide orebody at Tynagh was in the hanging wall of an E–W trending normal fault, with a maximum throw of about 600 m, which was active during hypogene mineralization (Moore, 1975). The fault forms the northern boundary of an Old Red Sandstone (Devonian) inlier. As at Silvermines (partly), Lisheen and Galmoy, the host at Tynagh for the ore is the Waulsortian limestone. Hypogene ore comprises galena, sphalerite and pyrite with minor chalcopyrite and tennantite, often interspersed with barite (Boast et al., 1981; Banks et al., 2002). Even if most of the mineralization is considered to be epigenetic, some has been described as early diagenetic. After the main phase of mineral deposition, renewed dolomitization occurred together with the precipitation of calcite, dolomite and minor chalcopyrite in veins and cavities.

The supergene mineralization in the so-called “Residual Orebody” of Tynagh consisted of a mixture of detrital as well as supergene sulfides, together with smithsonite, hemimorphite, cerussite, minor Cu carbonates and other exotic mineral species (Morrissey and Whitehead, 1971; Clifford et al., 1986; Boni and Large, 2003). Fragments of primary sulfide ores had the same composition as the primary stratabound ore. The original resource of the

nonsulfide Zn ore was 1.2 Mt at 4.66% Zn and 9.92% Pb, as compared to a sulfide resource of 3.76 Mt at 4.27% Zn and 4.76% Pb (Clifford et al., 1986). Further sulfide-enriched resources (2.80 Mt) occurred together with nonsulfides in the “Residual Orebody”. No samples from Tynagh Residual Orebody have been analyzed in the present study.

4.2. Silvermines

At Silvermines, sulfide ore is located on the northern margin of a Lower Palaeozoic inlier adjacent to the approximately E–W trending Silvermines fault system (Fig. 2). Three main faults in the deposit control the location of the hypogene ore and are believed to have acted as conduits for the hydrothermal fluids. The total northward downthrow of the main fault system was some 200 to 300 m (Taylor and Andrew, 1978; Taylor, 1984; Banks et al., 2002). The morphology of the ore is mostly stratabound, in places concentrated on faults, and the nature of the host rock is a dolomite breccia/limestone, derived from the Waulsortian limestone and the Argillaceous Bioclastic Limestones (limestone and dolomite, with shaly interbeds). The alteration comprises dolomitization and minor silica–hematite. Sphalerite and galena are the primary ore minerals. Barite (in the nearby Magcobar deposit) was also a significant resource and is also part of the same mineralizing system. Pyrite was a major component of the stratabound ores and minor sulfides included marcasite, chalcocopyrite, and arsenopyrite; sulfosalts also occurred. There is clear evidence, as at Tynagh, of both epigenetic and early diagenetic styles of mineralization.

The nonsulfide ore at Silvermines, consisting mostly of smithsonite and hemimorphite, was exploited intermittently from the 17th Century up until 1953. From 1866 onwards, high-grade ore (> 12% Zn) was treated in Wälz kilns to produce Zn-oxide. An evaluation of nonsulfide zinc ore made in 1933, determined a minimum resource of at least 0.5 Mt grading 21% Zn and minor lead. This was upgraded to 1 Mt after the work of Ennex International in the early 1990’s (Boland et al., 1992). The top of the water table at Silvermines before the start of the intensive mining operations would have been quite near to the surface, due to the current Irish climate.

Four significant deposits occur in the Silvermines area (Griffith, 1956), all hosted by the Lower Dolomite horizon (Courceyan). Of the deposits, three (G-Zone, K-Zone and Ballygown South) have been found in the hanging wall of the Silvermines fault. A fourth mineralized zone, at Cooleen, is some distance from the fault.

In each of these zones the residual mineralization is unconsolidated or semi-consolidated and developed in weathered-out, steep-sided troughs, replacing the primary sulfide lenses and, locally, the host carbonates. The main oxidized bodies are delimited by karstified and digitated margins, and by irregular fractures. The old workings exploited both the unconsolidated, cavity filling “calamine” concentrations and the replacements bodies (Griffith, 1956). The latter is concentrated within fracture zones, along fissures in the dolomite and in other easily permeated planes. Locally “the walls between two or more fissures and fractures have been completely replaced by large irregular masses of ore” (Griffith, 1956). Ore

mineralogy was described as zinc occurring in smithsonite and hemimorphite and lead occurring locally as cerussite and hydrocerussite (Griffith, 1956; Boland et al., 1992). The ore grades ranged from 3% Pb and 2–3% Zn in the gossan area, up to maximum values of 8% Pb and 15 to 20% Zn in smithsonite and hemimorphite orebodies. Hemimorphite is generally enriched in the Cooleen Zone, and in the uppermost parts of all deposits. Boland et al. (1992) concluded that the distribution of smithsonite and hemimorphite at Silvermines was a reflection of the oxidation level, with hemimorphite and goethite in the upper levels, and smithsonite progressively enriched at depth.

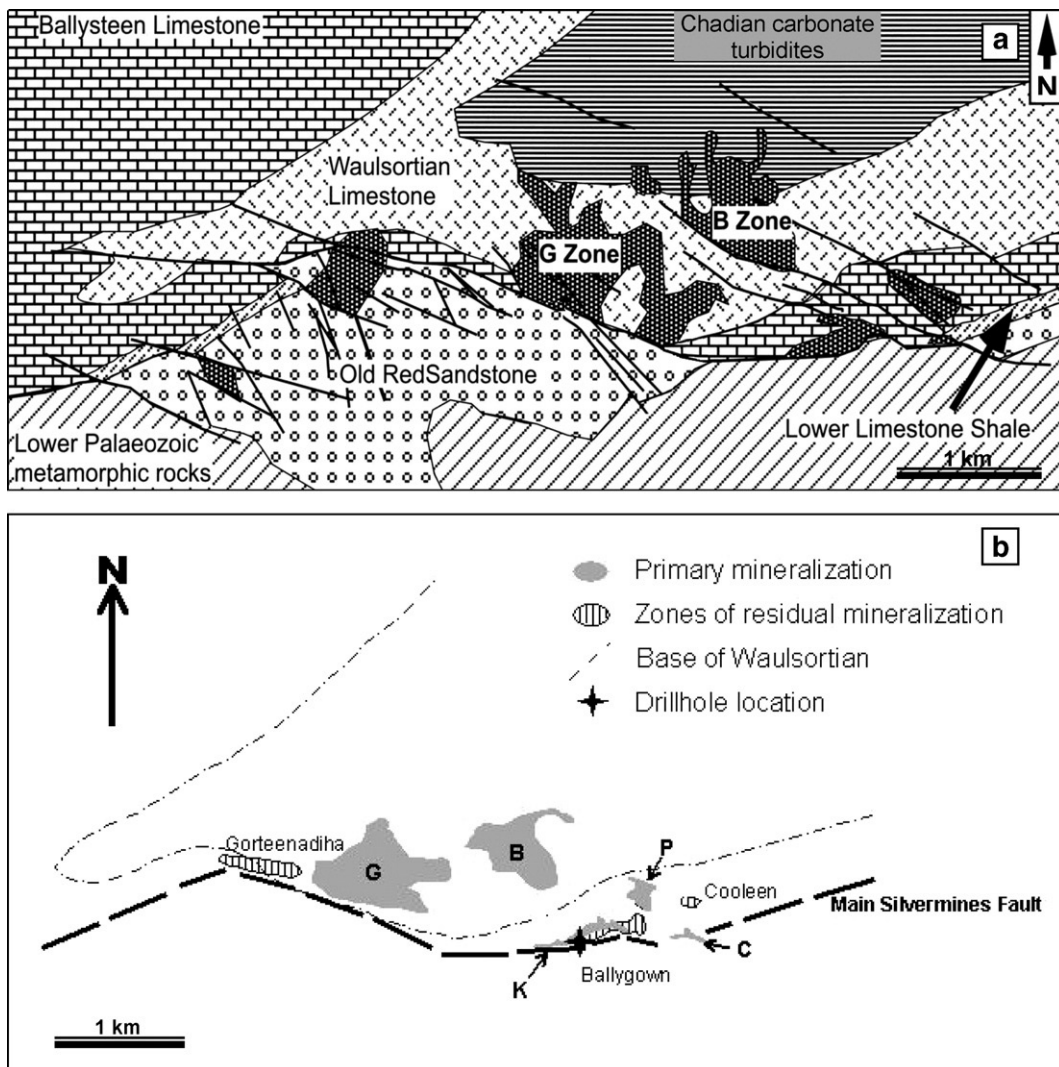


Fig. 2. (a) Geological map (modified after Hitzman and Beaty, 2003) and (b) location of drillholes of Figs. 4 and 5 (Knockanroe Townland) at Silvermines (after Boland et al., 1992).

4.3. Galmoy

The Galmoy orebody lies in a NE-striking belt of Lower Carboniferous carbonates in north Co. Kilkenny. The hypogene ore occurs as stratabound lenses of predominantly massive sulfides consisting of sphalerite, galena and pyrite/marcasite in variable proportions. The Galmoy orebodies are breccia-hosted and occur along the base of the regionally dolomitized Waulsortian Limestone Formation of Courceyan age (Lowther et al., 2003) (Fig. 3a, b). To the NW of the mine, the Waulsortian is predominantly undolomitized.

The CW and G orebodies were discovered in 1986 (Doyle et al., 1992), after drilling an Induced Polarization (IP) anomaly. The first hole intersected ore over 8.7 m and graded 7.39% Zn and 0.28% Pb. The K and R orebodies were discovered in 1995 and 2002, respectively. The reserve, as of 31st December 2005, stands at 3.55 Mt grading at 14.7% Zn and 4.1% Pb, with a measured and indicated resource exclusive of the reserve of 1.61 Mt

grading 10.9% Zn and 2.2% Pb. Mineralization in the G and R orebodies is directly related to the E–W trending G fault. The K and CW mineralization is indirectly related to the G Fault, fed through a NW striking, structurally-controlled, hydrothermal plumbing system (Lowther et al., 2003). The orebodies are tabular in shape with an average thickness of 5.8 m, and occur about 50 to 150 m below the surface, with the G orebody dipping gently to the N. The sulfide ores are predominantly sphalerite-rich in the CW and K orebodies, sphalerite- and galena-rich in the R orebody and sphalerite- and pyrite/marcasite-rich in the G orebody. Significant amounts of Cu–Ag sulfides have been identified in the footwall of the R orebody and in trace amounts at depth in drillholes in the southern part of the G orebody. The copper typically occurs as tennantite/tetrahedrite, with some minor chalcocopyrite, in the G orebody; silver occurs in the form of proustite. At both locations the host rock is the Ballysteen Limestone, with the Cu–Ag found at the base of the ore in the R Orebody and beneath the main zinc mineralization in the G orebody

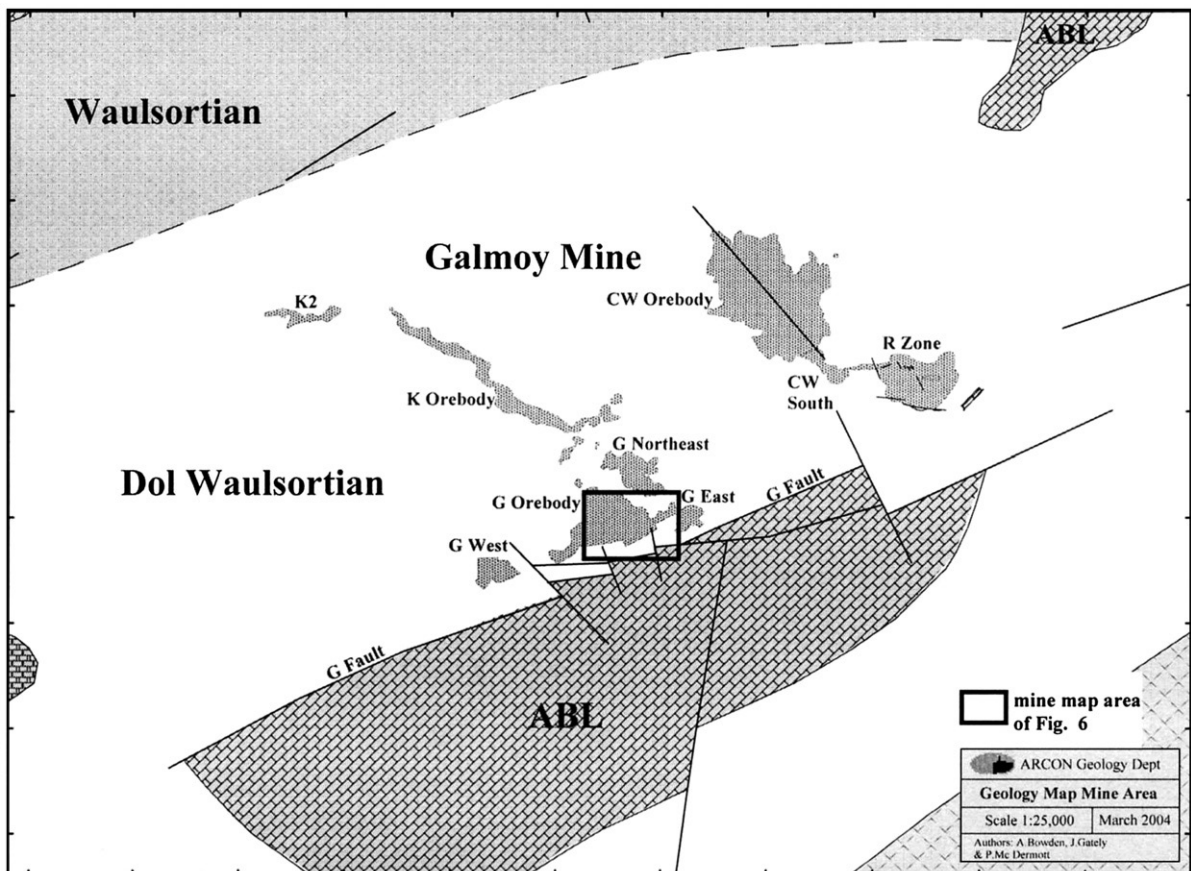
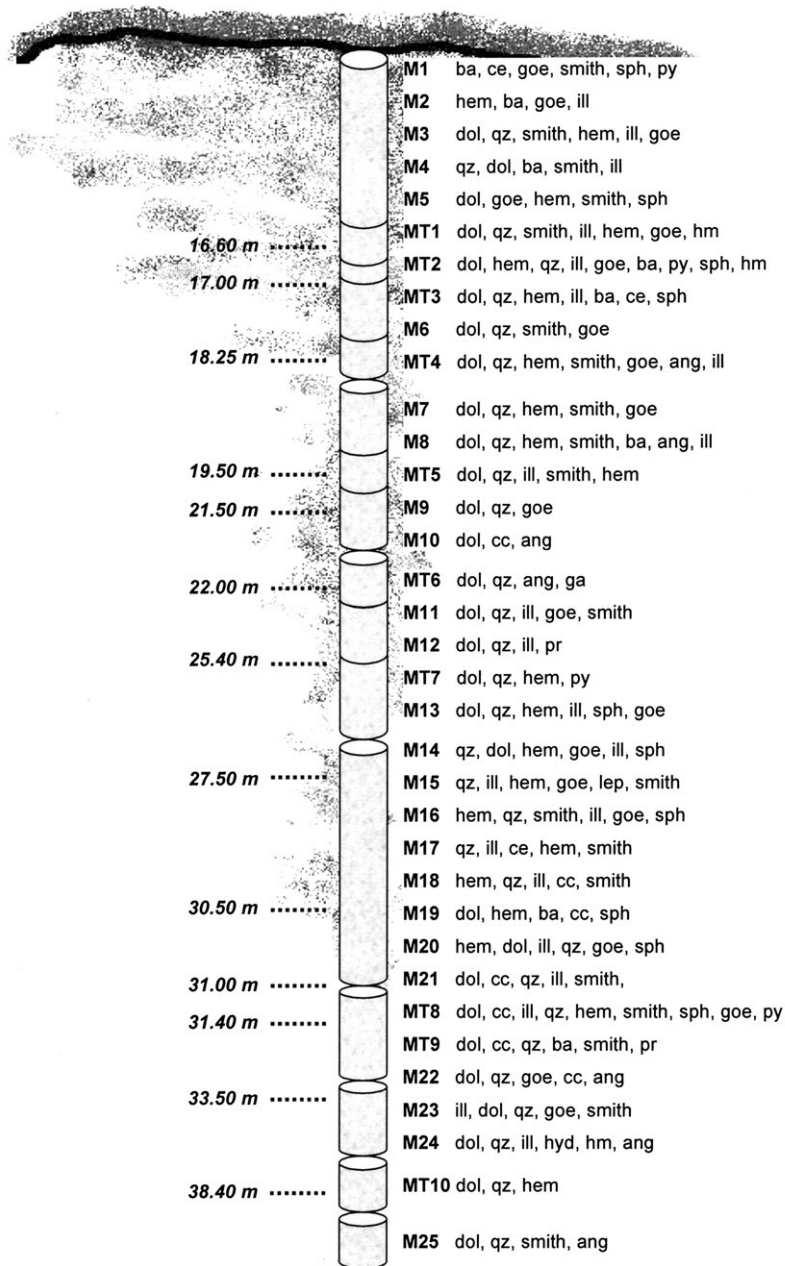


Fig. 3. Geological map of the Galmoy area with location of the orebodies.

(Doyle et al., 1992). Secondary minerals, recorded in the weathered ores, are smithsonite, cerussite and iron oxides and oxyhydroxides (hematite and goethite) (Lowther et al.,

2003). Prior to the commencement of mining in 1995, the top of the water table in the Galmoy area would have typically ranged from 1 to 30 m in depth below surface.

Borehole log 302/03 (Knockanroe Townland)



M1-M25 = sample #

ang=anglesite, ba=barite, cc =calcite, ce=cerussite, dol = dolomite, ga=galena, goe=goethite, hm=hematite, hem=hemimorphite, hyd=hydrozincite, ill=illite, lep=lepidocrocite, pr = pyrolusite, py=pyrite, qz = quartz, smith=smithsonite, sph=sphalerite

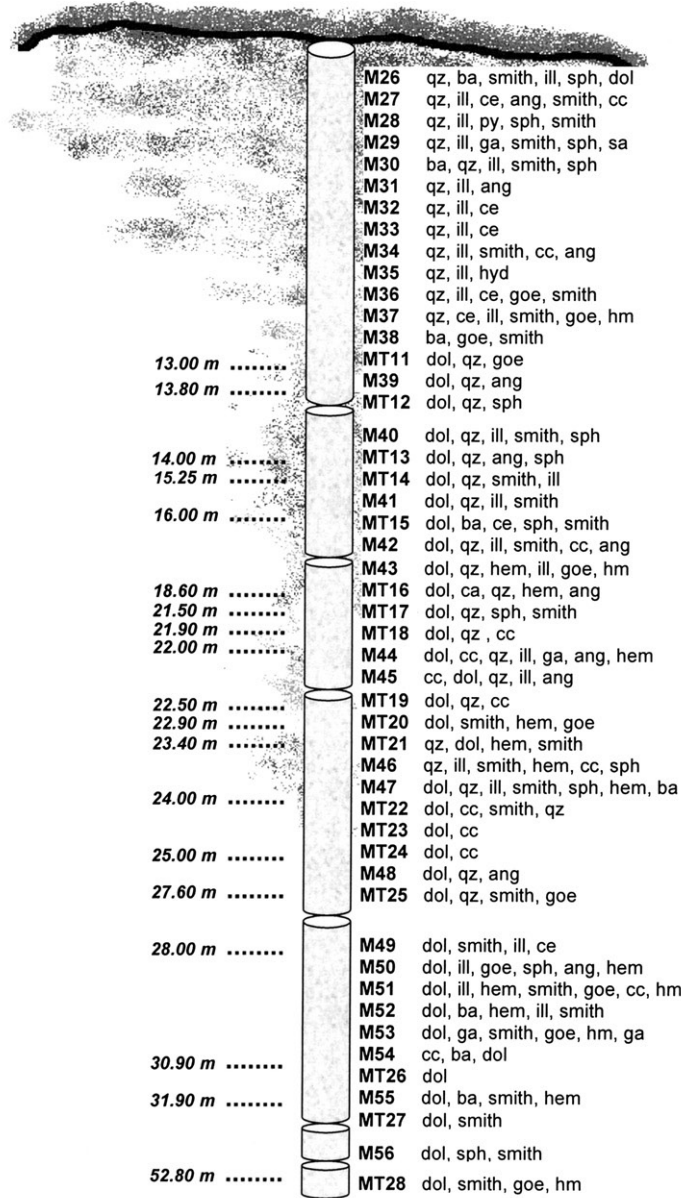
Fig. 4. Silvermines drillhole 302/3, with location of the analyzed samples and the corresponding mineral associations (minerals in order of decreasing abundance). The drillhole ends at a depth of 69.34 m.

5. Sampling and analytical techniques

Neither the old drill cores from 1933, nor the cores more recently obtained by Mogul Ltd. in the 1980s and containing the best intersections of the residual orebo-

dies at Silvermines, are available anymore. Therefore, in order to determine the real distribution of secondary Zn and Pb-bearing minerals, the Geological Survey of Ireland carried out additional drilling at Silvermines in November 2002. The aim was to obtain a good

Borehole log 303/03 (Knockanroe Townland)



M26–MT28 = sample #

ang=anglesite, ba=barite, cc= calcite, ce=cerussite, dol=dolomite, ga=galena, goe=goethite, hm=hematite, hem=hemimorphite, hyd=hydrozincite, ill=illite, lep=lepidocrocite, py=pyrite, qz=quartz, sa=sauconite, smith=smithsonite, sph=sphalerite

Fig. 5. Silvermines drillhole 303/3, with location of the analyzed samples and the corresponding mineral associations (minerals in order of decreasing abundance). The drillhole terminates at a depth of 69.12 m.

intersection containing both primary sulfides and oxides–residuum, where the relationship between these different phases could be examined (Balassone et al., 2005). Two drill cores (drillholes 302/3 and 303/3) were located in Knockanroe Townland at the periphery of the main orebody, (unfortunately) somewhat removed from the massive ore zone. They reached maximum depths of 69.34 m (303/2, Fig. 4) and 69.12 m (303/3, Fig. 5), respectively; however, clear evidence of oxidation (presence of supergene minerals) can be traced down only to 38.4 m in hole 302/3 and down to 52.8 m in hole 303/3. Eighty-two samples were prepared from the two diamond drill cores.

At Galmoy mine, all nonsulfide samples considered in the present study are from the G orebody. The oxidation in the G ore is concentrated in the southeastern part of the mineralization, along the hanging wall contact and where sub-vertical fissures cut through the orebody from the footwall up to the base of the Quaternary glacial deposits. The samples were collected in the areas of the G orebody where oxidation is most evident, at depths between 77 m and 93 m below surface (Fig. 6).

Optical microscopy (OM), secondary electron imaging by scanning electron microscopy (SEM, Jeol JSM-

5310) and powder X-ray diffraction (XRD, Seifert MZVI automated diffractometer equipped with the Rayflex software package, CuK α radiation, 3–75 $^{\circ}2\theta$ range and 0.5 $^{\circ}2\theta/\text{min}$ speed) were used to examine the samples. Semi-quantitative and quantitative microanalyses were carried out by energy-dispersive spectroscopy (EDS, Link Analytical 10,000, ZAF corrections on Jeol JSM-5310), using pure elements, oxides, sulfides, sulfates and silicates as standards (minimum detection limits, MDL, wt. %: ZnO 0.06, FeO 0.05, MnO 0.05, CaO 0.06, MgO 0.05, PbO 0.07, CdO 0.07). Operating conditions were 15 kV accelerating voltage and 10 μm spot size. Selected thin sections of different smithsonite generations and hemimorphite and cerussite-bearing assemblages were analysed by a full WDS microprobe Cameca SX50 electron microprobe (IGAG CNR Rome) operating at an accelerating voltage of 15 kV, 15 nA beam current and 10 to 20 μm spot size (MDL, wt. %: ZnO 0.008, FeO 0.009, MnO 0.009, CaO 0.008, MgO 0.009, PbO 0.007, CdO 0.008). Data were corrected using the PAP program (Pouchou and Pichoir, 1991). Minerals and pure elements were used as standards.

Selected major, minor and trace elements of some whole rocks from the Silvermines drill cores have been

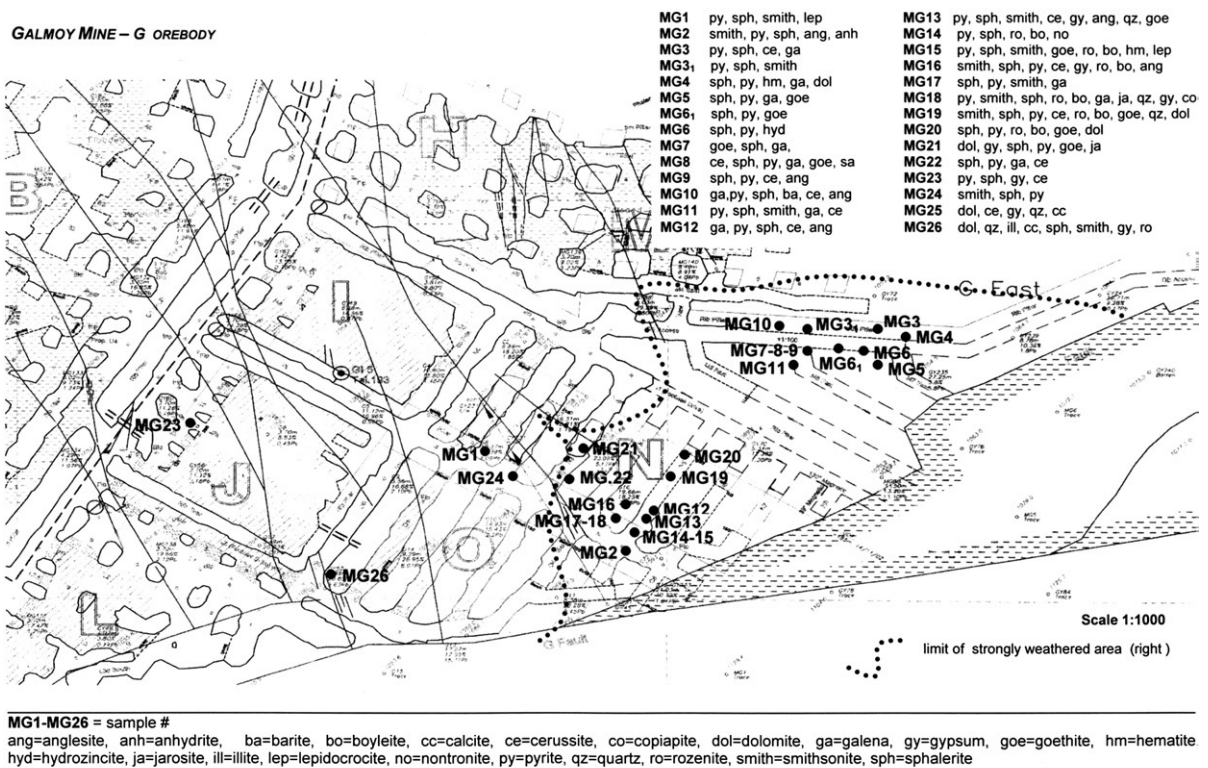


Fig. 6. Galmoy mine map (G orebody), showing sampling sites (GI5 Area), specimen labels and the relative mineral assemblages.

measured at ACME laboratories in Vancouver, Canada, with a Perkin Elmer Elan 6000 ICP-MS in the 7AR Group (24 elements). From each pulverized sample, 2 g has been analyzed by acid digestion. The OM and SEM examination and description of both suites of samples were carried out in order to characterize the mineralization at both sites and to compare the smithsonite single crystal and aggregate forms, with similar mineralogy investigated in Sardinian and Belgian nonsulfide zinc deposits (Boni et al., 2003; Coppola et al., 2007-this volume). This was carried out to investigate the possible variations in minor and trace elements contents among the different types and their paragenetic timing.

6. Mineralogical, petrographic and geochemical results

6.1. Silvermines

The mineralogy of the secondary ore is shown systematically in Figs. 4 and 5. Mineral abundance has been evaluated on the basis of a petrographic study coupled with XRD analysis. Nonsulfide zinc phases are fine-grained and dominated by smithsonite ($ZnCO_3$) and hemimorphite [$Zn_4Si_2O_7(OH)_2 \cdot H_2O$]. Hydrozincite [Zn_5

$(CO_3)_2(OH)_6$] was detected in only a few samples. In both drillholes, these minerals can occur together; in 302/03 both minerals are distributed equally throughout the entire section, whilst in drillhole 303/03, smithsonite is more common than hemimorphite, but the latter is more common at depth. Lead occurs as cerussite ($PbCO_3$) and rare anglesite ($PbSO_4$), whereas iron oxyhydroxides and oxides (mainly goethite and hematite) derived from the oxidation of pyrite are commonly present in “limonitic” boxworks and in small concretions with amorphous manganese minerals. Remnants of the primary ore mainly consist of sulfides (sphalerite, galena and pyrite/marcasite) and barite. We have not detected clear evidence of supergene sulfides in the Silvermines samples, as was the case at the Tynagh “Residual Orebody” (Morrissey and Whitehead, 1971). In both drillholes from Silvermines, the main gangue consists of crystalline ferroan dolomite, generally affected by intense oxidation and deposition of newly formed iron oxides; detrital and diagenetic quartz is ubiquitous, whereas calcite is only occasionally present. Among the clay minerals, illite is predominant, but also zincian clays (probably sauconite) were locally detected.

Smithsonite occurs in different generations and habits throughout both cores, ranging in color from milky white and light brown to dark gray. An extensive OM and SEM

Table 2

Morphological types of smithsonite single crystals and/or aggregates, relative abundance and compositional ranges of selected minor elements in the Irish nonsulfide Zn ores (S = Silvermines; G = Galmoy), with a comparison to SW Sardinian and Belgian deposits

| Morphological types | Abundance ^a | | | Minor element content (wt.%) | | | | |
|--|------------------------|------|--------------------------|------------------------------|------------|-----------|-----------|-----------|
| | Ireland | | SW Sardinia ^b | Belgium ^c | FeO | MnO | CaO | PbO |
| | S | G | | | | | | |
| Type I — rhombohedral, distinct idiomorphic, commonly zoned crystals (mean size 50–600 mm) | | | xxx | xxxx | 0.21–0.48 | 0.03–0.36 | 0.13–0.60 | – |
| Type II — tiny subhedral crystals (mean size between 20 and 400 mm) with curved and slightly rounded faces | xxx | | x | | 0.60–3.99 | 0.13–0.35 | 0.31–0.87 | – |
| Type III — rice grain shaped, with grain dimension in the range 250 mm–1 mm in length | xxxx | xxxx | xxx | | 0.00–1.02 | 0.05–0.11 | 0.19–1.10 | 0.04–1.15 |
| Type IV — roughly rounded to one-dimensional clusters (approximately between 10 and 600 mm across) showing well-developed rhombohedral faces | xxxx | xxx | xxx | | 0.13–10.49 | 0.00–2.02 | 0.08–1.14 | 0.00–0.85 |
| Type V — botryoidal aggregate, with more or less indiscernible crystal terminations (mean size of each rounded mass 100–300 mm across) | | xxxx | xx | xxx | 0.34–0.98 | 0.00–0.12 | 0.07–1.27 | 0.80–1.99 |
| Type VI — vuggy to drusy scalenohedral crystals (dimension along c-axis in the range of 30 mm–1 mm) | | | | xx | n.d. | n.d. | n.d. | n.d. |

“–”, Below detection limit.

n.d., Not determined.

^a xxxx common; xxx quite common; xx rare; x very rare (evaluated by OM and SEM).

^b From Aversa et al. (2002).

^c From Coppola et al. (2007-this volume).

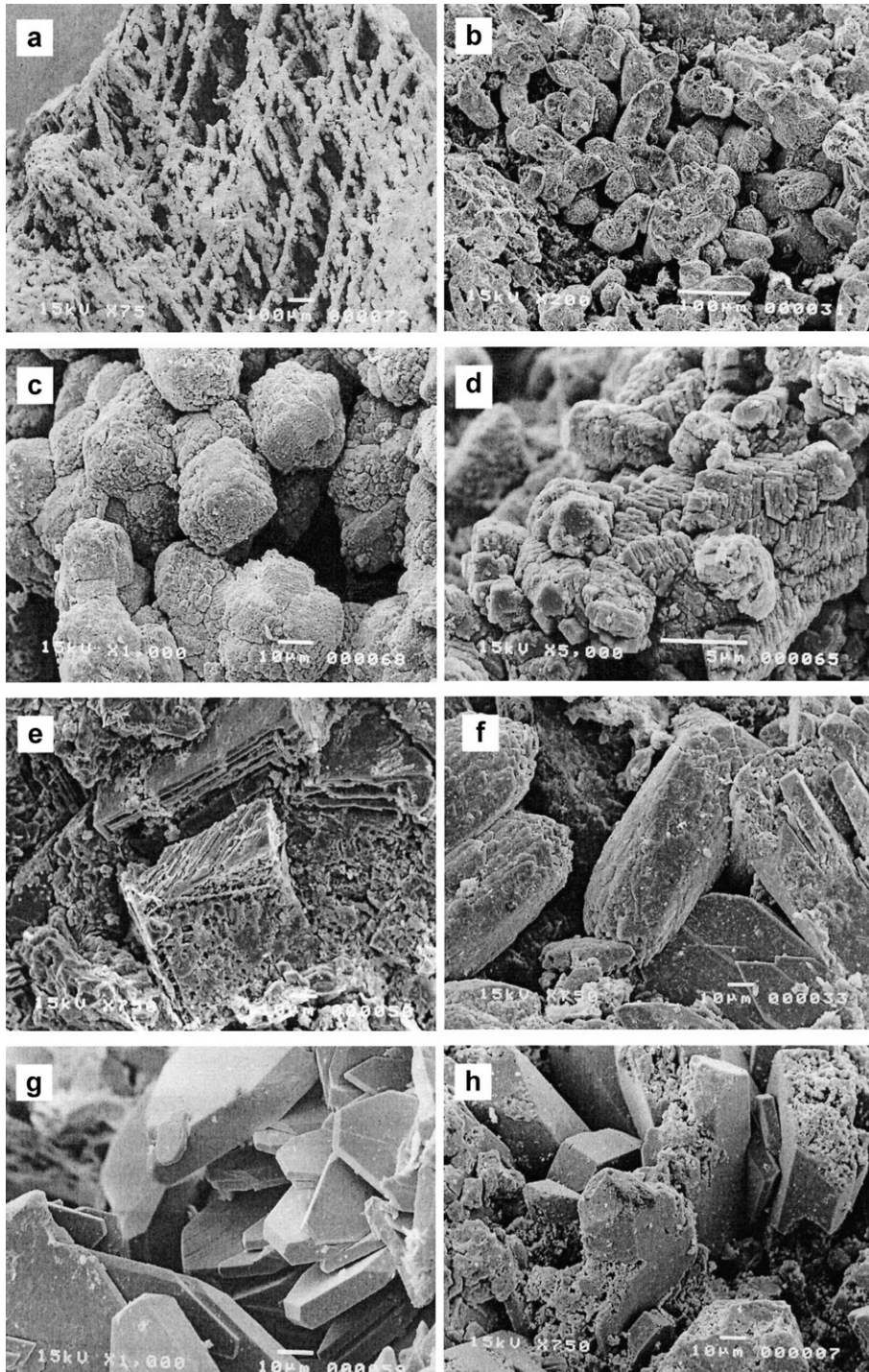


Fig. 7. Secondary electron microscopy micrographs of various smithsonite (classified as in Sardinia nonsulfide ores), and hemimorphite occurrences at Silvermines: (a) Type II smithsonite, (b) Type III smithsonite, (c) Type IV smithsonite, (d) Type IV, Fe-rich smithsonite, (e) dolomite partially replaced by Fe-bearing Type IV smithsonite, (f) idiomorphic hemimorphite with Type III smithsonite, (g) euhedral hemimorphite aggregates, (h) hemimorphite with clay minerals and Fe (oxyhydr)oxides.

study carried out on a large number of smithsonite-rich samples revealed three main morphological types of smithsonite, which have been compared with those recorded in the Sardinian and Belgian nonsulfide deposits (Boni et al., 2003; Coppola et al., 2007-this volume) (Table 2). Type I (idiomorphic rhombohedral crystals), quite common in Sardinia, has not been found in the Irish deposits. Type II smithsonite is fairly abundant at Silvermines, consists of subhedral tiny crystals with a mean size of 20 to 50 μm , and shows slightly rounded faces. This type coats irregular vugs and fractures and sometimes

may replace dolomite host rock (Fig. 7a). Type III “rice grain” smithsonite is also very common: the whitish grains can reach a maximum dimension of 1 mm in length. “Rice grains” encrust the surfaces of earthy, deeply red to brown calamine samples (Fig. 7b) and are often in association with euhedral hemimorphite (Fig. 7f). This type of smithsonite occurs in the upper parts of the drill cores and appears to be always the final phase to be precipitated. Its chemical composition corresponds to rather pure Zn carbonate. Type IV smithsonite has been frequently encountered in many Silvermines samples.

Table 3

Selected chemical analyses of smithsonites and hemimorphites from 302/03 and 303/03 Silvermines drill cores (average of five to eight point analyses); morphological smithsonite types observed on SEM are also reported (see text)

| Sample # | Smithsonite | | | | | | | | Hemimorphite | | | | |
|------------------------------|--|-------|---------|-------|----------|-------|---------|-------|--|-------|--------|-------|-------|
| | MT1 | | | | MT5 | | | | MT1 | | MT2 | | |
| | Type III | | Type IV | | Type III | | Type IV | | | | | | |
| ZnO | 63.55 | 63.48 | 63.99 | 63.54 | 63.70 | 63.61 | 64.15 | 64.01 | SiO ₂ | 24.76 | 24.94 | 24.51 | 24.69 |
| FeO | 0.38 | 0.42 | 0.13 | 0.23 | | | 0.45 | 0.54 | ZnO | 67.25 | 66.73 | 66.25 | 67.38 |
| MnO | 0.05 | 0.08 | | | | | 0.09 | | FeO | 0.10 | 0.21 | 0.22 | 0.31 |
| CaO | 0.34 | 0.26 | 0.36 | 0.57 | 0.58 | 0.57 | 0.36 | 0.21 | CaO | | | | 0.35 |
| MgO | 0.33 | 0.29 | 0.23 | 0.18 | 0.31 | 0.18 | | | MgO | | 0.18 | | |
| PbO | 0.06 | 0.04 | | | | | | | H ₂ O | 7.21 | 7.24 | 7.68 | 7.36 |
| CO ₂ ^a | 35.41 | 35.32 | 35.37 | 35.30 | 35.40 | 35.20 | 35.46 | 35.27 | | | | | |
| | 100.1 | | 100.0 | | | | 100.5 | 100.0 | | | | 100.0 | |
| Total | 2 | 99.89 | 8 | 99.82 | 99.99 | 99.56 | 1 | 3 | Total | 99.32 | 99.30 | 98.66 | 9 |
| | <i>Numbers of ions on the basis of 6 O</i> | | | | | | | | <i>Numbers of ions on the basis of 6 cations</i> | | | | |
| Zn | 1.94 | 1.95 | 1.959 | 1.950 | 1.949 | 1.958 | 1.959 | 1.966 | Si | 1.996 | 2.003 | 1.998 | 1.980 |
| Fe | 0.01 | 0.02 | 0.005 | 0.008 | | | 0.016 | 0.019 | Zn | 4.002 | 3.958 | 3.998 | 3.989 |
| Mn | 0 | 0 | | | | | 0.003 | | Fe | 0.007 | 0.014 | 0.015 | 0.021 |
| Ca | 0.02 | 0.01 | 0.016 | 0.025 | 0.026 | 0.025 | 0.016 | 0.009 | Ca | | | | 0.030 |
| Mg | 0.020 | 0.180 | 0.014 | 0.011 | 0.019 | 0.011 | | | Mg | | 0.021 | | |
| Pb | 0.001 | 0.001 | | | | | | | OH | 1.938 | 1.940 | 2.088 | 1.968 |
| C | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | | | | | |
| Sample # | MT8 | | | | MT20 | | | | MT28 | | | | |
| | Type IV | | | | Type IV | | | | Type II | | | | |
| | | | | | | | | | | | | | |
| ZnO | 63.52 | | 63.42 | | 52.82 | | 50.87 | | 60.57 | | 59.88 | | |
| FeO | 0.34 | | 0.68 | | 8.07 | | 10.49 | | 2.68 | | 3.99 | | |
| MnO | | | 0.54 | | 2.02 | | 1.79 | | 0.20 | | 0.13 | | |
| CaO | 0.53 | | 0.08 | | 0.40 | | 0.59 | | 0.87 | | 0.67 | | |
| MgO | 0.23 | | | | 0.97 | | 0.24 | | | | | | |
| PbO | | | | | | | | | | | | | |
| CO ₂ ^a | 35.38 | | 35.27 | | 36.27 | | 35.90 | | 35.35 | | 35.58 | | |
| Total | 100.00 | | 99.99 | | 100.55 | | 99.88 | | 99.67 | | 100.25 | | |
| | <i>Numbers of ions on the basis of 6 O</i> | | | | | | | | | | | | |
| Zn | 1.945 | | 1.948 | | 1.577 | | 1.534 | | 1.856 | | 1.823 | | |
| Fe | | | 0.024 | | 0.237 | | 0.358 | | 0.093 | | 0.138 | | |
| Mn | 0.012 | | 0.019 | | 0.069 | | 0.062 | | 0.007 | | 0.005 | | |
| Ca | 0.024 | | 0.004 | | 0.017 | | 0.026 | | 0.039 | | 0.030 | | |
| Mg | 0.014 | | | | 0.580 | | 0.015 | | | | | | |
| Pb | | | | | | | | | | | | | |
| C | 2.000 | | 2.000 | | 2.000 | | 2.000 | | 2.000 | | 2.000 | | |

^a Calculated from stoichiometry.

SEM studies reveal that the form of the latter type can vary from tiny rounded aggregates (Fig. 7c) to several clusters of thin platelets, distinctly stacked-up in one direction (commonly $40 \times 40 \times 150$ nm in size). These clusters have been mostly observed in the Fe-rich varieties (Fig. 7d), which also partly replace the dolomitic host rock (Fig. 7e). In both cases, the main feature of these aggregates is the strong development of the rhombohedral faces. Type IV occurs as cavity and fracture filling and has been also recorded in the Belgian nonsulfide Zn ores by Coppola et al. (2007-this volume) and reference therein. Unaltered idiomorphic hemimorphite occurs in cavity-lining aggregates (Fig. 7g) or partly corroded with minute crystals of clay minerals and Fe oxides (Fig. 7h). Type II and the two varieties of Type IV, belong to earlier generations and can be found equally distributed in both drillholes, even if the ferroan variety of Type IV is less frequent at Silvermines. Replacement of host rock dolomite by smithsonite has produced Fe-bearing types of Zn carbonate, e.g., the ferroan Type IV (up to 10.5 wt.% FeO) and Type II (up to

4.0 wt.% FeO). The determined paragenesis of the different smithsonite types at Silvermines is: Type II and IV \rightarrow Type III. In this latter generation, a quite remarkable decrease in the iron content is observed.

In Table 3 WDS microprobe analyses of representative smithsonites and hemimorphites from Silvermines are reported. Type III and IV smithsonites show a composition quite close to ideal smithsonite, with low contents of FeO (up to 0.42 wt.% in Type III and 0.68 wt.% in Type IV), CaO (up to 0.59 wt.% in Type III and 0.57 wt.% in Type IV) and minor and/or trace amounts of MgO, MnO, and PbO. Type II and the ferroan variety of Type IV (Fig. 7d) show high FeO contents, in the range 2.7 to 4.0 wt.% for Type II and of 8.1 to 10.5 wt.% for Type IV. MnO can reach up to 2.0 wt.% in Type IV. Hemimorphite displays a stoichiometric chemical composition, with SiO₂ varying between 24.8 and 25.0 wt.% and ZnO ranging between 65.3 and 65.2 wt.%, with only traces of Fe, Ca and Mg.

Whole rock chemical analyses of selected samples from drillholes 302/03 and 303/03 are shown in Fig. 8

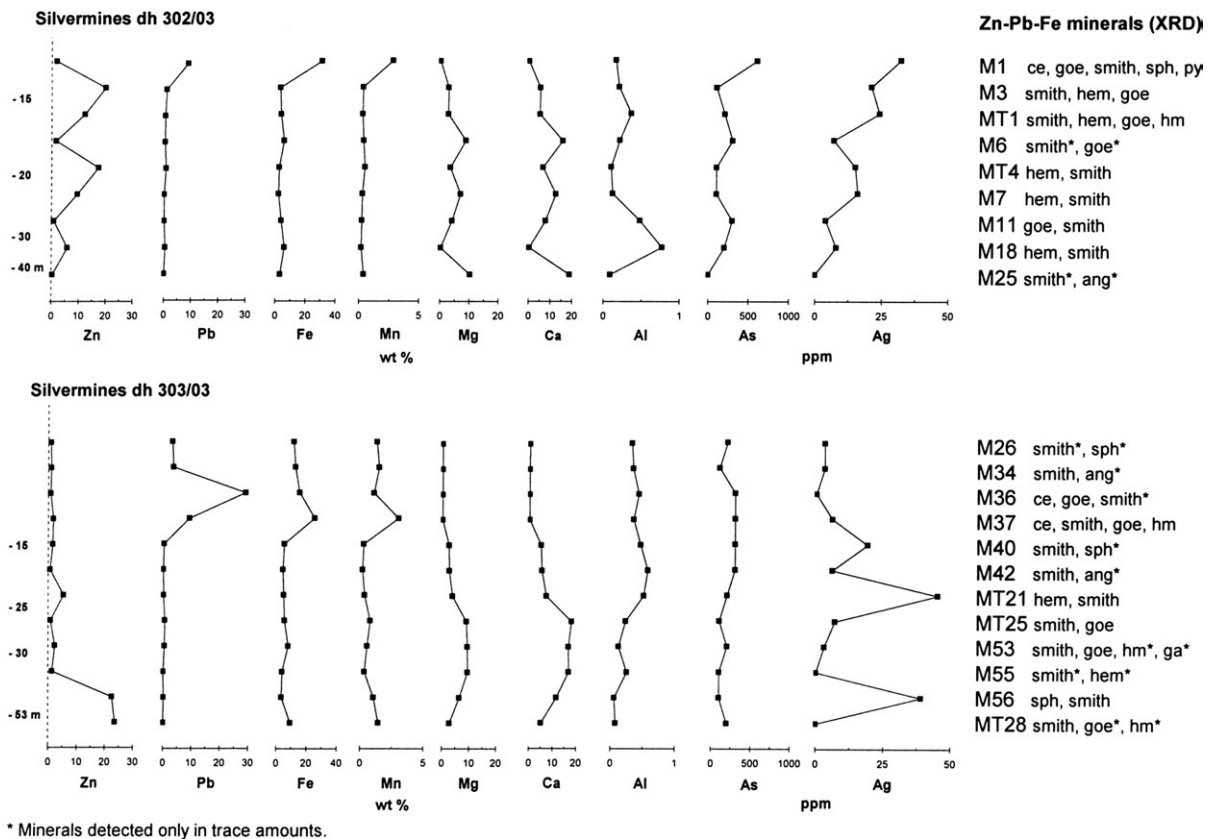


Fig. 8. Chemical analyses of selected samples from drillholes 302/03 and 303/03 at Silvermines, compared to Zn-Pb-Fe-bearing mineral associations inferred by X-ray diffraction (mineral abbreviations as in Fig. 4).

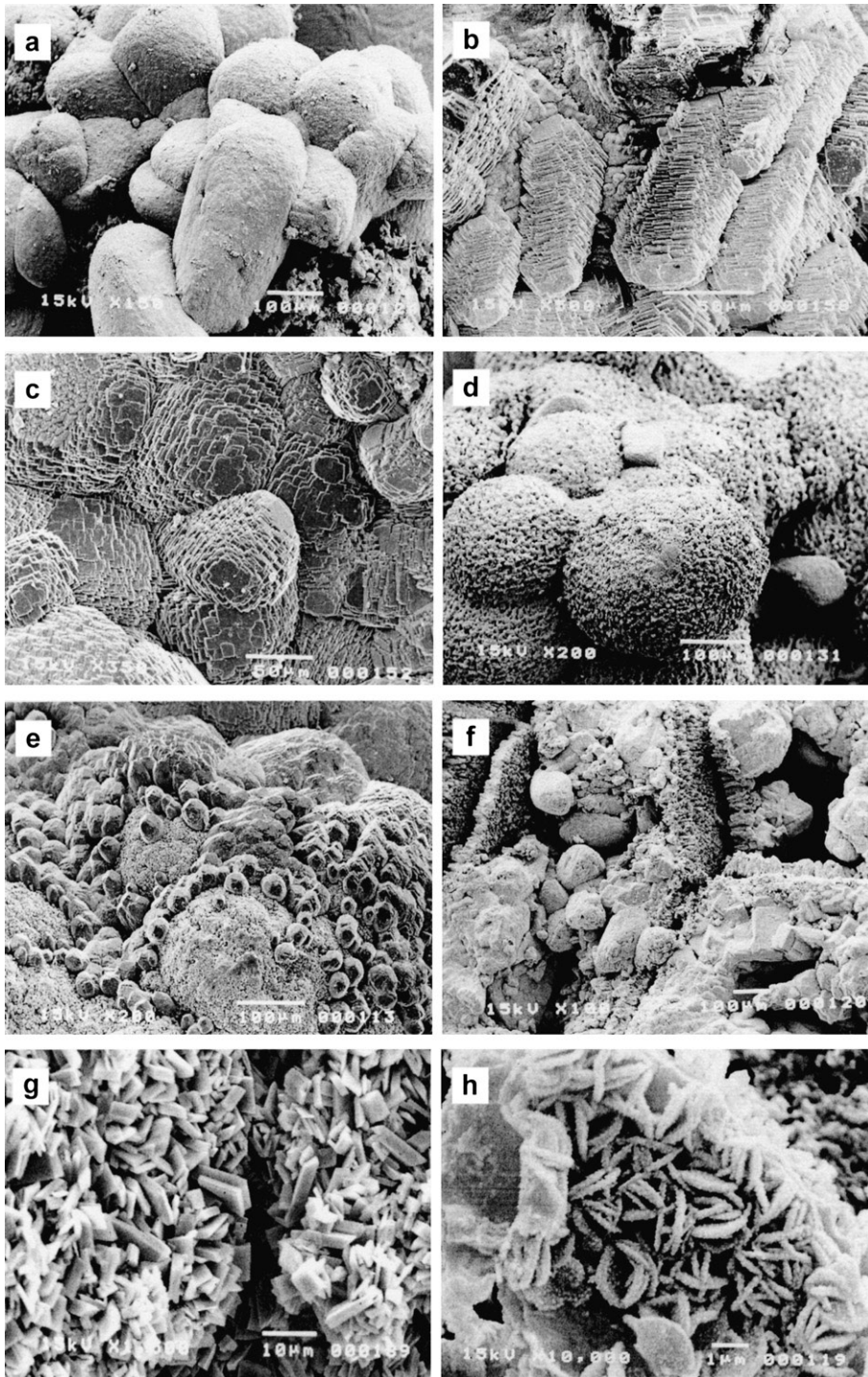


Fig. 9. Secondary electron microscopy images of different smithsonite forms and sulfates from Galmoy Mine: (a) Type III smithsonite, (b) Type IV (ferroan variety) smithsonite, (c) Type IV smithsonite, a variety with well defined rhombohedral faces, (d) Type V globular smithsonite, (e) Type IV smithsonite growing on Type V, (f) sulfides (the pyrite cubes, lower right corner) coated and partially replaced by Type IV and Type V smithsonite crusts; cavity-filling late Type III smithsonite, (g) boyleite growing on sulfides, (h) jarosite coating Fe (oxyhydr)oxides and clay minerals.

(values given in weight percent or ppm element). In both drillholes the Zn content is highly variable. In 302/03 Zn ranges from about 0.4 to 20.0 wt.%; Fe, Pb and Mn reach their maximum values in the top most sample (sample M1), with 30.9 wt.% Fe, 8.9 wt.% Pb, and 2.8 wt.% Mn. Ca and Mg are predominant in mostly dolomitic Zn-free samples (e.g., M6 and MT7). Cd and As are low (from below detection limit to not greater than 0.06 wt.%), and Ag content varies from 0 to 32 ppm, with the highest amount again in the M1 sample. In the uppermost oxidation zone (from the surface to 10 m below ground) of drillhole 302/03, Pb occurs as cerussite and coexists with Ag, Mn and Fe oxides. With depth, Zn (in form of smithsonite and hemimorphite) partly mimics the Ag content. Both Ag and As decrease with depth. In drillhole 303/03, Zn ranges from 0.9 to 23.6 wt.%. Fe ranges between 3.5 and 25.3 wt.%, with the higher contents in the upper levels of the drillhole (samples M26, M34, M36 and M37). Mn and Pb have approximately the same trend with up to about 3.00 wt.% Mn in M37. Locally high Pb values (M36) are related to the occurrence of cerussite (Fig. 5). Ca and Mg behave sympathetically as in drillhole 302/03. In the upper oxidation zone (from – 5 to – 15 m) of drill core 303/03, cerussite occurs together with Mn–Fe-(hydr)oxides. At depth (– 52 m) Fe–Mn-(hydr)oxides coexist with smithsonite and hemimorphite. In both 302/03 and 303/03 drillholes, Zn shows an inverse correlation with Ca and Mg: this might be due to the replacement of dolomite host rock first by primary and then by secondary Zn minerals.

6.2. Galmoy

Primary sulfides, still present at Galmoy in association with the oxidized phases, are mainly represented by pyrite, sphalerite and galena with no evidence of supergene sulfides. Locally barite also occurs as a primary or detrital phase. The main nonsulfide Zn–Fe–Pb phases are smithsonite, cerussite, Fe oxides and oxyhydroxides (goethite, hematite and lepidocrocite), anglesite and traces of hydrozincite. The presence of willemitte was mentioned in an unpublished mine report by Strongman (2003), but has not been confirmed in our study. Gangue minerals consist of dolomite, detrital quartz, calcite and clay minerals, including illite and trace amounts of nontronite. Smithsonite is widespread in the analyzed nonsulfide-bearing samples and occurs in different types of aggregates ranging in color from white, light yellow, light orange to dark gray. At Galmoy the smithsonite-rich samples are virtually hemimorphite free, in contrast to reported hemimorphite in the CW orebody at Galmoy and to Silvermines. SEM-EDS and OM studies revealed the

following three smithsonite types at Galmoy (Table 2). The “rice grain”-shaped Type III smithsonite is fairly widespread and occurs as whitish encrustations (Fig. 9a). It represents the last generation at Galmoy, as at Silvermines. It always occurs in cavities or coats earlier deposited smithsonite types. Type IV smithsonite is also common but recognizable only by SEM-EDS; it can occur in a variety enriched in Fe (Fig. 9b), as well as in Fe-poor aggregates (Fig. 9c). It is often coated by Type III smithsonite. Type V smithsonite is frequent. It ranges in color from light yellow to light orange and dark gray (Fig. 9d). In very few samples, the latter type seems to evolve laterally into crustiform aggregates. The globular Type V smithsonite is dominant at Galmoy. It appears to be the first deposited smithsonite generation. SEM and OM show evidence of replacement of sulfides by Type V smithsonite, mostly in form of thin crusts. The different smithsonite morphological types of the G orebody, often occur together with complex inter-relationships. Some crystal habits and aggregations are common to those of Silvermines, such as the “rice grain” and Type IV smithsonites. In some of the examined samples, Type IV smithsonite is growing on globular Type V (Fig. 9e). Pyrite crystals also occur, coated and/or partially replaced by both Type IV and Type V smithsonites, followed by a much later Type III in vugs (Fig. 9f). A likely paragenesis of the smithsonite types observed at Galmoy is: Type V → Type IV → Type III. Table 4 shows microchemical analyses of smithsonite and cerussite. “Rice grain” smithsonite generally displays low Fe content, in the range 0.12 to 0.35 wt.% FeO with the exception of sample MG18 (1.0 wt.% FeO). Lead and Ca reach up to ~ 1.0 wt.% each, while Mg and Mn contents are low. Both Fe-rich and Fe-poor varieties of Type IV smithsonite are found at Galmoy as at Silvermines. However, the ferroan variety has a maximum FeO content of only 1.16 wt.%, much lower than at Silvermines. Type V smithsonite shows high contents of PbO (up to ~ 2.0 wt.%) and CaO can reach up to ~ 1.3 wt.%. Traces of Mn, Mg, Ni and Co have also been observed. Cerussite composition does not show enrichments in any particular element, except for the presence of small traces of Cd, Zn and Fe.

Other secondary minerals are represented by a variegated sulfate assemblage, consisting of gypsum $\text{CaSO}_4 \cdot 2(\text{H}_2\text{O})$, boyleite $(\text{Zn}, \text{Mg})\text{SO}_4 \cdot 4(\text{H}_2\text{O})$, rozenite $\text{Fe}^{2+}\text{SO}_4 \cdot 4(\text{H}_2\text{O})$, jarosite $\text{KFe}^{3+}_3(\text{SO}_4)_2 \cdot (\text{OH})_6$ and copiapite $\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20(\text{H}_2\text{O})$. The tiny but well-formed crystals of sulfates, testifying to recent and/or ongoing sulfide alteration, have been encountered in several areas at Galmoy. Boyleite crystals coating primary sulfides have been detected by SEM (Fig. 9g), as well as white jarosite encrusting a Fe oxide- and clay

Table 4

Chemical analyses of representative smithsonites and cerussites from the Galmoy Mine — G orebody (average of five to ten point analyses), with indication of morphological smithsonite types (see text)

| Sample # | Smithsonite | | | | | | | | | | Cerussite | | | | |
|------------------------------|--|-------|----------|-------|---------|--------|----------|--------|---------------------|-------|--|-------|-------|-------|-------|
| | MG2 | | MG13 | | MG16 | | MG17 | | | | MG3 | | MG8 | | |
| | Type V | | Type III | | Type IV | | Type V | | Type IV | | | | | | |
| ZnO | 59.72 | 60.50 | 61.65 | 61.89 | 63.52 | 63.43 | 60.73 | 60.68 | 61.06 | 61.31 | PbO | 83.24 | 82.70 | 82.91 | 84.16 |
| FeO | 0.98 | 0.85 | 0.29 | 0.35 | 0.04 | 0.09 | 0.86 | 0.75 | 1.16 | 1.13 | ZnO | 0.03 | | 0.02 | |
| MnO | 0.07 | 0.10 | | | | | | 0.03 | | 0.07 | FeO | 0.02 | 0.06 | 0.02 | |
| CaO | 0.94 | 0.84 | 0.99 | 0.84 | 0.63 | 0.53 | 1.25 | 1.27 | 1.14 | 1.11 | CdO | 0.13 | 0.05 | 0.16 | 0.15 |
| MgO | 0.34 | 0.31 | 0.22 | 0.39 | 0.16 | 0.22 | 0.23 | 0.19 | 0.38 | 0.42 | CO ₂ * | 16.52 | 16.40 | 16.46 | 16.68 |
| PbO | 1.99 | 1.91 | 1.02 | 1.05 | 0.67 | 0.62 | 1.36 | 1.39 | 0.78 | 0.85 | | | | | |
| CO ₂ ^a | 34.59 | 34.82 | 34.89 | 35.13 | 35.33 | 35.29 | 35.02 | 34.92 | 35.38 | 35.54 | | | | | |
| | | | | | 100.3 | 100.1 | | | | 100.4 | | | | | 100.9 |
| Total | 98.63 | 99.33 | 99.06 | 99.65 | 5 | 8 | 99.45 | 99.23 | 99.90 | 3 | Total | 99.94 | 99.21 | 99.57 | 9 |
| | <i>Numbers of ions on the basis of 6 O</i> | | | | | | | | | | <i>Numbers of ions on the basis of 6 O</i> | | | | |
| Zn | 1.870 | 1.882 | 1.914 | 1.908 | 1.947 | 1.947 | 1.878 | 1.889 | 1.871 | 1.896 | Pb | 1.988 | 1.991 | 1.988 | 1.991 |
| Fe | 0.035 | 0.030 | 0.010 | 0.012 | 0.001 | 0.003 | 0.030 | 0.026 | 0.040 | 0.039 | Zn | 0.002 | | 0.001 | |
| Mn | 0.003 | 0.004 | | | | | | 0.001 | | 0.002 | Fe | 0.001 | 0.004 | 0.001 | |
| Ca | 0.043 | 0.038 | 0.045 | 0.038 | 0.028 | 0.024 | 0.056 | 0.057 | 0.051 | 0.049 | Cd | 0.005 | 0.002 | 0.007 | 0.006 |
| Mg | 0.021 | 0.019 | 0.014 | 0.024 | 0.010 | 0.014 | 0.014 | 0.012 | 0.024 | 0.026 | C | 2.000 | 2.000 | 2.000 | 2.000 |
| Pb | 0.023 | 0.022 | 0.012 | 0.012 | 0.007 | 0.007 | 0.015 | 0.016 | 0.009 | 0.009 | | | | | |
| C | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | | | | | |
| Sample # | MG18 | | MG19 | | | | MG24 | | | | | | | | |
| | Type III | | Type III | | Type V | | Type III | | Type V ^b | | | | | | |
| ZnO | 61.05 | 60.84 | 61.58 | 60.84 | 62.88 | 62.61 | 62.69 | 62.50 | 61.99 | 62.04 | | | | | |
| FeO | 1.02 | 0.99 | 0.65 | 0.29 | 0.34 | 0.44 | 0.17 | 0.12 | 0.46 | 0.36 | | | | | |
| MnO | 0.05 | 0.06 | 0.06 | 0.10 | 0.12 | 0.03 | 0.03 | 0.05 | 0.10 | 0.07 | | | | | |
| CaO | 1.10 | 0.98 | 0.92 | 0.98 | 0.55 | 0.61 | 0.60 | 0.70 | 0.85 | 0.80 | | | | | |
| MgO | 0.23 | 0.28 | 0.39 | 0.28 | 0.23 | 0.67 | 0.62 | 0.52 | 0.42 | 0.30 | | | | | |
| PbO | 1.15 | 1.12 | 0.88 | 1.12 | 0.94 | 0.80 | 0.58 | 0.82 | 1.00 | 1.10 | | | | | |
| CO ₂ ^a | 35.16 | 34.99 | 35.17 | 34.56 | 35.30 | 35.72 | 35.44 | 35.34 | 35.34 | 35.14 | | | | | |
| Total | 99.76 | 99.26 | 99.59 | 98.13 | 100.34 | 100.97 | 100.13 | 100.05 | 100.16 | 99.81 | | | | | |
| | <i>Numbers of ions on the basis of 6 O</i> | | | | | | | | | | | | | | |
| Zn | 1.881 | 1.883 | 1.896 | 1.907 | 1.930 | 1.898 | 1.916 | 1.916 | 1.900 | 1.912 | | | | | |
| Fe | 0.036 | 0.035 | 0.023 | 0.010 | 0.012 | 0.015 | 0.006 | 0.004 | 0.016 | 0.013 | | | | | |
| Mn | 0.002 | 0.002 | 0.002 | 0.002 | 0.004 | 0.004 | 0.001 | 0.002 | 0.004 | 0.002 | | | | | |
| Ca | 0.049 | 0.044 | 0.041 | 0.045 | 0.024 | 0.027 | 0.027 | 0.031 | 0.038 | 0.036 | | | | | |
| Mg | 0.014 | 0.018 | 0.024 | 0.018 | 0.014 | 0.041 | 0.038 | 0.032 | 0.026 | 0.019 | | | | | |
| Pb | 0.013 | 0.013 | 0.010 | 0.013 | 0.011 | 0.009 | 0.006 | 0.009 | 0.011 | 0.012 | | | | | |
| C | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | | | | | |

^a Calculated from stoichiometry.

^b NiO. up to 0.25 wt.%, CoO up to 0.22 wt.%.

mineral-rich matrix (Fig. 9h). The sulfates formed clearly later than most secondary Zn carbonates.

7. Discussion

The investigated Irish nonsulfide Zn–Pb mineralization shows all the characteristics of supergene deposition, related to intense (paleo)weathering processes of the primary sulfide orebodies. It is confirmed that the nonsulfide minerals at Silvermines are confined, even in the fringe of

the main orebody, to the upper parts of the oxidation zone (between 40 and 50 m below the present day surface), as already mentioned by Boland et al. (1992) for the top zone of the sulfide deposit. At Galmoy, the nonsulfide concentrations have been encountered at deeper levels, down to between 70 and 90 m below today's surface. In both sites the oxidation phenomena were particularly enhanced along the structural directions, which controlled the emplacement of the primary sulfides and probably also acted as conduits for oxidizing meteoric waters.

The assemblage smithsonite–hemimorphite is typical of the Silvermines drill cores, whereas smithsonite is dominant at Galmoy (G-orebody). The regular association between primary sulfides and secondary carbonates/silicates is also a common feature of the mineral assemblage at Silvermines: the secondary ore is never completely refined and free of sulfides, not even in the more gossanous zones of the drill cores. According to Boland et al. (1992), who evaluated the most central parts of the nonsulfide body, the distribution of smithsonite and hemimorphite at Silvermines is a reflection of the oxidation level, with hemimorphite and goethite in the upper levels and smithsonite progressively enriched at depth. Contrary to this statement, hemimorphite does not occur preferentially in the upper zones of the weathering profile in either of the peripheral cores, but is homogeneously distributed throughout drillhole 302/03 and is slightly enriched at depth in drillhole 303/03. This is evidence that silica-rich fluids could have reacted with sulfides at several levels during the oxidation process. The higher amount of silica-bearing phases (newly formed quartz, clay minerals and hemimorphite) detected from the analyses of the Silvermines drill cores, may be related to the reactions of the weathering solutions with rocks of mixed composition, varying between dolomites and argillaceous limestones (as the Argillaceous Bioclastic Limestones with their shaly interbeds, Taylor and Andrew, 1978), compared with the locally dolomitized limestones at Galmoy (Lowther et al., 2003).

An interesting result of this study is the direct correspondence between at least part of the morphological types of the smithsonite crystals and their content of minor and trace elements. In both Silvermines and Galmoy deposits, Type III “rice grain” smithsonite, represents the latest Zn carbonate generation. It was precipitated in open cavities and is remarkably depleted in Fe and other trace elements, whereas Type II, IV and V smithsonites are certainly older and locally rich in Pb, Fe and Mn. In the Silvermines drill cores, Type II and IV smithsonites generally replace the dolomite host rocks, whereas at Galmoy all the investigated smithsonite types seem to replace the primary sulfides (“direct replacement”; Hitzman et al., 2003) or precipitate in cavities derived from their dissolution. A possible evidence for direct sulfide replacement at Galmoy is the anomalous Pb content (up to 2.0 wt.% PbO) of the Zn carbonates.

The geochemical signal at Silvermines indicates slightly more reducing conditions during deposition of the early (Fe- and Mn-rich) Zn carbonates, as compared to the late “rice grain” Type III (Fe-poor) smithsonites, which coexist with hemimorphite and Mn and Fe oxides and oxyhydroxides. At high fO_2 conditions, at which

both Fe and Mn oxides are stable, the Fe and Mn concentrations should be very low in the circulating fluids, and consequently in the precipitated smithsonite. A steady increase on fO_2 during progressive oxidation and thus a change from Fe–(Mn)-rich to Fe-poor smithsonite, is expected in supergene deposits. This progressive oxidation is not observed at Galmoy, where the majority of the smithsonite types appear to have been deposited already in fairly oxidizing conditions.

In SW Sardinia, Boni et al. (2003) considered the different forms of smithsonite to be related to various depositional environments within the karstic system. Type I rhombohedral smithsonite, occurring both in SW Sardinia and in Belgium (Coppola et al., 2007-this volume), has been found to be typical of the upper phreatic zone, where it replaces limestone and dolomite in several mines. The lack of Type I smithsonite, both at Silvermines and Galmoy, might indicate that in Ireland the weathering profiles are relatively immature, with the absence of a deep, well developed karstic network. This immaturity had been already mentioned by Morrissey and Whitehead (1971), who described the Tynagh “Residual Orebody” as a concentration of transported secondary minerals and clays in a shallow doline. Therefore, although much more nonsulfide ore concentrations could theoretically still be lying beneath glacial overburden throughout the mineralized areas of the Irish Midlands, neither their tonnage, nor their grade are likely to be sufficiently high to warrant initiation of an exploration campaign.

Time constraints for the deposition of the nonsulfide ores are still unclear, since there is no unambiguous age indication of weathering related to the formation of nonsulfides at either Galmoy or Silvermines. We doubt that ^{40}Ar – ^{39}Ar or K–Ar dating of the jarosite discovered in the Galmoy mine could yield reliable formation on the age of nonsulfide ores, since the sulfates occur very late in the paragenetic sequence and are probably related to (sub)recent oxidation phenomena. The limited depth of nonsulfide occurrence, currently evidenced by oxidation levels down to less than 100 m in both mine sites, could possibly point to renewed uplift and significant erosion of the weathering profile before the deposition of the glacial cover rocks. We consider the Paleogene as the most likely period for sulfide weathering. During this period, the Paleocene basalts at Antrim, Northern Ireland, were transformed to laterites and even bauxites (Hill et al., 2001). Stable isotope studies on goethite, gibbsite, and organic matter in the Antrim laterites suggest a hot and humid climate at high paleo-latitude related to elevated atmospheric CO_2 concentration (Tabor and Yapp, 2005). This Early Tertiary weathering

phase might have extended also to other areas of continental Ireland and have produced the investigated nonsulfide concentrations on top of primary sulfide deposits. However, further reactivations of the weathering profiles, especially within the warm interglacial periods of the Quaternary (e.g., Proudfoot, 1958), cannot be excluded.

8. Conclusions

The nonsulfide zinc–lead mineralization at Silvermines and Galmoy represents an example of supergene oxidation of primary sulfide mineralization, redeposition and preservation under glacial till. At both sites, the dominant mineral composition of secondary ores is relatively simple with smithsonite–hemimorphite at Silvermines and smithsonite at Galmoy. Primary sulfides and secondary carbonates/silicates are generally associated at both localities, while fairly recent coatings of sulfates at Galmoy testify a recent and/or ongoing alteration. The age of the main weathering phase is still uncertain, but indirect geological evidence suggests Early Tertiary oxidation.

There is a direct correspondence between the smithsonite forms and their content of minor and trace elements (Fe–Ca–Mn–Pb). In both deposits, “rice grain” Fe-poor smithsonite coexisting with Fe and Mn oxides and oxyhydroxides represents the latest generation of Zn carbonate deposited at higher fO_2 than the earlier generations. At Silvermines, Zn carbonates and silicates replace host rock carbonates and grow in secondary porosity created by the dissolution process. At Galmoy, an anomalously high Pb content in smithsonite is possibly related to partial “direct replacement” of sulfides.

Lack of rhombohedral smithsonite, which characterizes the upper phreatic zone of analogous zinc–lead deposits in SW Sardinia and Belgium, may indicate the relative immaturity of the weathering profiles in Ireland and the absence of a well-developed karstic network that could have acted as a trap for secondary ores. In consequence, the nonsulfide concentrations of the Silvermines and Galmoy type, though very interesting for the study of paleoclimatic evolution in Western Europe, should still not be regarded as an attractive exploration target under present economic conditions.

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