

The mineralogy of the «Calamine» Ores in SW Sardinia (Italy): preliminary results

GASPARE AVERSA¹, GIUSEPPINA BALASSONE², MARIA BONI^{1*} and C. AMALFITANO³¹ Dipartimento di Geofisica & Vulcanologia, Università di Napoli «Federico II», Via Mezzocannone 8, 80134-Napoli, Italy² Dipartimento di Scienze della Terra, Università di Napoli «Federico II», Via Mezzocannone 8, 80134-Napoli, Italy³ Dipartimento di Scienze del Suolo, della Pianta e dell'Ambiente, Università di Napoli «Federico II», Via Università 100, I-80055 Portici, Italy*Submitted, February 2002 - Accepted, September 2002*

ABSTRACT. — Recently, due to new extraction technologies, there has been a marked revival of interest in the geology and exploration for non-sulfide zinc deposits in the world. The Iglesias area (SW Sardinia, Italy) is one of the oldest mining districts in the world. Significant occurrences of secondary non-sulfide Zinc ores, were exploited from the Iglesias district until the 1960's. Although this is one of the oldest mining districts in the world, there are very limited published data.

The most economically important non-sulfide zinc minerals (Zn-and minor Pb-carbonates and silicates) found at seven historical mining areas were characterized by combined XRD, SEM, EPM and FTIR investigations. Mineralogically the studied ores are composed mainly of smithsonite, which occurs in predominant microcrystalline, as well as concretionary and stalactitic forms. SEM analyses of the Zn carbonate have revealed interesting features, including six distinct habits (called I- to V-type and M-Type). Ongoing studies on C-isotopes ratios suggest that these are very variable, and may relate to the distinct crystal morphologies. Chemically the smithsonites are nearly pure Zn-carbonates, with traces of Fe, Mg, Mn and Cd and occasionally slightly higher Ca contents (up to 0.09 apfu Ca). Monheimite (M-type) shows a composition nearly intermediate between smithsonite and siderite, with

up to 0.74 apfu Fe. Microcrystalline to earthy hydrozincite, as well as hemimorphite and cerussite, represent the other common phases found in the secondary mineral assemblage. Hydrozincite is more abundant in the samples found in the higher levels of the mines and decreases with depth relative to the smithsonite concentrations. Their chemical compositions are also quite homogeneous, except for minor amounts of Ca and Zn in cerussite and of Cu in hemimorphite from the Sa Duchessa mine. XRD and FTIR analyses of the studied mineral phases are in agreement with the literature data.

RIASSUNTO. — In seguito allo sviluppo di nuove tecnologie estrattive, si è recentemente rinnovato l'interesse per la geologia e l'esplorazione delle mineralizzazioni a non-solfuri di Zn nel mondo. Nell'area dell'Iglesias (Sardegna SW, Italia), in assoluto uno dei più antichi distretti minerari, si trovano notevoli depositi minerari ad «ossidati» secondari di Zinco, coltivati fino agli anni sessanta, e sui quali esistono pochi dati nella letteratura moderna.

I più importanti minerali ossidati di Zn economici (carbonati e silicati di Zn e Pb) campionati in sette aree minerarie, sono stati caratterizzati mediante XRD, SEM EPM e FTIR. La smithsonite risulta la fase predominante e si presenta macroscopicamente in prevalenza come aggregati microcristallini, concrezioni e stalattiti. Lo studio al SEM ha rivelato aspetti interessanti; sono state distinte sei differenti morfologie (denominate I÷V-type ed M-type),

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

correlabili con diversi rapporti isotopici del C. I dati chimici rivelano una smithsonite generalmente corrispondente a $ZnCO_3$ puro; frequenti sono tracce di Fe, Mg, Mn e Cd, mentre in alcuni punti analitici si sono riscontrati più alti contenuti in Ca (fino allo 0.09 apfu Ca). La monheimite (M-type) presenta una composizione intermedia tra smithsonite e siderite, con contenuti in Fe fino allo 0.74 apfu. Idrozincite, cerussite ed emimorfite sono gli altri minerali economici comunemente rinvenuti nei depositi a Calaminari studiati. L'idrozincite è più abbondante nei campioni provenienti dai livelli sommitali dei profili di alterazione osservabili in miniera e decresce con l'aumento della profondità rispetto alla smithsonite. I dati chimici relativi ai tre minerali mostrano composizioni in pratica stechiometriche, con tracce di Ca e Zn nella cerussite e di Cu nella emimorfite della miniera di Sa Duchessa. Le analisi in XRD ed FTIR delle fasi studiate sono in accordo con i dati della letteratura.

KEY WORDS: *Secondary non-sulfide Zn-Pb ores, Calamine, SW Sardinia, scanning electron microscopy, electron microprobe, X-ray diffraction, infrared spectroscopy.*

INTRODUCTION

The Iglesias-Sulcis area in SW Sardinia (Fig. 1) is one of the oldest mining districts in the world, with production dating to pre-Roman times. Exploitation in the district was initially for silver-lead-copper and later for zinc and barium deposits. In the first decades of the twentieth century, there were more than 50 mines. Due to increasing economic difficulties, the last producing mine was closed in 1998.

The geology of SW Sardinia is dominated by Paleozoic lithotypes, of sedimentary as well as of igneous origin, overlain by Tertiary and Quaternary volcanics and sedimentary rocks. Among the Palaeozoic sedimentary rocks, Cambro-Ordovician lithologies predominate (fig. 1). These correspond to epizonal facies metamorphic rocks, belonging to the so-called «External Zones» of the Variscan orogen (Carmignani *et al.* 1994). Within the Cambrian sediments, limestones and dolomites of the Gonnese Group (Bechstädt & Boni 1994) are

the preferred hosts for both primary as well as secondary Zn-Pb ores.

Most of the primary mineralisation is pre-Variscan and stratabound (Sedex + Mississippi Valley Type, MVT) and consists of sulfides locally associated with barite. Hydrothermal alteration of the host rocks is limited to local dolomitization and silicification (Bechstädt & Boni 1994, Boni 1985, 1986, Boni *et al.* 1996, Boni *et al.* 2000). Post-Variscan ores, consisting of Ag-bearing galena and barite in hydrothermal veins, as well as of small Cu-Zn sulfide concentrations in skarn bodies, have been economic only in the past.

The so-called «Calamine» ores consist of a supergene mixture of zinc carbonates and hydroxyl-carbonates and silicates (with minor Pb), which cap in the whole area the primary sulfide mineralisation. Historically they were the principal source of zinc from this district.

The scope of this paper is a preliminary study of the mineralogic characteristics of a significative set of samples from the economically more significant Zn-oxide mining districts of SW Sardinia. It is well known that some of the most significant occurrences of secondary ore minerals in the world can be found in this area. However, they are poorly recorded in the modern literature. The results of this study, together with isotopic and geochemical studies that are in progress (Boni *et al.* in press b), will contribute to a better characterization of the Sardinian Zn-oxide ores.

THE «CALAMINE»

The «Calamine» ores are considered to be the result of the *in situ* oxidation of primary carbonate-hosted sulfide ores, and subsequent remobilisation and redeposition as internal sediments into dissolution vugs and karst cavities (Large 2001). The name «Calamine», deriving from the well known «La Calamine-Kelmis» Zn-deposit in Belgium (Dejonghe 1998), has been now generally dropped, due to the great confusion in differentiating the ore

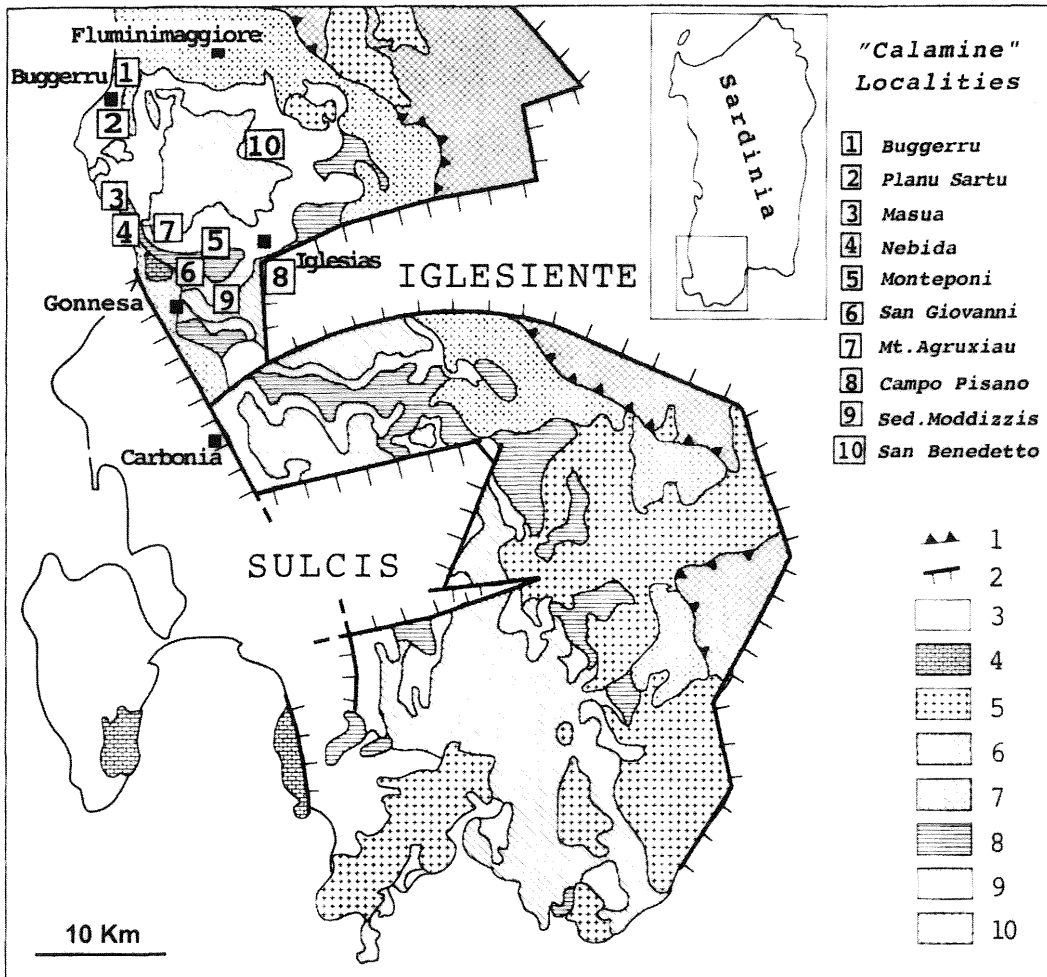


Fig. 1 – Sketch geological map of Southwest Sardinia and location of the main «Calamine» occurrences. 1 = overthrust, 2 = normal fault, 3 = Cenozoic, 4 = Mesozoic, 5 = Variscan granites, 6 = Palaeozoic (allochthonous), 7 = Ordovician to Devonian succession, 8 = Cambrian Iglesias Group, 9 = Cambrian Gonnesa Group, 10 = Cambrian Nebida Group (from Boni *et al.* in press, modified).

minerals identified by this term, in particular smithsonite and hemimorphite. Nevertheless, the name is still used to describe Zn-oxidation ores as a whole, especially in European countries.

In SW Sardinia the «Calamine» has been exploited extensively both in large open pits and in a maze of adits and/or winding trenches (fig. 2). This region is one of the few places in

the world where the association between «primary» Zn-Pb sulfides and «secondary» non-sulfide mineralisation can be well typified (Moore 1972, Boni *et al.* in press a,b). Historically, prior to the development of sulfide flotation in the early decades of 20th century, «zinc-oxide» ores were the principal source of zinc from this mining district (Fig.3a). The oxidation processes are apparently independent

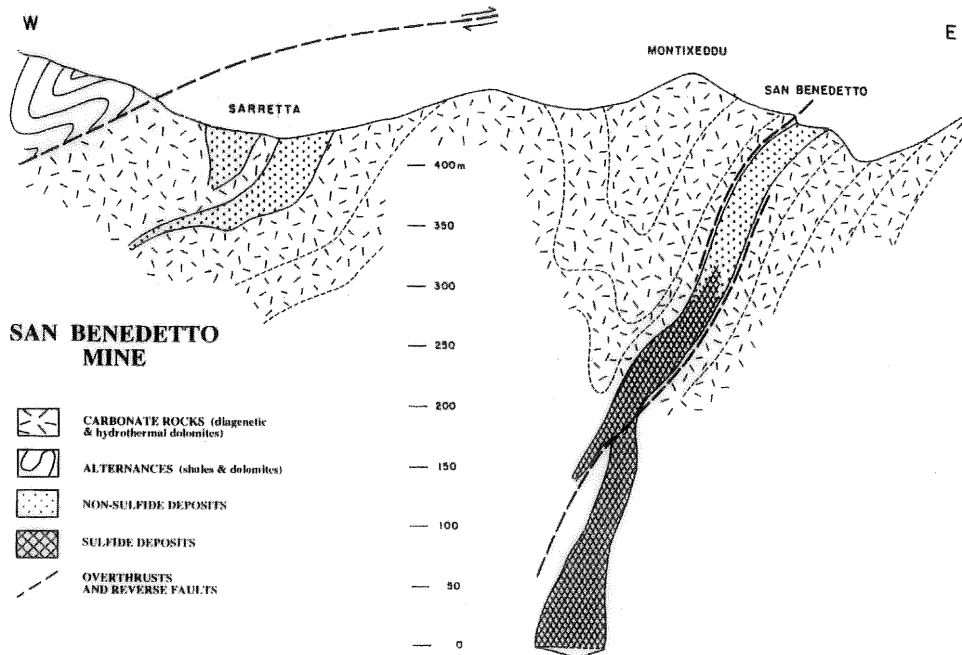


Fig. 2 – San Benedetto Mine: sketch section of the main orebody.

from the oscillations of the current water table, and should be related to Quaternary and even Tertiary geomorphologic settings. Several styles of «Calamine» mineralisation have been recognised in the district. These include both partial replacement of the host carbonates and stratabound primary sulfides, as well as concentrations of ferruginous, «earthy» smithsonite and hemimorphite-rich clays, that fill a maze of interconnecting karst cavities and open conduits in the upper levels of the mines.

The mineralogy of the oxidized ores is often very complex, comprising not only the most common Zn- and Pb-carbonates and silicates, but also very exotic species (Billows 1941, Zuffardi 1970, Moore 1972, Violo 1974, Stara *et al.* 1996) that are sought after by mineral collectors (Table 1). At the mesoscopic scale, smithsonite occurs as earthy, stalactitic, crustiform and perfectly crystalline varieties (Bonifazi and Massacci 1987, Boni *et al.* in press a, b), together with pseudomorphs after scalenohedric calcite (Moore

1972). The stalactitic concretions were characteristically abundant in the higher levels of the mines along the Nebida and Masua coast, where they are often seen altered to hydrozincite. Hemimorphite (fig. 3b) occurs together with smithsonite mainly in the upper part of the oxidation profiles. It is generally also concretionary in shape, and might locally be accompanied by quartz. Cu-bearing hemimorphite (fig. 3c) has been found in the areas where primary Cu-sulfides occur in the deeper parts of the old mines (e.g. the former skarn at Sa Duchessa).

ANALYTICAL METHODS

Each mineral phase was enriched by combined magnetic and gravimetric separation techniques, then carefully selected and examined under the stereomicroscope and polarizing microscope.

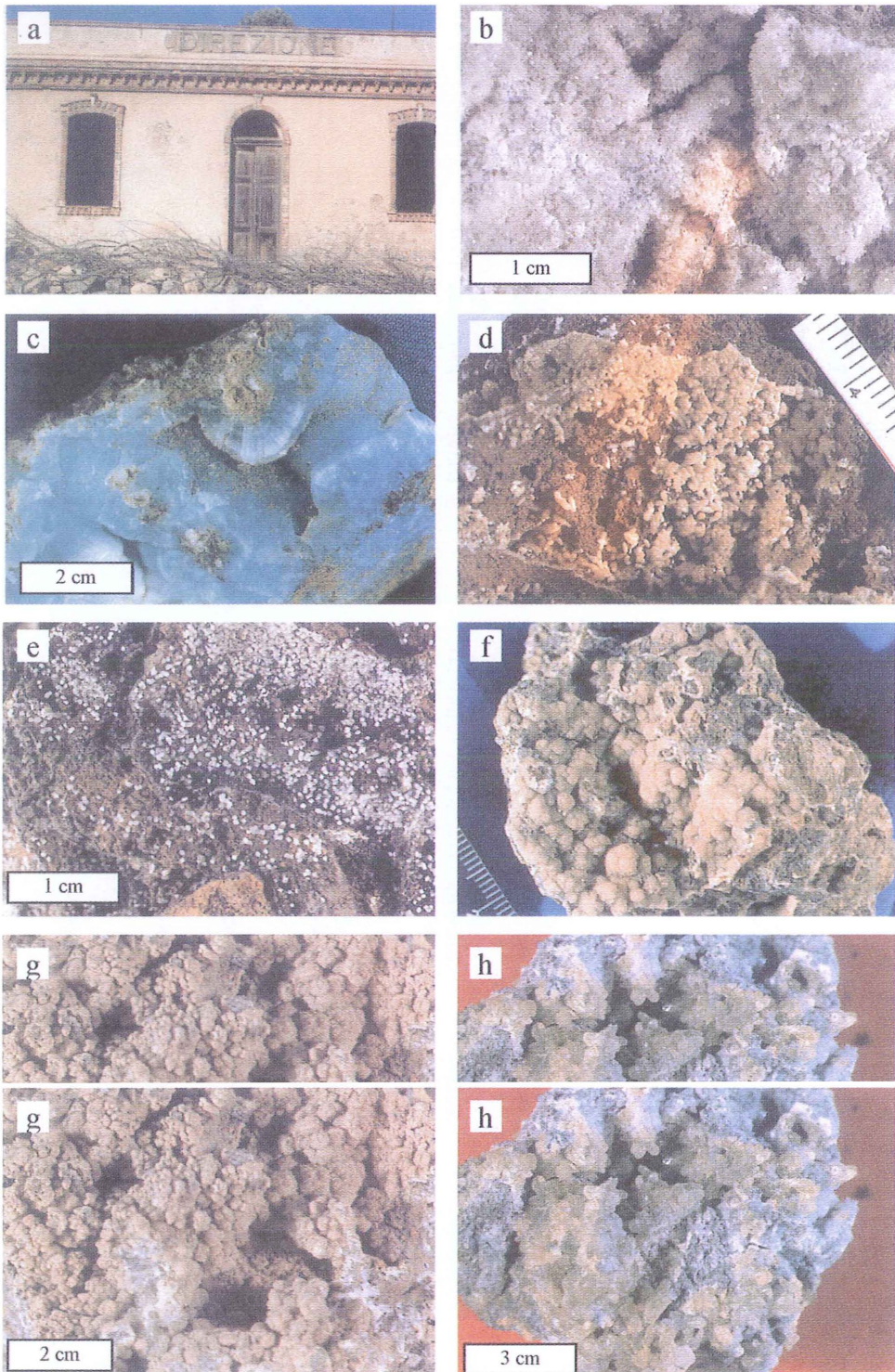


Fig. 3 – (a) Main office building at the old Seddas Moddizzis mine (Iglesias). (b) San Benedetto mine, thin tabular crystals of white hemimorphite. (c) Sa Duchessa mine, botryoidal Cu-hemimorphite. (d), (e) Mount Agruxiau mine, «rice grain» smithsonite crystals. (f), (g) S. Giovanni mine, botryoidal smithsonite. (h) Montevecchio mine, monheimite (Fe-rich smithsonite).

TABLE 1

Mineralogy of the supergene deposits in SW Sardinia; minerals in italics are economically significant (from Moore 1972 and Billows 1941, modified).

	supergene minerals								
	primary minerals	secondary sulfides	sulfates	carbonates	halides	oxides	silicates	other compounds	native metals
Lead	<i>galena</i>	galena	<i>anglesite</i> lanarkite	<i>cerussite</i> dundasite <i>iglesiasite</i> phosgenite leadhillite		minium massicot		wulfenite stolzite mimetite pyromorphite vanadinite beudantite bindehimitite descloisite	
Zinc	<i>sphalerite</i>	sphalerite	goslarite	<i>smithsonite</i> <i>hydrozincite</i> monheimite		zincite	<i>hemimorphite</i> Zn clays		
Copper	<i>chalcopyrite</i>	bornite chalcocite covellite	chalcantite brochantite celadonite spangolite connellite linarite	<i>malachite</i> auricalcite azurite rosasite		cuprite tenorite	chrisocolla plancheite	balydonite	native Cu
Iron	<i>pyrite</i> <i>magnetite</i> <i>hematite</i>	pyrite marcasite	melanterite	siderite		<i>limonite</i> goethite lepidocrocite hematite		simplesite scorodite phosphosiderite pharmacosiderite dufrenite	
Silver	<i>sulphosalts</i> argentite	<i>acantite</i>			cerargyrite embolite				native Ag
Barium	<i>barite</i>		<i>barite</i>						
Cadmium		greenockite				Cd oxides monteponite			
Nickel/cobalt	Ni/Co sulfides							erythrite annabergite	
Mercury		cinnabar							
Manganese				rhodochrosite		pyrolusite psilomelane manganite As oxides			
Arsenic	Arsenopyrite								

X-ray powder diffraction analysis (XRPD) was carried out between 5 and 75° (2θ) and 0.5° 2θ/min, on an automated diffractometer (SEIFERT MZVI) with CuKα radiation (1.5418 Å, 40 kV, 30 mA). Synthetic CaCO₃ (Mallinckrodt analytical reagent) was used as internal standard (the position of the 1014 reflection for CaCO₃ was taken as 3.035 Å, JCPDS-ICDD 5-586). The XDATA program (part of the XDAL 3000 software package from Rich. Seifert & Co.) was used to evaluate the analysed profiles. Diffraction patterns were compared with both the JCPDS-ICDD database and other literature data. Least-squares refinement of the setting angles of 2θ reflections was used for accurate unit-cell determination.

Scanning electron microscope (SEM) observations on morphology and major element analyses were performed on a Jeol JSM-5310 instrument in the energy-dispersive mode (EDS) (Link Analytical 10000). Data were reduced by a ZAF-4 correction program. Operating conditions were 15 kV acceleration voltage and 10 μm spot size, peak counting time 100s. Minerals and synthetic compounds were used as standards. The water content was evaluated by means of thermal analyses.

Fourier transform infrared spectroscopy (FTIR) was performed on various smithsonite samples, studied as KBr pellets. IR spectroscopic measurements were acquired by means of a Perkin-Elmer FTIR spectrometer 1720X. Background and sample spectra were obtained from 64 scans each, in air or in the respective crystal with 4 cm⁻¹ resolution. The data were processed with the IRDM program

RESULTS

The principal supergene zinc minerals of the present study are from mineralized rocks sampled from seven mining sites, where the depth of the oxidation zone extends several hundred meters below the surface. The samples were collected from the still accessible underground mines, mine dumps or from private collections. The specimen provenances

and mineral assemblages are reported in Table 2. The mineral phases consist of smithsonite (ZnCO₃), hydrozincite [Zn₅(CO₃)₂(OH)₆] and hemimorphite [Zn₄Si₂O₇(OH)₂·H₂O]. Cerussite (PbCO₃) also occurs in the mineral assemblage of the samples from Nebida and Monteponi mines. Minor amounts or traces of calcite, iron oxo-hydroxide (goethite, hematite), quartz, barite and galena have been locally observed or revealed by XRD.

Smithsonite and hydrozincite

Smithsonite is widespread and occurs in different types of aggregates ranging in color from greyish white, light yellow or pink to dark grey. An extensive SEM study carried out on a large number of smithsonite-bearing specimens, revealed the following occurrences of ZnCO₃:

- I-type: aggregates of idiomorphic rhombohedral smithsonite crystals;
- II-type: aggregates of small rounded, partly corroded smithsonite grains;
- III-type: lens-shaped, biconvex lumps of smithsonite («rice grains») (fig. 3 *d, e*);
- IV-type: crustiform, globular aggregates of platy smithsonite microcrystals (fig. 3 *f, g*);
- V-type: botryoidal smithsonite aggregates of colloform stalactites and crusts.

I-type corresponds to rhombohedral, distinct idiomorphic smithsonite individuals mainly found in the samples from the level +92 of the Nebida mine. They generally fill vugs and cavities or coat their most external surface, forming shining crystalline encrustations (fig. 4*a*). These perfect crystals range between 50 and 400 μm in size and always show the surface of the grains free from any corrosion evidence. Whitish rare calcite crystals and globular iron oxides/hydroxides occur locally interspersed among the rhombohedra. Bonifazi & Massacci (1987), in their SEM studies of the non-sulfide mineralizations of SW Sardinia (Buggerru-Caitas and San Giovanni deposits), also observed similar rhombohedral smithsonites, often intimately intergrown with calcite, or even associated with relicts of primary sphalerite.

TABLE 2
*Sample characterization and assemblage of the «calamine» rocks
 from Sardinian non-sulfide ore deposits.*

# of analyzed samples	Sample location and ore type	Mineral assemblage*
10	Monteponi mine massive "calamine" ore covered by a powdery white crusts and crystals	smithsonite, hydrozincite, cerussite, calcite, iron oxi-hydroxides, galena
10	Nebida mine massive to stalactitic "calamine" ore, with cavities filled by dark rhombohedral crystals or by a powdery white crust,	smithsonite, cerussite, calcite, quartz, galena
8	San Giovanni mine massive "calamine" ore, covered by orange-yellow botryoidal concretions or by powdery white crusts	smithsonite, hydrozincite, calcite
7	Mount Agruxiau red "earthy calamine" ore, often covered by "rice grain" light yellow crystal aggregates or with small lath-like transparent crystals	smithsonite, hemimorphite, calcite, iron oxi-hydroxides, barite
6	Seddas Moddizzis mine massive to red earthy "calamine" ores, with pinkish botryoidal concretions or with dispersed tiny white crystals	smithsonite, calcite, quartz, iron oxi-hydroxides
5	Sa Duchessa mine concretionary pale-blue "calamine"	hemimorphite, quartz
2	San Benedetto mine aggregate of lamellar crystals	hemimorphite, quartz
1	Montevecchio mine aggregate of elongated and intergrown yellowish-green crystals	Fe-rich smithsonite, quartz

* Mineral constituents listed in order of decreasing abundance.

II-type refers to poly-crystalline microaggregates of smithsonite individuals, often bearing curved and slightly rounded faces. These specimens have also been sampled in the Nebida mine. The crystal surfaces appear locally rough and corroded. Average crystal sizes are in the range of 200-400 μ m. This type of smithsonite crystal, coats irregular vugs in earthy greyish smithsonite masses (fig. 4b).

III-type - the so-called «rice grains» smithsonite (Stara *et al.* 1996) - has been observed in several specimens of red, earthy looking calamines from Mount Agruxiau mine and dumps. SEM study revealed that these forms seem to consist mainly of microcrystalline aggregates, but also of single elongated crystals (probably on the c-axis direction) with greater dimensions. Fig. 4c

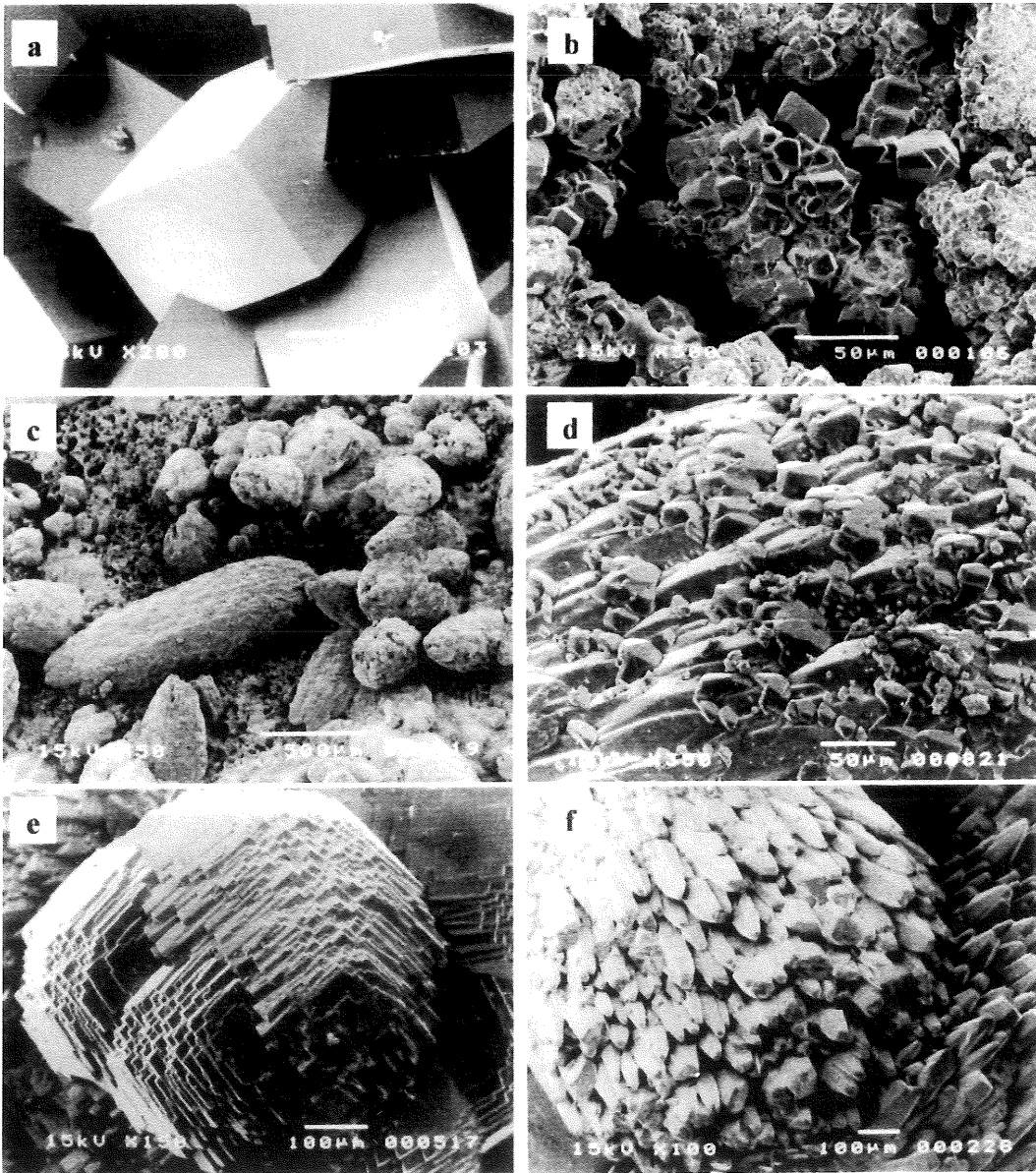


Fig. 4 – SEM micrographs of Sardinian smithsonites: (a) I-type, rhombohedral smithsonite crystals (Nebida mine); (b) II-type, rounded, microcrystalline rhombohedral smithsonite (Nebida mine); (c) III-type, «rice grained» smithsonite crystals (Mt. Agruxiau); (d) III-type coated by tiny $ZnCO_3$ crystals; (e) IV-type, globular «cluster» of smithsonite (S. Giovanni mine); (f) M-type, Fe-rich smithsonite (monheimite) in typical «bladed» aggregates (Montevecchio mine).

shows a typical cluster of «rice grains» smithsonite, with grain dimension varying from 1 mm to 250 mm. Fig. 4d shows an enlarged

detail of fig. 4c where III-type is coated by younger generations of tiny smithsonite crystals ranging from 20 to 50 mm in size.

IV-type samples consist of botryoidal aggregates characteristic of the San Giovanni Mine. SEM micrograph (fig. 4e) shows that IV-type consists of globular aggregates of 600 nm and distinct {1011} cleavage.

V-type is a particular variety of type-IV and corresponds to the stalactitic yellow-green smithsonites typically occurring in the Nebida and Masua mines, where it is known with the old name of «noble calamine» or «gel calamine» (Cavinato 1952).

M-type corresponds to monheimite (fig. 3h), the Fe-rich smithsonite (Palache *et al.* 1951, Zuffardi 1952, Sitzia 1965, Bak and Niec 1978, Bak and Zabinski 1981), collected in the

deeper part of the Montevecchio mine, a set of veins near the Arbus granite intrusions. M-type occurs as elongated aggregates frequently twinned, varying in color from light green to pale yellow. Fig. 4h it shows the typical parallel associations of crystals along the c-axis and the scalenohedric terminations.

The smithsonite cell parameters obtained by XRD analyses (Table 3) slightly differ from the data quoted in literature (Effenberger *et al.* 1981, Chang *et al.* 1996), with *a* and *c* in the ranges 4.659(4) - 4.665(3) and 15.038(2) - 15.050(5) Å. M-type presents cell dimensions slightly greater, with *a* 4.675(2) and *c* 15.180(2) Å. Fig. 5 confirms the trend of Bak

TABLE 3

Cell parameters of selected Sardinian smithsonite, hydrozincite, hemimorphite and cerussite (errors in brackets corresponding to the 2s standard deviation), compared with the literature data.

	a_0 (Å)	b_0 (Å)	c_0 (Å)	b (∞)	V (Å ³)
smithsonite	4.659(4)		15.040(2)		282.725(4)
	4.660(3)		15.038(2)		282.809(2)
	4.663(1)		15.042(1)		283.248(1)
	4.662(1)		15.044(2)		283.164(3)
	4.665(3)		15.045(1)		283.548(7)
	4.661(3)		15.050(5)		283.156(7)
<i>EFFENBERGER ET AL. 1981</i>	4.652		15.0257		281.68
Fe-smithsonite	4.675(2)		15.180(2)		287.320(2)
<i>SITZIA 1965</i>	4.68		15.20		288.314
hydrozincite	13.575(2)	6.300(2)	5.366(6)	95.58(2)	456.739(3)
<i>JCPDS-ICDD card # 19-1458</i>	13.58	6.28	5.41	95.60	459.18
hemimorphite	8.365(8)	10.711(6)	5.116(8)		458.381(2)
<i>McDonald & Cruickshank 1967</i>	8.37	10.72	5.120		459.36
cerussite	5.178(2)	8.497(1)	6.139(3)		270.100(3)
<i>CHEVRIER ET AL. 1992</i>	5.179(1)	8.492(3)	6.141(2)		270.082

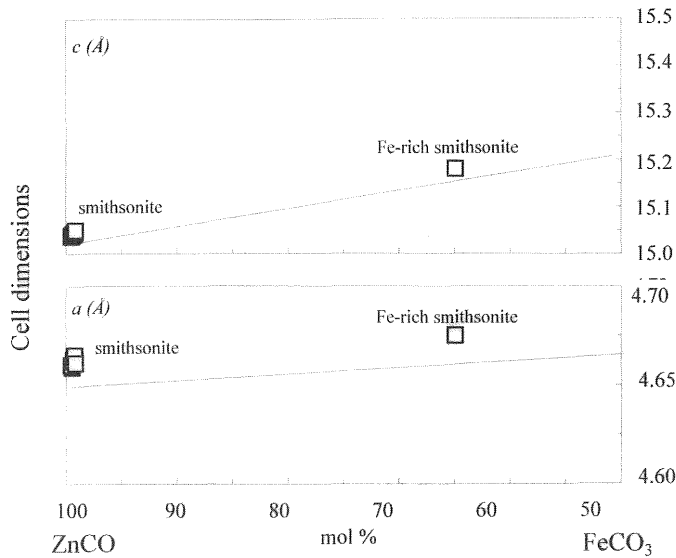


Fig. 5 – Cell parameters of Sardinian smithsonites vs their chemical composition. Dashed lines are the trends by Bak & Zabinsky (1981).

& Zabinski (1981) for the smithsonite-siderite series, i.e. a positive correlation between the cell dimensions and the FeCO_3 content.

EDS results of smithsonite are shown in fig. 6 and Table 4. The Zn content is in the range of 1.885-1.986 atoms per formula units (apfu), whereas amongst other trace elements only Ca^{2+} reaches significant amounts in few analytical points (up to 0.09 apfu). Contents in Fe and Mn can reach 0.024 and 0.012 apfu respectively, whereas the Mg content is in the range 0.005-0.017 apfu. M-type shows a composition nearly intermediate between smithsonite and siderite, with up to 0.74 apfu Fe.

Representative FTIR spectra of Sardinian smithsonites (fig. 7a, b) show predominant absorption bands around 1443, 870 and 744 cm^{-1} for the I to IV-types and a slight but significant shift of the three peaks for the M-type spectrum (absorption bands at 1414, 869 and 742 cm^{-1}). Their spectra fit well with the

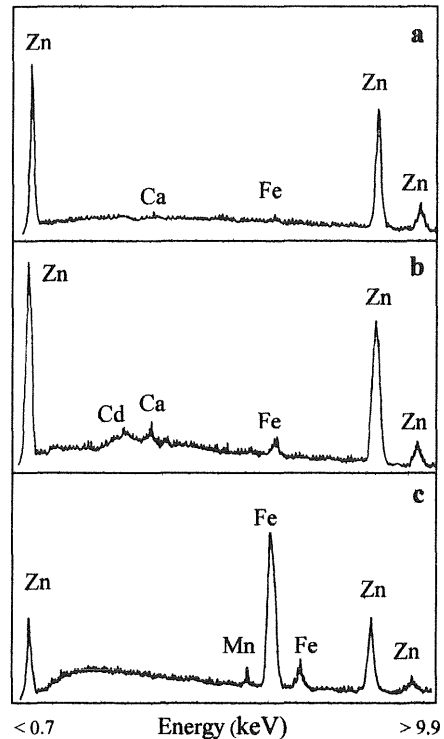


Fig. 6 – Energy dispersive spectra of the studied smithsonites. (a) Typical EDS spectrum of Sardinian smithsonites. (b) V-type smithsonite. (c) M-type smithsonite.

TABLE 4
Representative electron microprobe analyses and standard deviations of smithsonite from Sardinian Zn-Pb non-sulfide ores.

	smithsonite																		1 σ
	Monteponi		Nebida		San Giovanni		Mount Agruxiau		Seddas Moddizzis		Montevecchio								
	**																		
ZnO	63.99	63.85	62.18	64.15	62.74	64.05	64.25	64.31	64.21	64.50	64.03	64.21	64.28	64.52	63.81	42.01	43.56	ZnO	0.05
FeO	0.23		0.25	0.21	0.36	0.27			0.21		0.59				0.29	22.02	19.96	FeO	0.01
MnO						0.35									0.11		0.52	MnO	0.01
CaO	0.57	0.92	1.93	0.60	0.99	0.31	0.52	0.84	0.14	0.19	0.54	0.84	0.76	0.54	0.58	0.18		CaO	0.02
MgO			0.25			0.27	0.08											MgO	0.01
CO ₂ *	35.35	35.42	35.72	35.45	35.37	35.51	35.31	35.59	35.12	35.19	35.57	35.54	35.51	35.47	35.36	36.46	36.22		
total	100.14	100.19	100.33	100.41	99.73	100.57	100.08	100.74	99.68	99.88	100.73	100.59	100.55	100.53	100.15	100.67	100.26		
	number of ions on the basis of 6 oxygens																		
Zn	1.966	1.953	1.885	1.960	1.921	1.954	1.971	1.957	1.981	1.986	1.950	0.196	1.961	1.970	1.954	1.248	1.302		
Fe	0.008		0.009	0.007	0.012	0.009			0.007		0.024				0.011	0.741	0.676		
Mn						0.012									0.004		0.019		
Ca	0.025	0.041	0.085	0.027	0.044	0.014	0.023	0.038	0.006	0.008	0.021	0.037	0.034	0.024	0.260	0.008			
Mg			0.015			0.017	0.005												
C	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000		

* Calculated from stoichiometry

** Includes traces of Cd

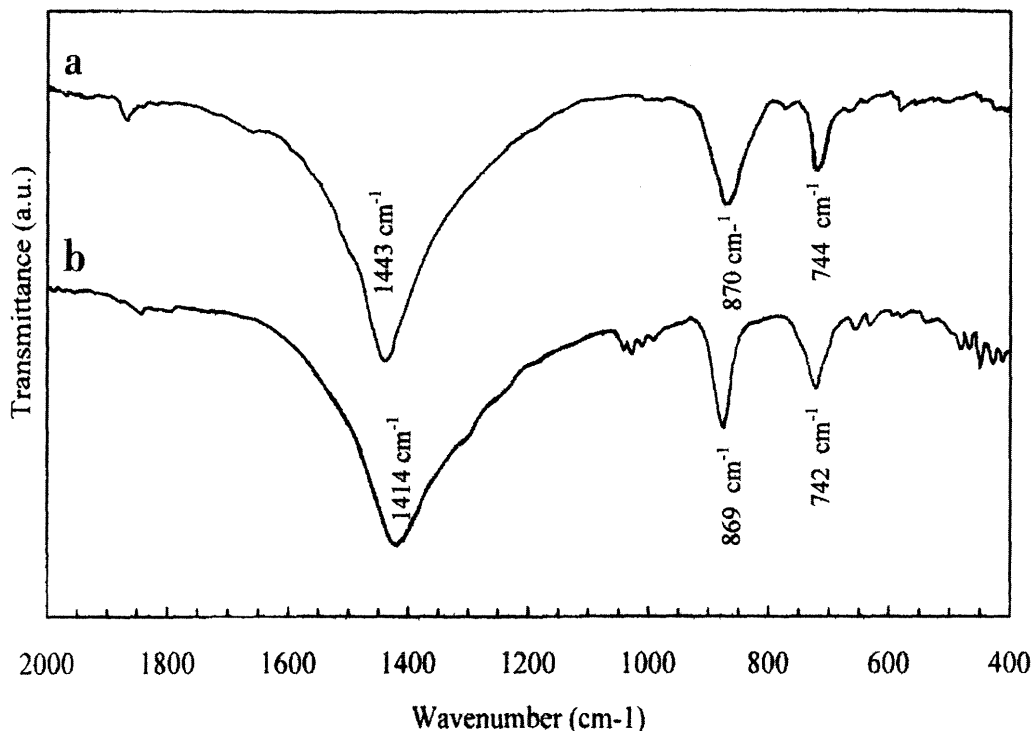


Fig. 7 – FTIR spectra of smithsonite of different composition. (a) Spectrum commonly observed for I to V-types. (b) Infrared spectrum of the M-type.

frequency trends of the Zn anhydrous carbonates (Chang *et al.*, 1996).

Hydrozincite is often associated with smithsonite and it commonly appears as whitish crustiform masses, locally growing directly on smithsonite (e.g. samples from Monteponi and San Giovanni mines) or smeared on the cerussite crystals (e.g. Monteponi sample). The SEM study revealed a micaceous habit trending to a more earthy variety (fig. 8a, b). XRD analyses do not show any significant discrepancies in their unit cells from the related JCPDS-ICDD data (Table 3). The same feature can be derived from chemical analyses, mostly close to the stoichiometric compositions. Only minor Ca-amounts were found to replace Zn in some EDS analyses of hydrozincite (Table 5).

Hemimorphite and cerussite

Other supergene minerals associated with the Zn-carbonates are hemimorphite and cerussite. While sphalerite is virtually absent in most samples, primary galena is often still associated to cerussite as well as anglesite, thus confirming the lower mobility of Pb during the supergene processes.

Hemimorphite consists of aggregates of idiomorphic thin tabular individuals or crystals with hemimorphic terminations (fig. 8c, d). It has been found as encrustations and open-space infill in massive hydrozincite. Hemimorphite spacings are always around a 8.365(8), b 10.711(6) and c 5.116(8) Å (Table 3), very similar to the values reported by the McDonald & Cruickshank (1967). The EDS analyses reveal homogeneous and practically

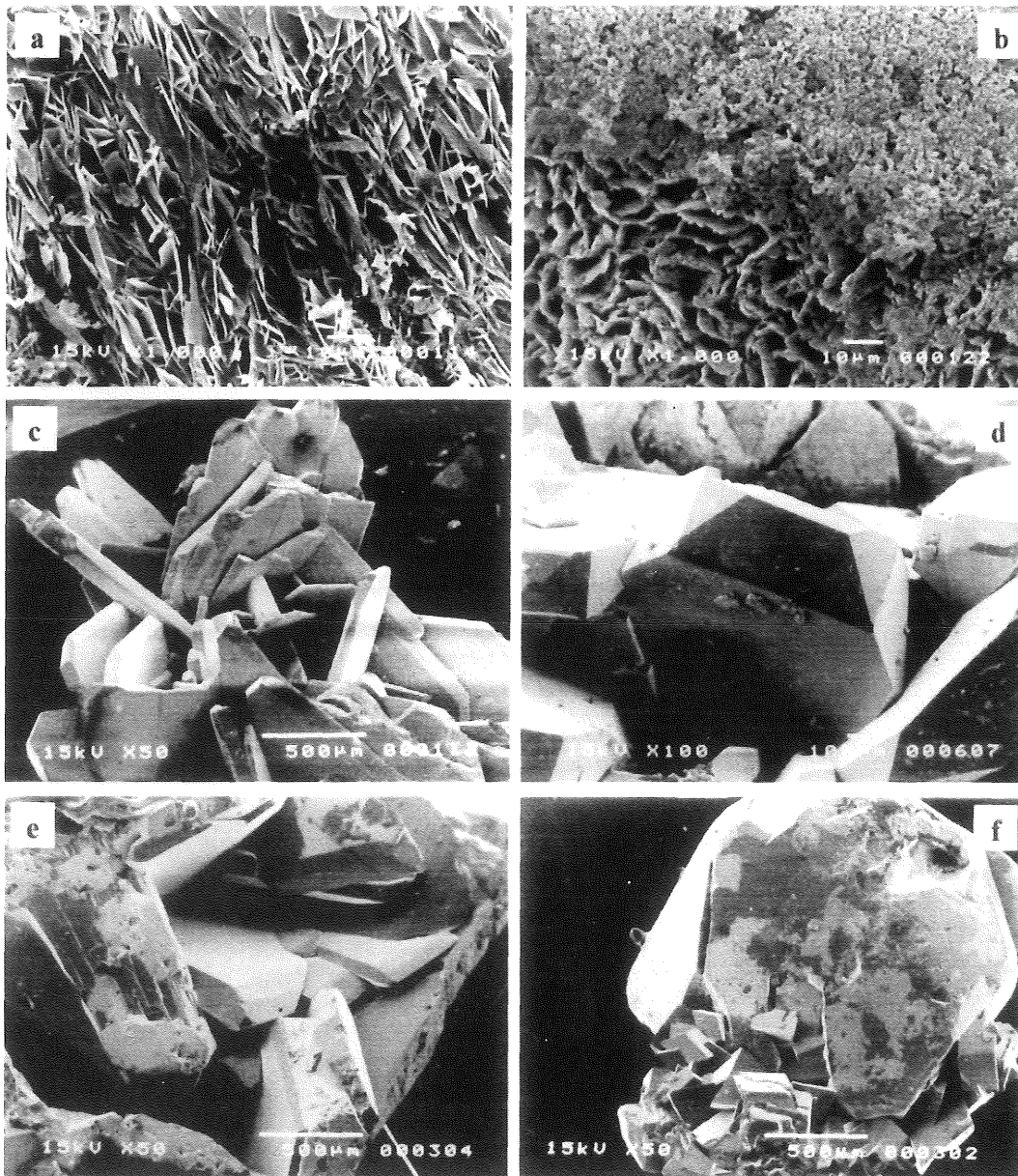


Fig. 8 – SEM micrographs of other economic minerals of Sardinian calamine ores: (a) typical foliated texture of hydrozincite crystals (Monteponi mine). (b) micaceous hydrozincite (left lower corner), progressively more massive (San Giovanni mine); (c) tabular hemimorphite aggregate (Mount Agruxiau); (d) Zn-silicate with typical hemimorphic terminations (San Benedetto); (e) tabular cerussite grains (Monteponi mine); (f) equant cerussite crystals with smithsonite rhombohedra (Nebida mine).

TABLE 5

Average compositions and standard deviations of hydrozincite, hemimorphite and cerussite from Sardinian Zn-Pb non-sulfide ores.

	<u>hydrozincite</u>				<u>hemimorphite</u>				<u>cerussite</u>				1σ			
	Monteponi		San Giovanni		Sa Duchessa **		San Benedetto		Monteponi		Nebida					
ZnO	74.35	74.18	74.21	74.30	SiO ₂	25.31	24.89	25.51	24.91	PbO	80.45	82.60	82.54	82.56	SiO ₂	0.05
CO ₂ *	16.16	16.12	16.12	16.14	ZnO	66.98	68.02	67.08	67.24	ZnO	0.65	0.05	0.45	0.36	ZnO	0.05
H ₂ O	9.87	9.81	9.87	9.91	H ₂ O	7.52	7.13	7.46	7.14	CaO	0.51	0.09	0.18		PbO	0.03
total	100.38	100.11	100.20	100.35	total	99.81	100.04	100.05	99.29	CO ₂ *	16.85	16.42	16.70	16.51	CaO	0.02
										total	98.46	99.16	99.87	99.43		
	numbers of ions on the basis of 12 O				numbers of ions on the basis of 10 O				numbers of ions on the basis of 6 O							
Zn	4.993	4.998	4.991	4.987	Si	2.022	2.011	2.034	2.021	Pb	1.908	1.985	1.951	1.973		
C	2.006	2.008	2.005	2.004	Zn	3.951	4.057	3.949	4.027	Zn	0.042	0.003	0.029	0.024		
OH	5.989	5.972	5.997	6.010	H ₂ O	1.002	0.961	0.992	0.966	Ca	0.048	0.009	0.017			
					OH	2.004	1.921	1.984	1.932	C	2.001	2.000	2.000	2.001		

* Calculated from stoichiometry

** Include traces of Cu

stoichiometric chemical compositions, except for the traces of Cu found in the specimens from Sa Duchessa mine, reflecting the Cu-sulfides exploited in the primary orebody (Table 5).

Cerussite has been found in several Nebida and Monteponi samples; it commonly occurs as whitish well-formed crystals (up to 0.3 mm in size), often as {110} twins and locally as incrustations on small nuclei of galena (fig. 8e, f). Average cell dimensions are a 5.178(2), b 8.497(1) and c 6.139(3) Å (Table 3), close to the structural parameters obtained from neutron diffraction refinement by Chevrier *et al* (1992). Most cerussite samples analysed for the present work are close in composition to ideal PbCO_3 . Minor amounts of Ca^{2+} and Zn^{2+} were found (Table 5).

DISCUSSION AND CONCLUSIONS

The investigated Sardinian carbonate-hosted non-sulfide ore deposits are mostly characterized by smithsonite-rich «Calamine», in microcrystalline, concretionary and stalactitic assemblages on the hand specimen scale. The mineralogical data for the Zn carbonate derived by the SEM study reveal the existence of different morphologies, ranging from rhombohedral (I-type), to rounded, partly corroded aggregates (II- and III-types), to botryoidal and stalactitic morphologies (IV- and V-types). Fe-rich smithsonite (monheimite, M-type) presents a totally different habit. Ongoing studies on C-isotopes ratios show that they are variable and reflect the distinct crystal morphologies and position within the weathering profile (Boni *et al.*, in press b). In contrast, O-isotopes of Sardinian smithsonites of all types do not show particular differences among them (Boni *et al.* in press a, Gilg *et al.* 2001). Both XRD and FTIR tests on I- to V-types showed a substantial agreement with the literature data. Slightly higher 1014 spacings probably resulted from the substitution of Zn by larger cations, such as Ca (Birch 1986), whereas cell dimension values slightly increase

with the Fe content. According to Chang *et al.* (1996), considerable quantities of Fe^{2+} and variable amounts of Mn^{2+} , Pb^{2+} , Ca^{2+} and Cd^{2+} are recorded from smithsonites from different parts of the world. Indeed, mineral chemistry study demonstrated that the majority of the Sardinian varieties are nearly pure Zn-carbonates. Slightly higher Ca contents have been found in few point analyses, whereas trace amounts of Mn seem to be correlated to other elements that occur occasionally, such as Cd in IV-type concretions, and Fe^{2+} in M-type. Mineral composition of hydrozincite, which is more abundant in the samples from the higher levels of the mines and decreases with depth, cerussite and hemimorphite did not show significant concentrations of trace elements with respect to their stoichiometry, except for only minor amounts of Ca and Zn in the Pb-carbonate and Cu in the Sa Duchessa Zn-silicate. XRD results are comparable with the literature data.

It is well known that solubilities of transition metals (e.g. zinc, lead and copper) are important factors in assessing possible mechanism for the formation of economic secondary minerals in natural waters close to primary sulfides (Takahashi, 1960; Shvartsev *et al.*, 1975; Giblin, 1978; Mann and Deutscher, 1980; Sangameshwar and Barnes 1983; Gotor *et al.*, 1998; Gamsjäger *et al.*, 1998; Preis *et al.*, 2000; Preis and Gamsjäger, 2001a, b; Brudruga *et al.*, 2001). This concept can also be used as a possible exploration tool (White, 1968; Cameron, 1977). Furthermore, their thermodynamic properties play a major role for a better understanding of industrial processes and for minimizing the environmental consequence of mining these metals (indeed some are ecotoxic as well as mentioned by Nuttal and Younger, 2000). The alteration mineral assemblages are mainly controlled by the initial mineralogy, the composition and flow rates of ground water and the permeability of the ores and host carbonates (Sangameshwar and Barnes, 1983). In general terms, as the SW Sardinian secondary non-sulfide ores are in carbonate

terrains, the pH of the ground water is expected to be relatively high (6-8 or possibly higher), thus stabilizing the carbonates, smithsonite, hydrozincite and cerussite. The fugacity of CO₂ is high as well (*f* CO₂ around 10^{-2.0} bar; Mann and Deutscher, 1980). In order to obtain a better understanding of the genesis of the «Calamine» ores of SW Sardinia, a thermodynamic study of the stability and solubility fields of the complete mineral assemblages, including relevant equilibrium diagrams is in progress.

ACKNOWLEDGMENTS

The authors thank the IGEA company (Iglesias, Sardinia) for having granted access to their properties and R. Sarritzu for help and discussions. H.A. Gilg (Technische Universität München) is thanked for fruitful discussions. Special thanks are expressed to G. Manunta and E. Cocco for providing samples from their collections, and to A. Canzanella (CISAG, Università di Napoli «Federico II») for assistance with SEM-EDS analyses. W. Preis (Institut für Physikalische Chemie, Leoben) kindly provided literature data. Thanks are also due to G. Sorrentino and M. Amendola (Istituto di Bioimmagini e Biostrutture, CNR Napoli) for their precious support during a set of XRD analyses and to D. Large for checking the english.

REFERENCES

- Bak B. and NIEC M. (1978) — *The occurrence of monheimite in the Boleslaw Zn-Pb ore deposits near Olkusz*. Min. Polonica, **9**, 123-128.
- BAK B. and ZABINSKI W. (1981) — *On the continuity of the solid solution series smithsonite-siderite*. Min. Polonica, **12**, 75-80.
- BECHSTÄDT TH. and BONI M., Eds. (1994) — *Sedimentological, stratigraphical and ore deposits field guide of the autochthonous Cambro - Ordovician of Southwestern Sardinia*. Memorie Descrittive Carta Geologica d'Italia, v. XLVIII, Servizio Geologico d'Italia, 434 p.
- BILLOWS E. (1941) — *I minerali della Sardegna ed i loro giacimenti*. Rendiconti Università di Cagliari, 331-335.
- BIRCH W.D. (1986) — *Zinc-manganese carbonates from Broken Hill, New South Wales*. Mineral. Mag., **50**, 49-53.
- BONI M. (1985) — *Les gisements de type Mississippi Valley du Sud Ouest de la Sardaigne (Italie): une synthèse*. Chron. Rech. Min. BRGM, **489**, 7-34.
- BONI M. (1986) — *Pb-Zn-Ba ore deposits in the Sardinian Cambrian: a comparison with the Irish Carboniferous*. IAEG Meeting, Dublin Conference, 677-684.
- BONI M., IANNACE A. and BALASSONE G. (1996) — *Base metal ores in the Lower Palaeozoic of South-Western Sardinia*. Econ.Geol. 75th Anniversary Volume, Special Publication, **4**, 18-28.
- BONI M., AVERSA G., BALASSONE G. and GILG H.A. (in press a) — *The Zn-Pb ore deposits in SW Sardinia (Italy): from sulfides to «calamine»*. - In: *The Geology and Genesis of Europe's Major Base Metal Deposits*, Andrew, C.J., Ashton, J.H., Boland, M.B., Earls, G., Kelly, J. and Stanley, G.A. (Eds.), Irish Association for Economic Geology.
- BONI M., GILG H.A., AVERSA G. and BALASSONE G. (in press b) — *The «calamine» of SW Sardinia (Italy): geology, mineralogy and stable isotope geochemistry of a supergene Zn-mineralisation*. Econ. Geol.
- BONI M., PARENTE M., BECHSTÄDT TH., DE VIVO B. and IANNACE A. (2000) — *Hydrothermal dolomites in SW Sardinia (Italy): evidence for a widespread late-Variscan fluid flow event*. Sedim. Geol., **131**(3-4), 181-200.
- BONIFAZI G. and MASSACCI P. (1987) — *Characterization of oxidized zinc (calamine) ores by scanning electron microscopy and electron microprobe analysis*. Scanning Microscopy, **1**(1), 73-83.
- BUDRUGEAC P., CRIADO J.M., GOTOR F.J., POPESCU C. and SEGAL E. (2001) — *Kinetic analysis of dissociation of smithsonite from a set of non-isothermal data obtained at different heating rates*. Journal of Thermal Analysis and Calorimetry, **63**(3), 777-786.
- CAMERÓN, E. M. (1977) — *Geochemical dispersion in lake waters and sediments from massive sulphide mineralizations, Agricola Lake area, Northwest Territories*. J. Geochem. Explor., **7**, 327-348.
- CARMIGNANI L., CAROSI R., DI PISA A., GATTIGLIO M., MUSUMECI G., OGGIANO G. and PERTUSATI P.C. (1994) — *The Hercynian chain in Sardinia*. Geodin. Acta, **5**(4), 217-233.
- CAVINATO, A. (1952) — *I fenomeni di ossidazione nelle miniere dell'Iglesiente in Sardegna*. Res. Sed. Ass. Miner. Sarda, **57**(6), pp. 9-18.
- CHANG L.L.J., HOWIE R.A. and ZUSSMAN J. (1996) — *Rock-forming minerals. Non-silicates: sulphates, carbonates, phosphates, halides*. **5B**, 2nd ed. Longman, London, 383 pp.
- CHEVRIER G., GIESTER G., HEGER G., JAROSH D.,

- WILDNER M. and ZEMANN J. (1992) — *Neutron single-crystal refinement of cerussite, PbCO₃, and comparison with other aragonite-type carbonates*. Z. Krist., **199**, 67-74.
- DEJONGHE L. (1998) — *Zinc-lead deposits of Belgium*. Ore Geology Reviews, **12**(5), 329-354.
- EFFENBERGER H., MERREITER K. and ZEMANN J. (1981) — *Crystal structure refinement of magnesite, calcite, rhodocrosite, siderite, smithsonite and dolomite, with discussion on some aspects of the stereochemistry of calcite-type carbonates*. Z. Krist. **156**, 233-243.
- GAMSIÄGER, H., KÖNISBERGER, E. and PREIS W. (1998) — *Solubilities of metal carbonates*. Pure & Appl. Chem., **70**(10), 1913-1920.
- GIBLIN, A. M. (1978) — *Experiment to demonstrate mobility of metals in waters near base-metal sulphide deposits*. Chem. Geol., **23**, 215-223.
- GILG H.A., AVERSA G. and BONI M. (2001) — *A stable isotope study of smithsonite with application to Pb-Zn deposits of SW Sardinia, Italy*. XI EUG, Strasbourg, p. 515.
- GOTOR F.J., MACIAS M., ORTEGA A. and CRIADO J.M. (1998) — *Simultaneous use of isothermal, nonisothermal, and Constant Rate Thermal Analysis (CRTA) for discerning the kinetics of the thermal dissociation of smithsonite*. International Journal of Chemical Kinetics, **30**(9), 647-655.
- LARGE D. (2001) — *The geology of non-sulphide Zinc Deposits – an Overview*. Erzmetall., **54**(5), 264-276.
- MANN A.W. and DEUTSCHER R.L. (1980) — *Solution geochemistry of lead and zinc in water containing carbonate, sulphate and chloride ions*. Chem. Geol., **29**, 293-311.
- MCDONALD W.S. and CRUICKSHANK D.W.J. (1967) — *Refinement of the structure of hemimorphite*. Z. Krist., **124**, 180-191.
- MOORE J.Mc.M. (1972) — *Supergene mineral deposits and physiographic development in southwest Sardinia, Italy*. Trans. Instn. Min. Metall, (Sect. B: Appl. Earth Sci.), **71**, B59-B66.
- NUTTALL C.A. and YOUNGER P.L. (2000) — *Zinc removal from hard, circum-neutral mine waters using a novel closed-bed limestone reactor*. Water Research, **34**(4), 1262-1268.
- PALACHE C., BERMAN H. and FRONDEL C. (1951) — *The system of mineralogy*. New York, (J. Wiley and Sons), 1124 pp.
- PREIS W., KONIGSBERGER E. and GAMSJAGER H. (2000) — *Solid-solute phase equilibria in aqueous solution. XII. Solubility and thermal decomposition of smithsonite*. J. Chem. Thermodyn., **29**(7), 605-618.
- PREIS W. and GAMSJAGER H. (2001a) — *Solid-solute phase equilibria in aqueous solution. XIII. Thermodynamic properties of hydrozincite and predominance diagrams for (Zn₂₊+H₂O+CO₂)*. J. Chem. Thermodyn., **33**(7), 803-819.
- PREIS W. and GAMSJAGER H. (2001b) — *Thermodynamic investigations of phase equilibria in metal carbonate-water-carbon dioxide system*. Monatsh. Chemie, **132**(11), 1327-1346.
- SANGAMESHWAR S.R. and BARNES H.L. (1983) — *Supergene processes in zinc-lead-silver sulfide ores in carbonates*. Econ. Geol., **78**, 1379-1397.
- SHVARTSEV, S. L., UDODOV, P.A. AND RASSKAZOF, N. M. (1975) — *Some features of the migration of microcomponents in neutral waters of supergene zone*. J. Geochem. Explor., **4**, 433-439.
- SITZIA R. (1965) — *Osservazioni su alcune ferrosmithsoniti di Montevecchio*. Atti Symposium Problemi Geo-Minerari Sardi, Cagliari-Iglesias Ottobre 1965, Ass. Min. Sarda, 434-437.
- STARA P., RIZZO R. and TANCA G.A. (1996) — *Iglesiente-Arburese, Miniere e Minerali*. Ente Minerario Sardo, vol. **I**, 238 pp.
- TAKAHASHI T. (1960) — *Supergene alteration of zinc and lead deposits in limestone*. Econ. Geol., **55**, 1083-1115.
- VIOLO M. (1974) — *La zonalità nei giacimenti metalliferi: una conseguenza delle variazioni paleogeografiche durante la sedimentogenesi e la diagenesi*. Soc. Ital. Mineral. Petrol., **33**(2), 1109-1132.
- WHITE, D. E., (1968) — *Environments of generation of some base metal deposits*. Econ. Geol., **63**, 301-335.
- ZUFFARDI P. (1952) — *Il giacimento piombo-zincifero di Monte Agruxiau*. Industria Min., **3**, 1-12.
- ZUFFARDI P. (1970) — *La metallogenese du plomb, du zinc et du barium en Sardaigne: un exemple de permanence, de polygenetisme et de transformisme*. Ann. Soc. Geol. Belgique, **92**, 321-344.