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G. Bonifazi
Universitá di Roma "La Sapienza"

P. Massacci
Universitá di Roma "La Sapienza"

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CHARACTERIZATION OF OXIDIZED ZINC (CALAMINE) ORES BY SCANNING ELECTRON MICROSCOPY AND ELECTRON MICROPROBE ANALYSIS

G. Bonifazi and P. Massacci*

Dipartimento di Ingegneria Chimica, dei Materiali, delle Materie Prime e Metallurgia
Universita´ di Roma "La Sapienza", via Eudossiana 18, 00184 Roma, Italy

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Abstract

Textural and structural features of Sardinian oxidized zinc (calamine) ores have been established by scanning electron microscopy and electron microprobe analysis, the elements analyzed being Zn, Pb, Ca and Fe. The surface composition of grains produced by comminution has also been determined, especially with reference to the presence of smithsonite and cerussite.

The methodological approach adopted has revealed intimate intergrowth of the mineral species present and contamination of the main mineral by inclusions of other species, which explains why it is so difficult to obtain good recoveries and high-quality concentrates by beneficiation processes.

Key words: Optical microscope, Electron microscope, Electron microprobe, Calamine ore, Cerussite, Smithsonite.

*Address for correspondence:
For reprints and other information contact
P. Massacci at the address above.
Phone no.: 39-6-4687337

Introduction

Approximately 90 percent of all lead and zinc marketed today comes from sulfide ores. However renewed interest is being shown in utilizing oxidized lead and zinc ("calamine") ores because of the discovery of new deposits in recent years.

The beneficiation of calamine ores is difficult owing to their texture and structure, which leads to low metal recoveries (less than 50 percent in some cases). There are several reasons for such poor results: a) extensive intergrowth of the two main species - smithsonite ($Zn\ CO_3$) and cerussite ($Pb\ CO_3$) - with one another and with other minerals, especially iron oxides; b) wide range of variability in texture of the zinc and lead phases present in the ores, resulting in dispersion of these grains and associations of particles of diverse minerals, which adversely affects subsequent beneficiation processes (flotation), and makes recovery more difficult); c) presence of clays, oxides and hydroxides of iron, which necessitates complex preliminary desliming to remove these materials that would interfere with flotation, and d) limited selectivity of conventional flotation agents with regard to mineral surfaces present in the pulp. In order to design a flow-sheet for a reasonable ore treatment, it is extremely important to have a complete picture of the chemical, mineralogical, textural and structural characteristics of the ores. Textural and structural relationship among the various mineral phases can be properly assessed by using SEM and electromicroprobe analysis, as demonstrated in this study.

Such techniques must be adopted to supplement the information which can be acquired by means of optical analysis using reflected and transmitted light. It is notoriously difficult or even impossible to differentiate carbonate minerals by the usual petrographic methods (FRIEDMAN, 1959) (WARNE, 1962) (BELARDI & BONIFAZI, 1985). With transmitted light, zinc carbonate can, of course, be distinguished from carbonate gangue minerals (calcite and dolomite) whose reflectivity is considerably weaker, but confusion among cerussite and other carbonates is always possible (RAMDOHR, 1980).

Yet even when such techniques permit easy identification of the mineral particles they do not provide sufficient information on coating by impurities or micro-intergrowths, which play a decisive role in separation processes that involve surface phenomena (flotation, for instance). This kind of information has to be collected at micron scale, which can be done by means of SEM techniques and microprobe analysis (REED, 1975) (FISHER, 1964).

Ores studied

The study covered two oxidized lead and zinc ores (calamine ores) from Sardinia, one consisting mainly of smithsonite (Zn CO_3) from the Buggerru Caitas deposit (Ore A), and the other of mixed Pb-Zn oxidized species from the San Giovanni deposit (Massa Pozzo 4, Sublevel +168.00 m above sea level) (Ore B).

Chemical and mineral composition of the ores are given in Table 1 (VIOLO, 1974), (ZUFFARDI, 1952, 1968, 1969, 1970).

Buggerru-Caitas deposit

Most of the rocks in the Buggerru area are of Cambrian or Ordovician age, though there are also some sediments attributable to the continental phases of the Permo-Triassic, while Quaternary alluvial and eluvial materials occur, as to volcanics of various kinds (BONI, 1978) (COCOZZA et al., 1974).

Three characteristic Cambrian formations are found in the Iglesiente-Sulcis area: from the bottom upwards, these are the Nebida, the Gonnesa and the Cabitza (BONI & MARINACCI, 1980). The mineralizations dealt with here are "located" in the Gonnesa Formation, being the result of syngenetic deposition in epicontinental carbonate platform sedimentary environments; they are connected with small lagoon environment carbonate facies formed where there was a relative lack of oxygen and a moderate contribution of detritus. The mineralizations occupy a relatively constant position in the Gonnesa carbonate sequence, but they have been dislocated, orientated and sometimes concentrated by tectonic action, particularly by the N-S Hercynian phases. The original sedimentary structure of these mineralizations has been obliterated in some cases, especially where tectonic action or recirculation has been most intense.

At Buggerru, the mineralizations are found in the laminated fossiliferous white limestones and, to some extent, the grey limestones and the "flame" limestones. These lithofacies are between 50 and 100 m thick and lie at a somewhat variable distance from the contact with the grey basal dolomites, depending on the positions of the basins.

The mineralized masses as a whole strike N-S and dip almost vertically. They are separated by virtually barren zones of limestone. Most mineralizations are of the oxide type, but the sulfide content increases with depth (sphalerite for the most part and a little galena). The limits of the oxidation are not regular, however, unaltered sulfide nuclei being found even at the highest levels. There is also an outcrop of massive sulfides (sphalerite and pyrite) in the "laminar" limestones, surrounded by belts of oxidized minerals at the highest points.

The oxidized mineral have a very vuggy appearance and often occur as concretions and geodes.

Table 1: Chemical and mineralogical composition, resulting from normative calculations, with reference to the mineral species identified by X-Ray diffraction analysis.

Chemical composition

Element	Content (%) ore A	Content (%) ore B
Zn	12.83	5.45
Pb	1.27	2.60
Ca	27.35	23.16
Mg	0.09	4.40
Fe	0.35	3.15
Si	0.27	3.61
Al	0.02	0.21
S	0.20	0.26
LOI	43.44	39.37

Mineralogical composition

Pure minerals	Content (%) ore A	Content (%) ore B
Calcite ($CaCO_3$)	67.38	39.72
Dolomite ($CaMg(CO_3)_2$)	0.68	33.35
Smithsonite ($ZnCO_3$)	24.61	10.45
Cerussite ($PbCO_3$)	1.64	3.35
Hemimorphite ($Zn_4(OH)_2(Si_2O_7)H_2O$)	tr	tr
Quartz (SiO_2)	0.27	3.61
Sphalerite (ZnS)	tr	tr
Galena (PbS)	tr	tr
Goethite ((FeO)OH)	0.56	5.00

LOI = Loss On Ignition

tr = trace

From the mineralogical point of view they consist almost exclusively of smithsonite, though there is some hemimorphite and a very small amount of hydrozincite. Cerussite is almost always found together with smithsonite, though in smaller amounts. Pyrite with various degrees of alteration is present too.

In the residual sulfide zones, somewhat light-colored sphalerite is present either impregnating the limestone or as a stratiform deposit.

San Giovanni deposit

This deposit lies 4 km WSW of Iglesias on the southern limb of the Iglesias syncline of the Sardinian Cambrian series (BONI & GANDIN, 1979) formed of shales, limestones, dolomities and sandstones, the Pb and Zn mineralization being mainly in the limestones (BRUSCA et al., 1968).

Horizontal zoning is encountered in the mineralized horizons. This zoning is indicative of paleogeographic variations in the transition from the marginal platform environment with its mainly carbonate sedimentation to the west, to more enclosed environments in sporadic contact with the open sea to the east.

There are various types of mineralization in the San Giovanni deposit:

a) sphaleritic masses in which predominate sphalerite accompanied by variable amounts of galena and very little pyrite
b) contact vein, consisting essentially of galena with a low Ag content
c) irregular masses - mainly lodes - of Ag-rich galena in the higher part of the deposit
d) barite masses forming the gangue of the Ag-rich ore but also occurring as small superficial pockets in the dolomites
e) oxidized masses of Pb and Zn which occur as a continuation of the sphaleritic masses.

The oxidized material owe their origin to the effects of denudation of the carbonate block and the onset of new karstification. This resulted in the establishment of groundwater flows of various origins, but mainly meteoric, facilitated by the intense tectonic fracturing, leading to the generation of Zn and Fe sulfates (HOLLAND, 1959). The zinc sulfates then reacted with the carbonates to form smithsonite and hydrozincite, while the iron sulphates reacted with the limestones to form yellow dolomites.

Part of the lead of the galena, instead, remained in situ as unaltered galena or was transformed into cerussite and perhaps into virtually insoluble anglesite and pyromorphite, while part of it was dissolved as chloride or complex chloride salts which were reprecipitated as galena by the action of H_2S of biochemical origin. This interpretation fits in well with the presence of galena in the bottom of the oxidation pockets, in the tectonic collapse breccia and in karst cavities where there was insufficient oxygenation.

Sample preparation

Lump ore and crushed ore samples were embedded in cold epoxy resin in a 25.4 mm diameter teflon specimen holder, which was then placed in a muffle furnace at 60-80 C in order to: a) fluidize the resin so as to ensure better coating of the material (this procedure is especially important in the case of granular samples), and b) promote polymerization.

The mass was then removed from the teflon cylinder and ground flat to uncover the surface of the material to be analyzed.

It was then machine polished using finer and finer emery paper, after which it was hand polished using a series of diamond pastes starting from 3 µm and finishing at 1 µm. After optical study and prior to using the SEM and electron microprobe, the specimen was coated with graphite, by vacuum evaporation, and a silver-collared specimen holder was then positioned. The analyses were run on small fragments of the ores in the "as-mined" condition, various screen-sizes classes of crushed ores, and on polished sections in zones considered to be of interest.

Prior to SEM analysis the fragments of "as-mined" or crushed ores were mounted on an aluminum specimen holder and metallized with gold by vacum evaporation.

Specimens having surface dimensions of about 8x8 mm and 2 mm thick were also taken, mounted and metallized with gold as indicated above (JONES, 1974) (GOLDSTEIN and YAKOWITZ, 1975) (GULSON and LOVERING, 1968).

Methods of investigation

Optical microscope observations

A Zeiss Neophot II microscope was employed for optical analysis using reflected light, and a Zeiss WL polarizing microscope for transmitted light.

Optical examination was performed to acquire preliminary information to facilitate subsequent SEM and electron microprobe analyses.

Scanning electron microscope examinations

All SEM investigations were carried out using a Cambridge 150 Stereoscan Electron Scanning Microscope equipped (with a Geos 6010 energy dispersive analytical system). The analysis was obtained at a stabilized voltage of 20 kV and current of 20 mA.

The SEM was used for textural, structural and morphological characterization of the mineralogical associations, adopting procedures proposed by REED (1970) and GOLDSTEIN and YAKOWITZ (1975).

The elements analyzed in both ores were Zn, Pb, Ca and Fe. The main purpose of the examinations was to ascertain the existence of idiomorphic forms of smithsonite and cerussite: well-crystallized forms of ore minerals are of great importance for subsequent beneficiation operations, owing to the different physico-chemical behaviour of grain surfaces (presence of polar sites, cleavage, etc.).

Electron microprobe analyses (REED, 1970)

The analyses were performed using a JEOL JXA-SOA wavelength dispersion (WDS) microprobe, which has SEM capabilities.

The most interesting zones on each specimen

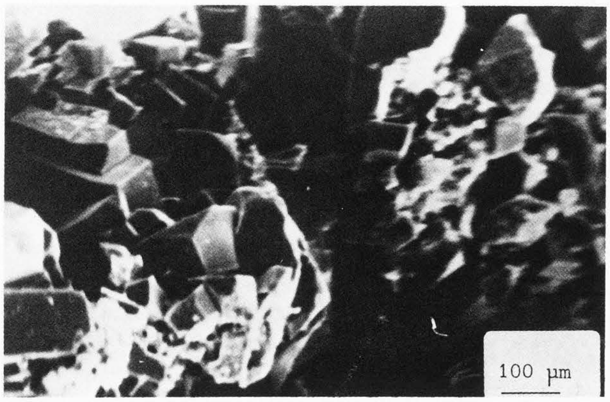

Fig.1: Mainly smithsonite ore (A): as mined SEI. Note the presence of idiomorphic minerals, presumably calcite, smithsonite and sphalerite.

Fig.2: Mainly smithsonite ore (A): as mined SEI. Higher magnification than Fig.1, punctiform microanalysis reveals presence of:

element	**Ca, Fe, Zn**	**Ca**	**Zn**	**Zn**	**ZN**
point	**1**	**2**	**3**	**4**	**5**

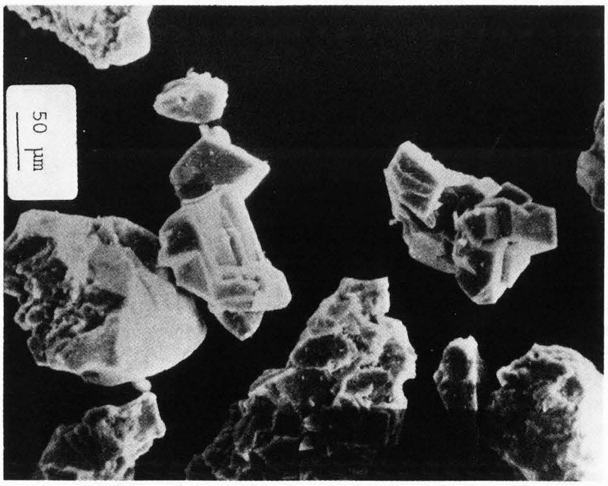

Fig.3: Mainly smithsonite ore (A): grain size fraction less than 125 μm after comminution SEI. Smithsonite present in idiomorphic form and twinned calcite intergrowth still marked.

(lump ores and ground ores) were examined by a back-scattering electron image (BEI), and by X-ray mapping (XRM) of the selected elements.

The electron microprobe was used to establish the compositions of the grains examined and the distribution of elements in the mass of the mineral particles, so as to identify the chemical composition.

The elements Zn, Ca, Pb and Fe were mapped in order to determine: a) amount of intergrowth of the ore minerals; b) distribution of minerals within the samples; c) presence of lead and zinc sulfides and iron oxides, and d) existence of coating forms (punctiform and/or patches) on the mineral particles identified macroscopically.

Zn-Kα_1, Pb-Kα_1, and Ca-Kα_1 were analyzed using an LIF 200 (lithium fluoride) crystal which has very high reflecting power and virtually fluorescence effects. The Fe-L α_1 spectral line was analyzed using a RAP (Rubidium Acid Phthalate) crystal which is particularly suitable for detecting Fe-Lα_1 radiation due to its medium-high reflecting power.

Results

Analysis of smithsonite ore

Examination under the optical microscope (500x) showed the material to consist of a series of intergrown microgranular aggregates of smithsonite and calcite with some iron oxides. Quite irregular vugs and cavities ranging in size 30-40 μm up to 200 μm and beyond affect the whole material. The iron oxides frequently fill the cavities.

SEM analyses reveal the presence of well-crystallized forms of smithsonite ($ZnCO_3$) and calcite; sphalerite (ZnS) sometimes occurs as a relict in the smithsonite. These species also occur in the form of complex, highly intergrown aggregates. The idiomorphic aggregates and forms are found mainly in the cavities and vugs in the ore (Fig.1).

Point microanalyses show that replacement has occurred in some cases. Microanalysis reveals that crystals similar to sphalerite (cubic system, hexacisoctahedral class) are actually smithsonite (rhombohedral system, ditrigonal scalenohedral class) (Fig.2).

Even the smallest grains resulting from comminution occur as poly-crystalline aggregates. Intergrowth between species, especially between smithsonite and calcite is always very intimate (Figs. 1 and 2), Smithsonite grains are almost always idiomorphic (Fig.3); grains consisting of idiomorphic aggregates of this carbonate have been found in numerous samples. Microprobe analysis of the lump ore reveals a pronounced interpenetration of calcite and smithsonite (Fig.4).

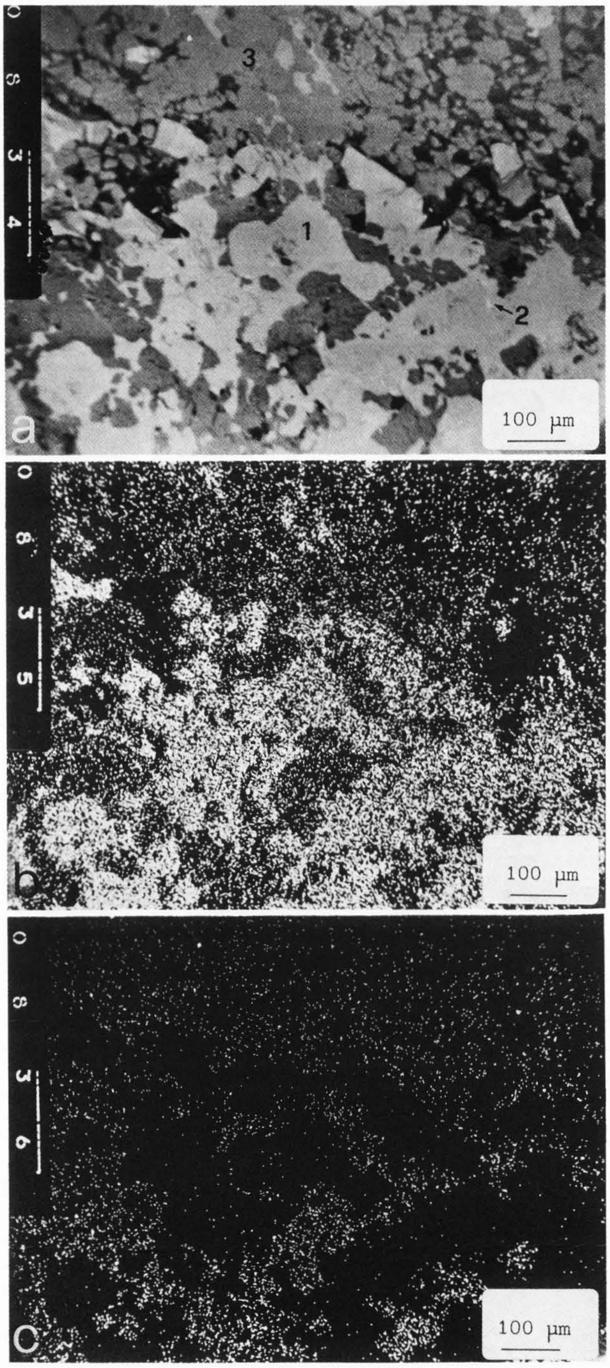

Fig.4: Mainly smithsonite ore (A): as mined 4a=BEI; 4b=XRM (Zn,Kα_1); 4c=XRM (Ca,Kα).
Note the presence of idiomorphic smithsonite (phase 1=mid grey) and also of sphalerite (phase 2=light grey) within the smithsonite. Gangue consists virtually of calcite (phase 3=dark grey) alone. It is evident from 4a the material is highly vuggy and that mineral species are intimately intergrown.

Sphalerite is found as inclusions which are sometimes finely disseminated in the smithsonite (Fig.4).

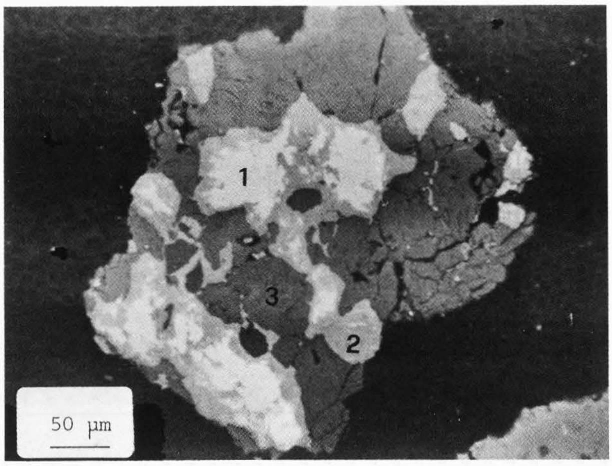

Fig.5: Mainly smithsonite ore (A): grain-size fraction between 250 and 500 µm after comminution BEI.
Note the presence of sphalerite (phase 1 = lighter grey) intimately associated with smithsonite (phase 2=mid grey). Gangue consist virtually of calcite (phase 3=dark grey) alone.

Analysis of samples of crushed and ground ore shows that in the 250-500 µm size-fraction, the mineral phases are highly intergrown, and are elongated or roundish in shape. Grains of single phases are rare. Smithsonite occurs in the form of idiomorphic microgranular aggregates. Numerous grains have been found in which sphalerite is present owing to incomplete oxidation, as shown in Fig.5.

In the fraction between 38 and 75 µm in diameter free particles of smithsonite are encountered with some frequency, as illustrated in Figs.6a and 6b. Most smithsonite detected in the fraction less than 38 µm would appear to be liberated, i.e., to occur as individual grains, even though some grains exibiting intergrowth with sphalerite and/or calcite are still present.

The analysis becomes increasingly more difficult at finer sizes owing to evaporation of the epoxy resin due to electron bombardment which causes deterioration in image quality.

Analysis of mixed oxidized Pb and Zn ore

Optical microscopy shows that the ore has a brownish colour owing to the presence of goethite, which was identified by X-ray diffraction. Polycrystalline masses of iron hydroxides are always vuggy with fillings of cerussite aggregates. The cerussite is usually associated with dolomite and smithsonite, while intergrowths of cerussite and iron hydroxides have been found in many cases. The cerussite sometimes has an elongated habit with straight extinction. Aggregates of cerussite and barite have been encountered in some instances, especially in the cavities. Galena is often seen as a relict in cerussite, but rarely as a phase in its own right. Sphalerite, wurtzite and hemimorphite occur as accessory minerals with smithsonite in calcareous or dolomite gangue.

Quartz is ubiquitous and sometimes has metal-

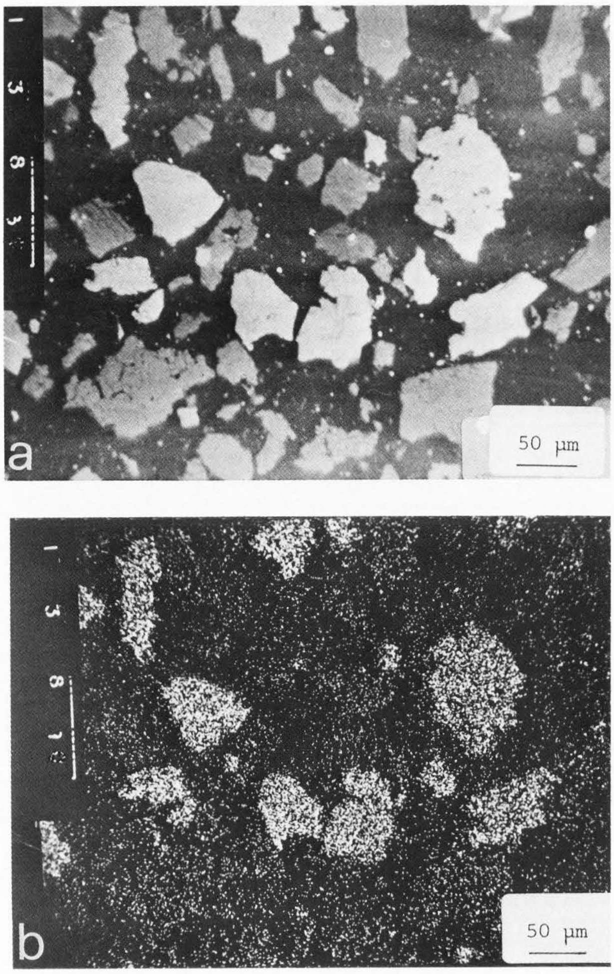

Fig.6: Mainly smithsonite (A): grain-size fraction between 38 and 75 µm after comminution 6a=BEI; 6b=XRM ($Zn, K\alpha_1$). Comparison reveals evident presence of numerous liberated smithsonite grains, though intergrown form (calcite) still occur.

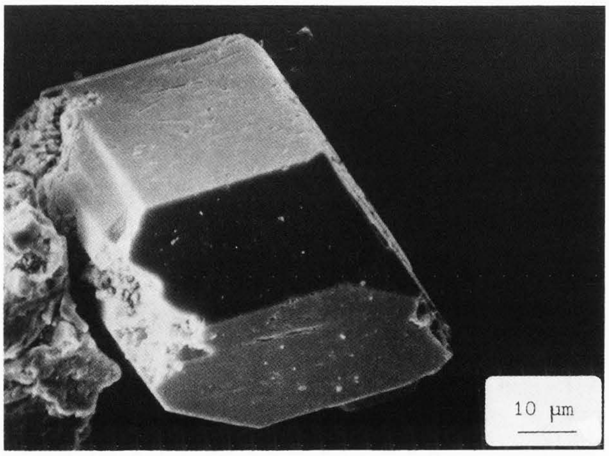

Fig.7: Mixed Pb-Zn oxidized ore (B): grain-size fraction less than 38 µm after comminution. Cerussite crystal.

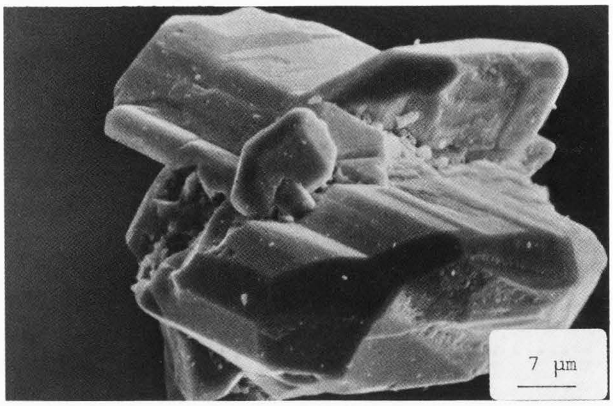

Fig.8: Mixed Pb-Zn oxidized ore (B): grain-size fraction less than 38 µm after comminution. Cerussite twin.

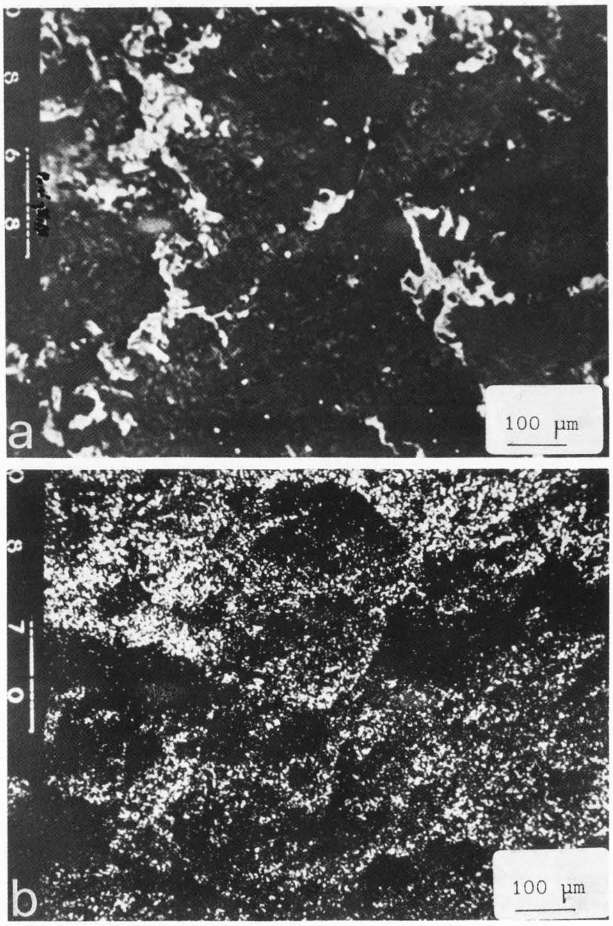

Fig.9: Mixed Pb-Zn oxidized ore (B): as mined 9a=BEI; 9b=XRM ($Zn, K\alpha_1$).
Smithsonite present as finely disseminated form into dolomite matrix.

lic inclusions. Most of the smithsonite is associated with calcite, much less being associated with dolomite. Smithsonite is also associated with cerussite.

SEM analysis of this ore reveals that idiomorphic forms of cerussite occur, though not to the

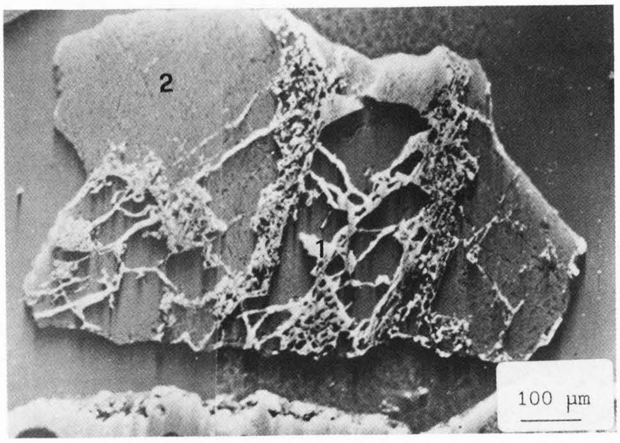

**Fig.10: Mixed Pb-Zn oxidized ore (B): grain-size fraction between 500 and 1000 μm after comminution BEI.
Note the presence of cerussite (phase 1=light grey) in variously orientated veins in grains of dolomite (phase 2=mid grey). Both the dolomite and cerussite appear in relief owing to the high excitation voltage needed to detect presence of Pb (from 30 to 35 kV).**

same extent as in the smithsonite ore.

Point microanalysis of numerous samples does not reveal any replacement phenomena. Cerussite occurs in the form of individual idiomorphic crystals (Figs.7 and 8).

Microprobe XRM analyses of elements Zn, Pb and Fe were run on all the samples examined. The element Ca was not mapped, as in the case of smithsonite ore, since the presence of calcite and dolomite, as the sole gangue species, had already been identified by other investigations (X-ray diffraction, chemical analysis and optical microscopy).

In most cases smithsonite and cerussite are associated with calcite and dolomite: there is a very considerable amount of intergrowth among the Pb and Zn carbonate species and between them and other minerals. Both smithsonite and cerussite have a variety of textures in this ore.

Smithsonite occurs as patches of various sizes (Figs.9a and 9b), from 40 to 200 μm, in finely disseminated form and as veins. Smithsonite has also been found associated with cerussite; in no case, however is it found in idiomorphic crystals or aggregates, as is the case in the calamine ore. Cerussite is sometimes present as patches but it occurs more frequently in finely-disseminated form (Figs.9a and 9b) within a calcite-dolomite gangue.

Examination of samples of various screen-size classes resulting from comminution shows that the grains have the same textures and associations as in the lump ore. No free particles are found in the screen-size classes ranging from 1000 to 250 μm (Figs.10, 11a and 11b).

Intergrowth remains also in the finer size-classes, especially in the case of cerussite (Figs.12, 13, 14, 15a and 15b).

With these samples, too, the vaporization effect of the epoxy resin is felt particularly in the finer screen-size classes.

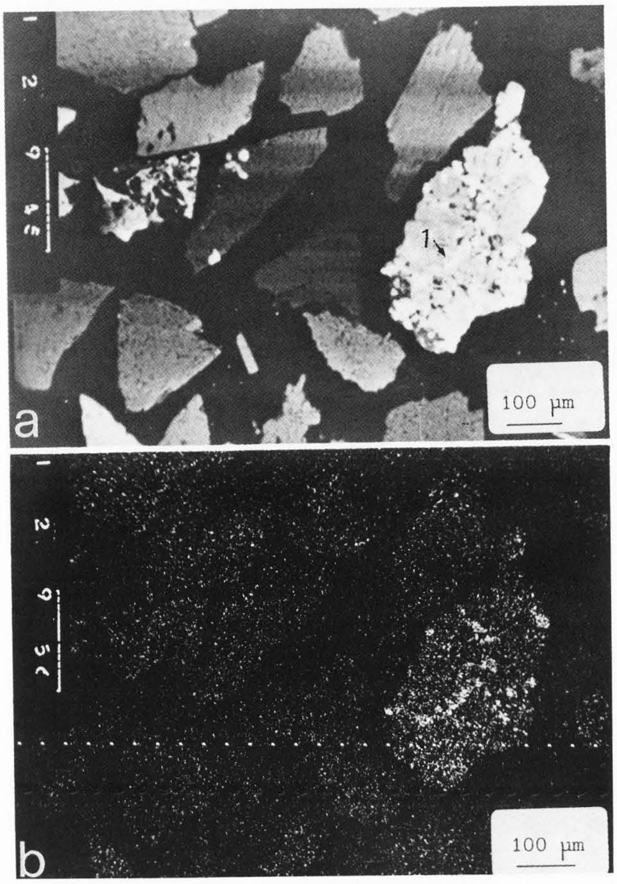

**Fig.11: Mixed Pb-Zn oxidized ore (B): grain-size fraction between 125 and 250 μm after comminution. 11a=BEI; 11b=XRM $(Pb,L\alpha_1)$.
Comparison of images reveals presence of cerussite (phase 1=white) which appears white in BEI owing to the high excitation voltage used on specimen).**

Applicability of results

The results of the investigations have been used to design comminution flowsheets and to evaluate processes for separating the valuable minerals from their gangue.

For the ores examined it is not possible to identify a liberation size, even when comminution produces very small grains. At best the grains consist of particles of one mineral species contaminated by inclusions of other minerals. This explains the relative lack of success of beneficiation processes and the difficulty in obtaining good recoveries of high grade concentrates. The treatment limits of these ores thus depend not so much on the type of flowsheet adopted and process control, but on the intrinsic characteristics of the grains themselves. In fact the presence of such phenomena as replacement, micro-intergrowth and the coating of one mineral species with another results in very complex structures. So even if very elaborate comminution circuits are adopted, "definite mixtures" are always obtained,

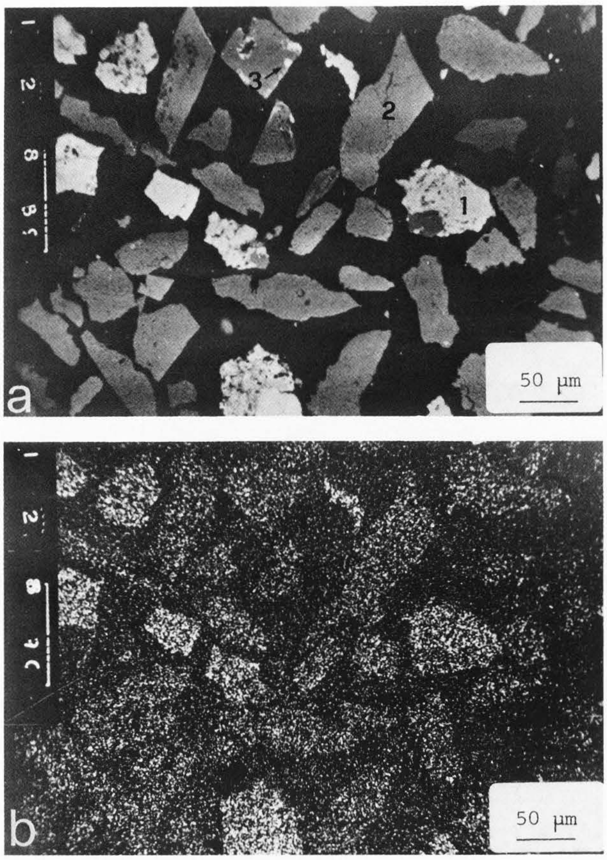

Fig.12: Mixed Pb-Zn oxidized ore (B): grain-size fraction between 75 and 125 µm after comminution. 12a=BEI; 12b=XRM (Pb, $L\alpha_1$).
Note the presence in photo 12a of grains with highly intergrowth cerussite (phase 1=light grey) and calcite (phase 2=dark grey). Galena (phase 3= white) is also present. The other grains consist almost entirely **of calcite.**

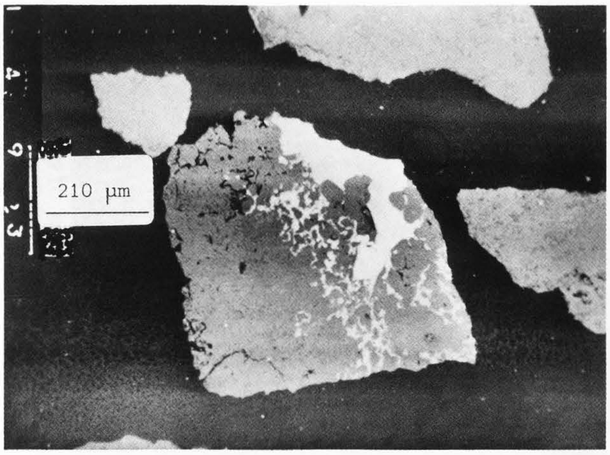

Fig.13: Mixed Pb-Zn oxidized ore (B): grain-size fraction between 500 and 1000 µm after comminution BEI.
Cerussite in finely disseminated form in a calcite grain.

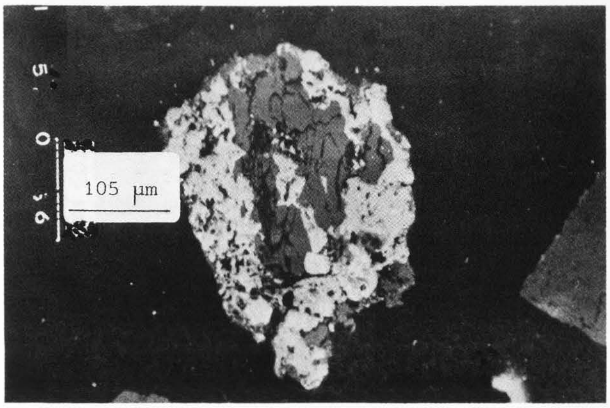

Fig.14: Mixed Pb-Zn oxidized ore (B): grain-size fraction between 250 and 500 µm after comminution BEI.
Highly intergrowth of cerussite and calcite.

namely the grains are always contaminated regardless of their size.

The analytical techniques employed provide useful indications at different size scales, enabling information to be acquired on the qualitative distribution of the elements and minerals on the surface of the grains resulting from comminution. In other words, starting from the ore, an evaluation can be made of the possible configurations of elemental and mineralogical particle distribution obtained in a size reduction simulation process.

Application of the techniques described to complex ores has permitted through examination of the quantitative relationships of the various mineral species present in lump and comminuted ore, revealing structures and textures that are difficult to identify by conventional methods of investigation (optical microscopy).

The electron microprobe reveals the existence of a crystal habit of the valuable minerals even when these happen to derive from alteration of primary minerals (e.g., smithsonite pseudomorph after sphalerite). It can be deduced from this observation that the fractures which cause separation of the grains during comminution propagate along surfaces orientated on planes parallel to the cleavage planes, namely the planes of the crystal boundaries. Even so, owing to the texture and intergrowth situation revealed by the other analytical techniques this favourable condition alone is not sufficient to ensure an acceptable degree of liberation.

Conclusions

The examination techniques adopted have revealed structures and textures that are difficult to identify by conventional methods of investigation. It has thus been possible to make an exhaustive, in-depth evaluation of the magnitude and complexity of the mineralogical associations present in the lead and zinc ores studied.

It is evident from the results of the analyses that the lack of success in obtaining high re-

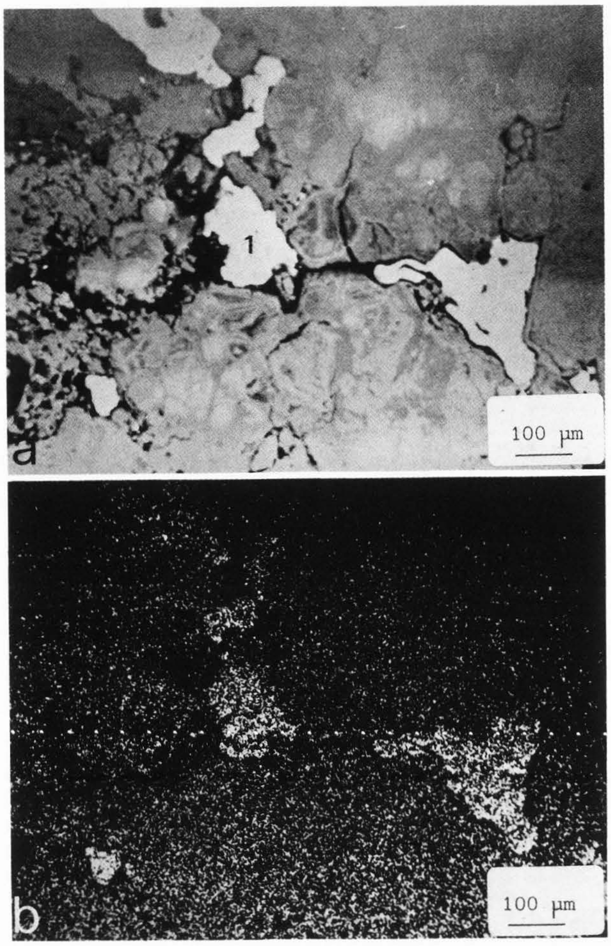

Fig.15: Mixed Pb-Zn oxidized ore (B): as mined. 15a=BEI; 15b=XRM Goethite is present (phase 1 = white). Note that element Fe was excitated (18kV). This results **in a very high background radiation.**

coveries of minerals when processing ores of this type is attributable not so much to the type of technology or process adopted as to the wide variety and intense intergrowth of the minerals involved, namely to intrinsic characteristics of the ores.

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Discussions with Reviewers

A.M. Bence: The precursors to the Pb-Zn carbonate ores studied were sphalerite, galena and (or no) pyrite assemblages. This requires that, during weathering there be major fluxes of elements both in to and out of the system (e.g.,S, Fe, C, O).

From your results, have you attempted to compute the magnitude of these fluxes using mass balance considerations?

For example, where have the S and Fe gone?

Authors: Ore paragenesis of the Cambrian carbonate rocks of Sardinia consists mainly of Fe, Zn, Pb and Ba. During the post-Hercynian peneplanation (i.e., in permo-Triassic times) the Cambrian rocks were partly eroded and their metal content was partly oxidized, transported and redeposited. Weathering of the carbonate rocks provided the bicarbonate anion, while oxidation of the sulfides furnished S anions, namely sulfuric acid. The S anions reacted to form sulfates, more particularly barium sulfate and iron sulfate (soluble). Lead sulfate is also found locally, especially in mineralized zones where there are no carbonate rocks. The bicarbonate reacted with the Zn to form smithsonite, while the other sulfates were partly solubilized and washed out, except for the barite which is insoluble.

J. BACK: You mention that Zn, Pb, Ca, and Fe were mapped, but no Fe X-ray maps are presented. Have you looked to see if iron is present in sphalerite and smithsonite (iron can substitute for Zn in both of these phases, RAMDOHR, 1980, p.506 and 1107), and how iron concentrations in these phases might be related to iron oxides in your sample? If smithsonite is pseudomorphous after sphalerite (as you indicate) and contains less iron than sphalerite, perhaps the iron oxide is a byproduct of oxidation of zinc ore? Is there any textural, as well as chemical, evidence to indicate the relationship of iron oxide to the ore phases or to the host rock?

Authors: Fe has never been found in association with smithsonite in any of the samples analyzed. The Fe content of the sphalerite is always very low, though there are variations depending on whether the mineralization is in the lower or upper part of the Cambrian series. The iron which is found both as oxides and in the Yellow Dolomite derives mainly from the ore paragenesis (pyrite). Most of the iron present in the ores is thus in the form of goethite as cement in the vugs and cavities of the mosaic of minerals forming the ore (Fig.15).

A.M. BENCE: Are sulphates (e.g., gypsum, barite) important in the rocks peripheral to the bodies? Are siderite or ankerite important gangue minerals?

Authors: Gypsum is not present but barite is. Ankerite is the basic mineral of the supergene epigenetic dolomitization process that transformed the Cambrian limestones into yellow dolomite during the Permo-Triassic peneplanation.

In some samples of ore from San Giovanni Mine, characterized by a cavernous type of structure, cerussite sometimes associated with barite has been found in the cavities. The presence of this sulfate, which occurs as shiny, glassy crystals having a tabular habit, could be due to the $SO_4^=$ content of the ground-waters which precipitated their barium in the limestones and went into solution with the weathering of the latter.

J. BACK: Have you analyzed the various phases present in the ores with the SEM and electron microprobe to determine the presence and quantities of minor and trace elements? According to RAMDOHR (1980), varieties of sphalerite may contain greater than 10% Fe (p.506) and smithsonite may contain Fe, Mn, and Cd (p.1107). Might the presence of these phases affect grade and beneficiation procedures? In addition, if Mg is present in calcite associated with smithsonite ore, it might effect potential methods for separating smithsonite from calcite; smithsonite and dolomite [$CaMg(CO_3)_2$] are resistant to cold HCl, while calcite is not. Perhaps Mg would also be an interesting element to examine.

Authors: X-ray fluorescence analysis was used for Bi, Ca, Cd, Fe, HG, Pg, Pb and Zn, a Philips PW 1110 X-Ray Spectrometer being employed for the purpose. The research for minor and trace elements in the minerals present in the two ores studied was tackled with reference to the two principal minerals of interest. In the mainly smithsonite ore (Buggerru-Caitas) the smithsonite was analyzed, while on the mixed oxidized Pb-Zn ore (San Giovanni) the cerussite was analyzed, the results being as follows:

Ore	**Mineral**	**Minor and trace elements found**
1	Smithsonite	Fe, Ca, Cd, Mg, Bi, Hg & Pb
2	Cerussite	Fe, Mn, Zn, Bi, Ca & Hg

1. Mainly smithsonitic (Buggerru-Caitas)
2. Mixed Pb-Zn oxides (San Giovanni)

Some of the elements indicated were found only as traces. Experience acquired in treating Sardinian "Calamine" ores shows that the presence of these phases in the ores is not important in the flotation process. The presence of iron oxides, on the contrary, is decidedly important, because even if the iron minerals are liberated from the others, iron may still occur as a coating on the valuable minerals, thus modifying the surface characteristics of the oxidized lead and zinc species (especially the smithsonite). In the treatment processes usually adopted aliphatic amine in the presence of Na_2S the type of gangue carbonates associated with the smithsonite is of no importance. However, collector selectivity is greatly influenced by the presence of iron oxides and clayey slimes, as well as by fine particles of any kind, and of course by the presence of "definite mixtures" (ABRAMOV, 1962) (BILLI & QUAI, 1963) (GATY, 1942, 1946).