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CHEMICAL AND MINERALOGIC CHARACTERISTICS OF *BOROGYPSUM* PRODUCED BY ACID DISSOLUTION OF COLEMANITE AT LARDERELLO (ITALY)

Abstract - *Chemical and mineralogic characteristics of* borogypsum *produced by acid dissolution of colemanite at Larderello (Italy).* Large amount of *borogypsum*, the by-product of the acid boric industrial extraction from colemanite, were produced at Larderello industry and discharged into the environment during the last century, before the regulations for environmental concern were established. In this study we investigate the chemical and mineralogical characteristics of the waste, to define geochemical tracers of this source for environmental application.

Key words - Boric acid production, colemanite, borogypsum, environmental pollution, Larderello (Tuscany, Italy).

Riassunto - *Caratteristiche chimiche e mineralogiche del* borogesso *prodotto per dissoluzione dell'acido dalla colemanite a Larderello (Italia).* Grandi quantità di *borogesso*, scarto industriale del processo di produzione dell'acido borico dalla colemanite, sono state riversate nell'ambiente dall'industria chimica di Larderello, prima dell'emanazione della legislazione a favore della tutela ambientale. In questo studio vengono presentate le caratteristiche chimiche e mineralogiche del *borogesso*, allo scopo di definire dei traccianti geochimici da applicare nelle ricerche ambientali indirizzate al riconoscimento di questo inquinante.

Parole chiave - Produzione acido borico, colemanite, borogesso, inquinamento ambientale, Larderello (Toscana).

Introduction

After boric acid (known with the name of «sedative salt of Homberg») was identified as a natural phase (sassolite) at Monterotondo by Höefer (1977), the production of boric acid from the boron-rich geothermal fluids of Larderello was envisaged by Mascagni in 1812 and the first tons of boric acid finally produced in 1819 (Cappelo & Culivicchi, 2010). In the mid '50, the industrial production of boric acid moved worldwide towards extractive processes from boron minerals. The dissolution mechanisms and kinetics of boron minerals were extensively investigated (Kurtbas *et al.*, 2006 and references therein), and colemanite became one of the most important minerals used around the world for boric acid production.

Colemanite ($CaB_3O_4(OH)_3$ H_2O) is a complex inoborate in which the chains of composition $[B_3O_4(OH)_3]^{2-}$ extend along [100]. In these chains tetrahedra and triangles, centred by boron atoms and linked through corners to form rings of composition $[B_3O_5(OH)_3]^{4-}$, are present.

Ores are found in Anatolia (Turkey) and California (USA), where the mineral is stratabound in Tertiary rocks (Helvaci, 1977); colemanite also occurs in the salars of Argentina and Bolivia (Helvaci & Alonso, 2000). Colemanite was considered a secondary mineral formed after original deposition of borax (Helvaci, 1977), until a primary origin was recognized by Helvaci and Alonso (2000).

For industrial application, boric acid is generally produced by dissolving colemanite (50.81 % B_2O_3) in a sulfuric acid solution, according to the following reaction:

$$2CaB_3O_4(OH)_3 \cdot H_2O + 2H_2SO_4 + 6H_2O = 2CaSO_4 \cdot 2H_2O + 6H_3BO_3$$
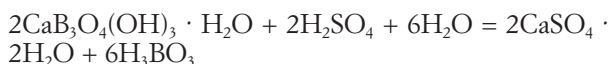
After reaction, boric acid is crystallized from the solution (Kurtbas *et al.*, 2006), while the so called *borogypsum* (which consists mainly of gypsum crystals and boron compounds) precipitates as industrial by-product.

Data on the X-ray diffraction pattern and the chemical composition of the waste produced by the boric acid industry were reported by Elbeyli & Piskin (2004) for samples from Eti Holding Bandirma Borax and Boric Acid Palnts, in Turkey. The X-ray diffraction pattern is dominated by gypsum. The chemical analyses indicate that the boron content of the solid waste is generally in the order of several units wt%, and varies on the basis of the relative yield of each industrial extraction procedure.

Large amounts of *borogypsum* waste have been discharged by the boric acid industry into the environment, mainly in weastern Turkey, were about 62% of the world's boron ores are found (Elbeyli and Piskin, 2004). In Tuscany, the Larderello area represents a site were significant discharges have also occurred during the 20th century. In this area, during the '60s the boric acid production from geothermal fluids was converted into extraction from colemanite imported from Western Anatolia (Cappelo & Culivicchi, 2010). After a period in which the extraction was performed by using ammonium bicarbonate, the production of boric acid at Larderello moved towards the acid procedure, which used locally produced (at Scarlino) sulfuric acid

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(Cappello & Culivicchi, 2010). The amount of boron in the *borogypsum* waste produced in Tuscany was inversely correlated with the yield of B-extraction, that increased in time from 60% up to 90% (Cappello & Culivicchi, 2010). Favored at the time by the lack of awareness for environmental protection, about 70,000 tons/year of boron-rich waste have been released in the Possera creek, left tributary of the Cecina River, that crosses the Larderello village, where the industrial activity was concentrated (Grassi & Squarci, 2004). After the regulations were established, and till the industrial process was active (up to 2002), the waste was disposed in a local landfill, where it is still confined.

The unregulated dump of *borogypsum* contaminated shallow and groundwaters through bank infiltration. In the '70 of 20th century, the boron content in surface waters of the Possera stream increased up to about 400 mg/L, and up to 10 mg/L in groundwater extracted from local wells (Grilli Cicilioni *et al.*, 1995; Grassi *et al.*, 2004). The contamination of the Cecina aquifer and the isotopic characteristics of boron and strontium in colemanite, *borogypsum* and groundwaters were discussed in Pennisi *et al.* (2006a), and the isotopic signatures of B and Sr used to constraint the origin of colemanite (Emet ore).

In this study we investigate the mineralogical and bulk chemistry of *borogypsum* with the aim to: a) highlight the B-bearing phases eventually associated to sassolite; b) identify those elements that are associated to boron (and calcium and sulfur), and that could eventually trace *borogypsum* in the environment.

EXPERIMENTAL DATA

Mineralogical data

The X-ray powder pattern of *borogypsum* revealed only the presence of gypsum. A weak peak at 5.9 Å (that represents the most intense diffraction peak in the X-ray powder diffraction pattern of sassolite) suggested the presence of traces of sassolite (boric acid).

Microprobe EDS-SEM analyses of the heavy fraction of *borogypsum*, obtained by means of a saturated solution of sodium politungstate ($D = 2.9$ g/cm^3) revealed the presence of not negligible amounts of celestite and realgar as accessory phases.

Experimental procedure

To verify the occurrence of any residual soluble boron-bearing phases within the mass of *borogypsum*, 200 grams of this material were powdered, put into a becker with 500 ml of cold water, and stirred for 2 minutes. Once the insoluble part settled, the solution was filtered and evaporate up to complete dryness. At the end of evaporation we observed at the bottom of

becker a tiny crust of minute tabular colourless crystals that successive EDS-SEM and XRPD with Gandolfi camera investigations revealed to be sassolite, natural boric acid (Fig. 1).
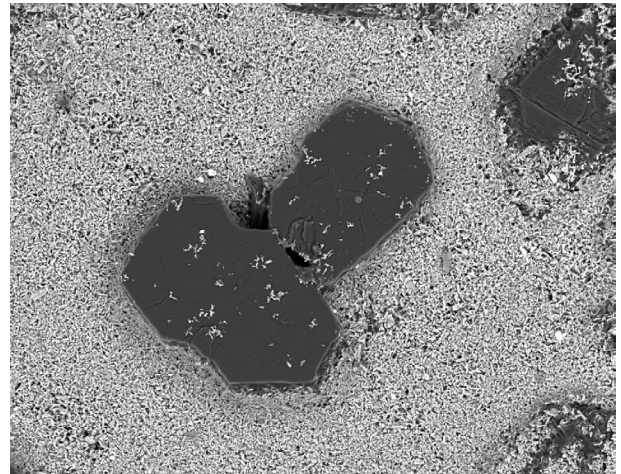

Fig. 1 - Dark gray pseudo-hexagonal sassolite crystals, up to 2 mm in diameter, associated with white microcrystalline gypsum crystals. Back-scattered SEM photo.

On the basis of these data, we can state that *borogypsum* consists of a white microcrystalline powder formed by the aggregation of finely interwoven tiny acicular crystals of gypsum, and including minutes micaceous crystals of sassolite (Fig. 2).

Chemical characteristics of borogypsum

The bulk chemical characterization of *borogypsum* was performed by means of X-ray fluorescence method using about 3 grams of materials previously heated at
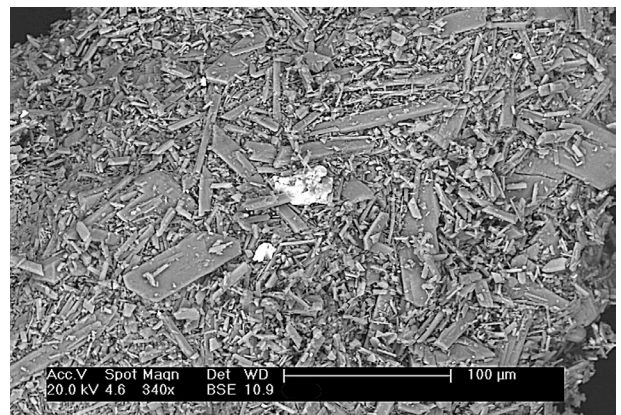

Fig. 2 - *borogypsum*: aggregate of pale gray microcrystalline tiny acicular crystals of gypsum associated with sporadic minute white fragments of celestite and realgar. Back-scattered SEM photo.

200°C for five hours. Major elements were analysed using Cu Kα radiation while a Mo Kα radiation was used for trace elements. Boron was analysed by Prompt Gamma Neutron Activation (PGNA) at Act-labs, Canada.

The chemical analysis of *borogypsum* produced at Larderello is reported in Tab. 1. Associated to SO_3 (42.3%), CaO (30%), and B_2O_3 (2%), *borogypsum* contains, in decreasing order, subordinated SiO_2 (5%), MgO (2.4%), Al_2O_3 and Sr, (0.7%), Fe_2O_3 (0.35%), K_2O (0.3%), As (0.2%), and Na_2O (0.1%). Ti, Ba, Zr, Ce, La, and Rb were also detected, but in concentration lower than 100 μg/Kg.

Tab. 1 - Chemical composition of borogypsum produced at Larderello. Isotopic composition of boron and strontium (Pennisi *et al.*, 2006) and sulfur (Amadori, 2009) are included.

Borogypsum		This sudy	Elbeyli *et al.* 2004	Alp *et al.* 2009
wt %	Na_2O	0.11	0.1	0.06
	K_2O	0.21	0.79	0.04
	CaO	28.1	25.2	28.41
	MgO	2.25	0.88	1.06
	Al_2O_3	0.68	1.37	0.75
	SiO_2	4.91	7.74	6.99
	TiO_2	0.03	nd	0.1
	Fe_2O_3	0.33	0.74	0.72
	SO_3	40.0	35.6	40.1
	B_2O_3	2.07	7	2.8
	As_2O_3	0.93		1.45
	SrO	0.23		0.66
	Pc	20.1		17.83
μg Kg-1	Pb	7		
	Ba	34		
	Zr	97		
	Ce	17		
	La	13		
	Rb	29		
permil	$\delta^{11}B*$	-13.3		
	$\delta^{34}S**$	1.2		
	$^{87}Sr/^{86}Sr*$	0.70942		

The B_2O_3 component represents the residual boric acid (sassolite) not recovered by the industrial production, while high As and Sr are relict of the realgar and celestite associated to colemanite in the Turkish ore deposits (Helvaci and Alonso, 2000). The silicatic component has to be referred to the matrix of the ore deposit.

The comparison with the chemical data from Elbeyli *et al.* (2004) and Alp *et al.*, (2009) shows that *borogypsum* wastes differ in terms of boron content (B_2O_2 = 2.1, 7, and 2.8%, respectively), and confirms that the boron-recovery is peculiar for the industrial sites. Alp *et al.*, (2009) also measured an As_2O_3 content of 1.45 mg/kg in *borogypsum*, and accordingly define it as «ar-

senical borogypsum waste». The authors suggested that the arsenic in realgar and orpiment occurring in the ore could partialy dissolve during the leaching process (with concentrate H_2SO_4) and be removed as insoluble Ca/Fe arsenate. Aydin *et al.* (2003) evidenced that over 99% of As present in the feed remains in the *borogypsum*, increasing the environmental risk by this waste.

The B, Sr and S isotopic values (expressed as $\delta^{11}B$, $^{87}Sr/^{86}Sr$ and $\delta^{34}S$, respectively) of the *borogypsum* produced at Larderello (colemanite from Emet deposit) measured by Pennisi *et al.* (2006a) are added in Table 1. *Borogypsum* has a negative $\delta^{11}B$ value of –13‰, a $^{87}Sr/^{86}Sr$ ratio of 0.70942, and a $\delta^{34}S$ of 1.2‰.

DISCUSSION

The *borogypsum* waste produced at Larderello from industrial treatment of colemanite from Emet ore deposit is mainly composed by sulfur, calcium and boron, with associated strontium and arsenic, from celestite and realgar. *Borogypsum* consists of a dense network of gypsum crystals in which the boric acid (not recovered during the industrial process of acid attack of colemanite) is trapped in the form of minutes micaceous crystals. The amount of sassolite crystals in *borogypsum* is controlled by the recovery yield of the industrial process that differs at each productive site.

The isotopic signatures of B, and Sr significantly differs from those of the local geogenic fluids ($\delta^{11}B$ = +13‰ ± 4, Pennisi *et al.*, 2006b, $\delta^{34}S$ = 6‰ ± 0.9, Amadori, 2009; $^{87}Sr/^{86}Sr$ = 0.7086 ± 1; Pennisi *et al.*, 2006a), suggesting that these parameters could be sensitive tracers of *borogypsum* in the environment.

The $\delta^{11}B$, and $^{87}Sr/^{86}Sr$ isotopic signature represents a potential tools to evidence environmental contamination, in those sites where - as in the Larderello area - Emet colemanite was used for boric acid production. In contrast, the $\delta^{34}S$ signature univocally reflects the isotopic signature of the H_2SO_4 used at each specific site for the industrial extraction.

High arsenic and boron content, associated to the dissolution of gypsum in water (Kuechler *et al.*, 2004; Colombani & Bert, 2007), makes *borogypsum* a waste of high environmental concern, and its storage a huge problem for the industry. However, it was shown that the use of arsenical *borogypsum* as an additive in lightweight concrete or in Portland cement clinker increases its compressive strength (Boncukcuogly *et al.*, 2002; Elbey & Piskin, 2004; Kavas *et al.*, 2005; Alp *et al.*, 2009). Accordingly, the addition of *borogypsum* in cement production could represent an useful remediation, because of the restricted mobility shown by boron and arsenic in new-formed solid phases after calcination.

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