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Petroarcheometry of copper smelting slag in Trentino; provenance and process data

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ABSTRACT - Smelting slag collected at various sites in Trentino reveal a provenance of the raw material from the phyllitic basement of Valsugana (Gabàn, Acquaviva, Romagnano of the Copper Age; Luserna, of the Late Bronze Age), or from the Permian volcanites (Val Fersina, Late Bronze Age), based on lithic fragments, chemical composition and process products within the slags. In the metallurgic process a great deal of quartz was added as a reagent to scorify the iron of the chalcopyrite, by fixing it into silicate neominerals, and smelt the metal into a copper matte.

KEY WORDS: Smelting slag, Copper Age, Bronze Age, Gabàn, Trentino

PAROLE CHIAVE: Scorie di fusione, Età del Rame, Età del Bronzo, Trentino

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Fortysix samples of prehistoric slags from Trentino smelting areas were examined and attributed partly to the Copper (or the Early Bronze) Age (Riparo Gabàn, Acquaviva, and Romagnano), and partly to the Late Bronze Age (Luserna and Val Fersina). (ANGELINI *et al.*, 1980; BAGOLINI & PEDROTTI, 1995; DE MARINIS & PEDROTTI, 1997; FASANI, 1988; MARZATICO, 1997; PERINI, 1989, 1992; PREUSCHEN, 1973).

The aim of the study (D'AMICO *et al.* 1998) was to identify the ore provenance and refurnishment from the numerous ore deposits of the adjacent Trentino area (cfr. PERNA, 1964a,b). The data also suggested some reflection on the metallurgic process that produced the slag, starting with copper-iron sulphides, in particular chalcopyrite.

The slags, with the usual appearance ranging from greatly to fairly blistered (prevalent) to flattened (rare), have a variable quantity of lithic fragments (10-40%), process products (40-70%, up to 90% in flat slags) and blistering holes (10-30%).

The lithic relics are always thermoclastically fractured, corroded and transformed by the smelting process. They belong to two different typologies according to the distribution areas (Fig. 1).

In the Chalcolithic slags from Gabàn (12 samples), Acquaviva (10 samples), Romagnano (3 samples) and in the slags from Luserna (12 samples) of the Late Bronze Age, the fragments consist exclusively of phyllite relics, melted in their micaceous-chloritic-albitic portions and rich in corroded quartz residues, and of relics of metamorphic quartz, from the usual nodules in the phyllites. These relics do not belong to lithologies outcropping in the smelting areas, and therefore indicate importation of the ores from other places.

In the late Bronze age slags from Val Fersina (9 samples) the lithic fragments are less evident and consist of Permian volcanites, which outcrop in the area, and abundant hydrothermal quartz.

In both cases, the quartz is so abundant that it is logical and inevitable to think that it was intentionally added to the smelting mixture. The mineral relics, determining at SEM/EDS, are mainly chalcopyrite, sometimes pyrite and rarely covelline.

The process products essentially confirm what was described by PIEL *et al.* (1992) and consist of a blackish vitreous matrix and neominerals that have developed in this matrix, in mutually variable quantities. The vitreous matrix is very rich in Fe (SEM/EDS), with a substantial silicate component, and relatively high quantities of Zn and Ca. The neominerals consist mainly of ferriferous olivine, (hyalosiderite and fayalite SEM/EDS), with minor contents of Ca and Zn mostly in skeletal forms and rarely complete, and to a lesser extent of clinohypersthene (see Fig. 2).

The bulk composition of the process material, with some inevitable contamination by minute residues of lithic material, is shown in the table. It is characterized by very high percentages of Fe, which together with Cu, Zn and S (+ lesser quantities of Co, Pb, etc.) seems to be essentially derivated from the ore minerals, while the silicate component is derived from partially melted lithic relics. A small addition of $CaCO_3$ is deduced from the high quantity of CaO not compatible with phyllite chemical compositions.

It can be inferred from the chemical data that the ore sources were rich in Fe, according with the corroded relics of chalcopyite and pyrite mineralogically observed.

The petrographic characteristics of the slags containing phyllite relics at Gabàn, Acquaviva, Romagnano, and Luserna indicate that the sources of the material must have been in the phyllite basement of Valsugana, where chalcopyrite and sphalerite bearing pyritiferous deposits, compatible with the chemical and mineralogical characteristics found in the slags, are known. The largest deposit is at Calceranica, where levels rich in chalcopyrite and sphalerite (MORRA, 1964; PERNA, 1964b; OGNIBEN, 1966) are known, particularly if one imagines its original appearence before the massive exploitation of the last four centuries. Another possible source, logistically and mineralogically less probable, is the Vetriolo area, while the small chalcopyrite deposits of Val Sella (PERNA, pers. com.) are also worthy of consideration, particularly for the supply of the nearby smelting area of Luserna. These mineral sources seem to have lasted for a long time, from the final Chalcolithic period for Gabàn, Acquaviva and Romagnano, to the late Bronze Age for Luserna, and involve transport routes of 5-15km.

The Bronze age slags of Val Fersina, with volcanites and hydrothermal quartz relics, seems instead to be local (<5km), from some of the various hydrothermal deposits connected to the Permian volcanics of the area (cfr. PERNA, 1964b).

It should be noted that Gabàn, rather close to hydrothermal deposits, was supplied instead from more distant phyllite sources. It can thus be inferred that the volcanite-hydrothermal sources were not known regionally in the early Metal Age.

The high quantities of intentionally added quartz were clearly used as a reagent to fix the Fe of the sulphydes, in particular $CuFeS_2$, in the silicate bonds of the Fe-olivines and Fe-pyroxenes, eliminating S as SO_2 by oxidation and exhalation, and releasing the copper matte by smelting. This suggests a metallurgic extraction process which is simpler than that usually considered for copper smelting (cfr. e.g. TYLECOTE, 1992; MADDIN, 1996), which foresees a first roasting stage before smelting. This seems somewhat incompatible with the enormous presence of Fe-olivine in the slags, since most iron would oxidize to hematite and/or magnetite during roasting, requiring a subsequent difficult reduction to Fe to obtain the Fe-olivines observed. A single-stage process for the extraction of the copper matte from the chalcopyrite would seem to be more in agreement with the data, especially if contaminated by pyrite. The same would apply to the bornites.

The situation differs for the exploitation of covelline or chalcocite, in which the addition of quartz to scorify the Fe would seem superfluous, and for the exploitation of malachite/azurite, where the roasting stage seems in fact to be necessary.

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SUMMARY - Smelting slag collected at various sites in Trentino reveal a provenance of the raw material from the phyllitic basement of Valsugana (Gabàn, Acquaviva, Romagnano of the Copper Age; Luserna, of the Late Bronze Age), or from the Permian volcanites (Val Fersina, Late Bronze Age), based on lithic fragments, chemical composition and process products within the slags. In the metallurgic process a great deal of quartz was added as a reagent to scorify the iron of the chalcopyrite, by fixing it into silicate neominerals, and smelt the metal into a copper matte.

RIASSUNTO - Scorie di fusione raccolte in vari siti trentini rivelano, in base ai frammenti litici contenuti, al loro chimismo e ai prodotti di processo, una provenienza dal basamento filladico della Valsugana (Gabàn, Acquaviva, Romagnano dell'Eneolitico; Luserna, del Bronzo recente), o dalle vulcaniti atesine locali (Val Fersina, del Bronzo recente). Nel processo metallurgico molto quarzo è aggiunto come reagente per fissare il ferro della calcopirite in neominerali silicatici, ossidare lo zolfo e liberare per estrazione fusoria il metallo come rame grezzo.

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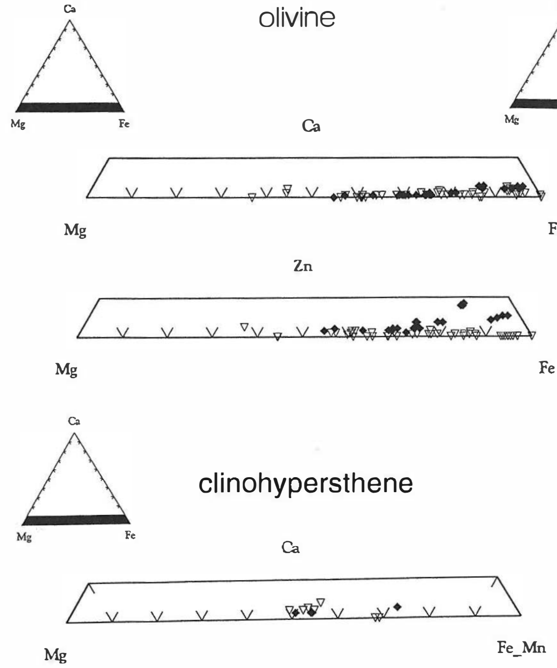

Fig. 1 – Ternary diagrams of mafic minerals

TABLE 1

	Acquaviva (10 camp.)		Gaban (12 camp.)		Romagnano (3 camp.)		Fersina (9 camp.)		Luserna (12 camp.)	
SiO_2	33.0	46.7	23.2	43.2	37.8	42.4	35.9	52.3	28.8	53.2
TiO_2	0.21	0.24	0.15	0.41	0.20	0.3	0.10	0.37	0.14	0.33
Al_2O_3	6.1	7.7	4.3	8.8	5.2	7.9	4.6	10.2	5.1	7.7
Fe_2O_3	34.0	46.3	33.9	58.2	36.7	45.1	30.8	44.2	24.9	49.5
MnO	0.17	0.23	0.15	0.26	0.22	0.2	0.23	0.79	0.09	0.30
MgO	3.2	4.6	1.9	4.9	3.1	3.9	0.55	4.0	1.5	5.0
CaO	1.9	5.2	1.3	7.6	2.3	4.4	1.6	5.7	3.0	6.8
Na_2O	0.09	0.70	0.07	0.39	0.12	0.1	0.20	1.03	0.17	0.45
K_2O	0.47	0.86	0.42	1.8	0.46	0.5	0.69	3.6	0.85	1.5
P_2O_5	0.07	0.11	0.12	0.34	0.12	0.15	0.14	0.57	0.12	0.22
S	0.64	3.0	0.45	2.0	0.77	1.3	0.09	1.6	0.79	2.3
Cu	0.83	3.5	0.75	2.7	1.3	1.8	0.60	1.8	0.35	1.9
Zn	1.0	1.5	0.38	2.8	0.31	1.9	0.03	1.8	0.36	1.5
H_2O	1.6	4.0	1.6	4.0	0.43	2.1	0.31	4.1	0.37	4.7
V	29	46	14	53	30	41	23	53	23	38
Cr	25	30	26	57	20	42	15	52	24	50
Co	137	260	108	451	202	354	72	2479	88	497
Ni	71	155	85	327	44	49	3	49	9	45
Rb	13	31	10	47	8	16	25	177	19	57
Sr	16	28	16	50	11	26	39	130	25	62
Zr	95	123	75	154	85	139	11	140	58	182
Nb	4	8	5	13	7	8	4	10	3	16
Ba	15	158	57	482	4	44	125	675	61	140
Pb	45	69	72	231	194	3400	51	2400	100	1950
As	30	91	13	97	55	255	35	1670	44	174

Table 1 – Range of chemical composition of smelting slag