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Article

# Slags as Evidence for Copper Mining above Casaccia, Val Bregaglia (Central Alps)

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**Abstract:** Slags from the remote Mota Farun locality above Casaccia (Val Bregaglia, Swiss Alps) have been analyzed with scanning electron microscopy, X-ray powder diffraction and microfocus synchrotron X-ray diffraction to determine mineralogical composition and microstructures. Non-magnetic slag samples are largely composed of euhedral and dendritic iron-rich olivine in a glassy matrix. Locally there are zones with globular inclusions rich in bornite ((Cu<sub>5</sub>Fe)S<sub>4</sub>) and locally metallic copper. Some regions display dendritic pentlandite ((Fe,Ni)<sub>9</sub>S<sub>8</sub>). Magnetic samples are mainly composed of fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) and wüstite (FeO), with minor magnetite (Fe<sub>3</sub>O<sub>4</sub>). The mineralogical composition indicates that slags were the product of copper smelting. The slag compositions and morphologies are analogous to slags described from the Oberhalbstein (Graubünden, Switzerland) and the Trentino Alps (Italy) which are attributed to metallurgical exploitations of the Late Bronze Age. While the origin of the ore could not be determined, it may be related to ore deposits of chalcopyrite in greenschists and serpentinites in the vicinity, such as Alp Tgavretga (Septimer Pass) and Val Perossa (Val Bregaglia).

**Keywords:** copper smelting; slags; Swiss alps; Casaccia; scanning electron microscopy; synchrotron X-rays

## 1. Introduction

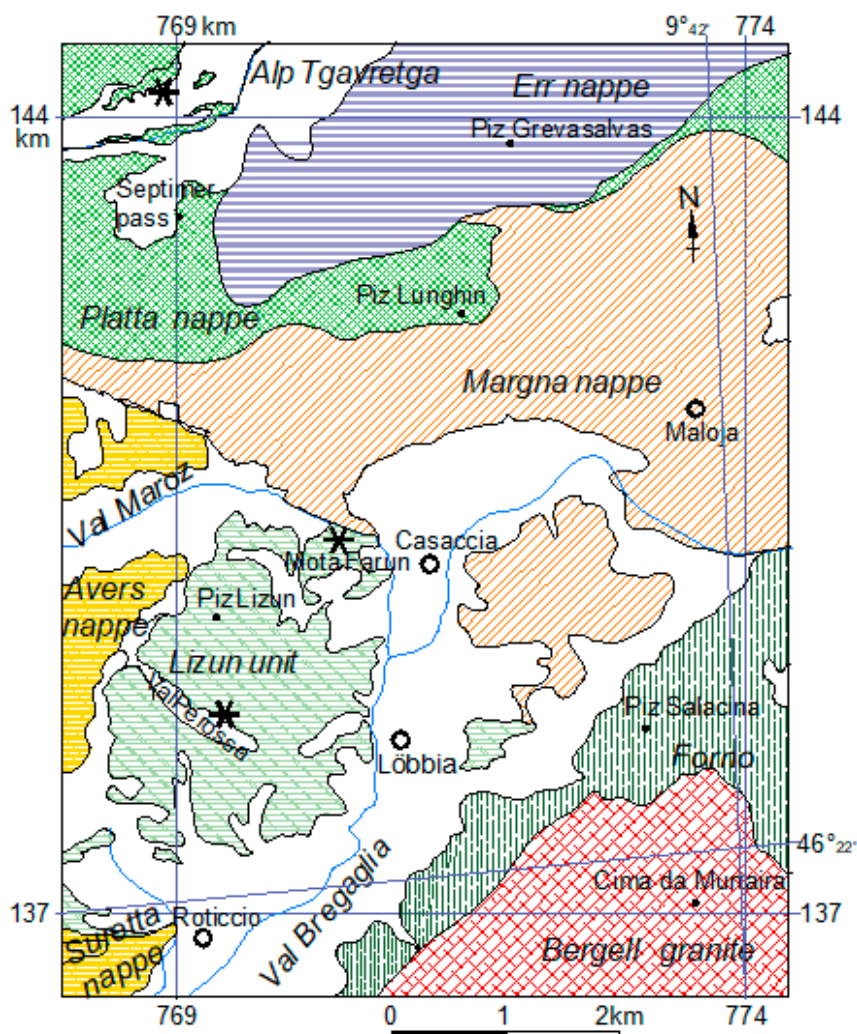
Ancient metallurgy in Europe has been of longstanding interest [1–11] and particularly prehistoric copper production in the eastern Alps received a lot of attention such as the the Oberhalbstein in Graubünden (Switzerland) [12], Montafon [13,14], the Silvretta region [15], Kitzbühel [16], Mitterberg [16,17] and Obersteiermark [18] in Austria and the Trentino region in northern Italy [19–22]. Similar Bronze Age activities have been described from the Western Alps [23]. Copper smelting slags are often found at remote places, corresponding to local mineral deposits, mainly of chalcopyrite.

In 1972 Remo Maurizio [24] described slags from a locality above Casaccia, Val Bregaglia, in the Swiss southern Alps. These slags were never analyzed in any detail and attracted our interest in connection with geological fieldwork [25].

The Casaccia locality is not very far from other mining sites further north in Graubünden where metal mining and processing started in the Bronze age [26], continued through the Middle Ages to the late 19th century [27–30]. Compared with other metallurgical mining operations in the Alps described in the literature [11], Casaccia slags originate from a very small and local operation.

Casaccia is in uppermost Val Bregaglia, which has been an important trading route for a long time. While there is currently no evidence for prehistoric habitation, Romans traversed the Alps from Italy through what is now Casaccia, both over Septimer Pass and over Maloja-Julier Passes, with some relics preserved such as pillars on Julier Pass as well as remains of roadways.

Figure 1 shows a map of upper Val Bregaglia with principal tectonic units compiled from previous studies [25,31,32]. The geology is rather complex, with lower Pennine nappes on the southwest overlain by Austroalpine nappes on the northeast. The Pennine nappes (Suretta, Lizun, Avers and Platta) are composed largely of muscovite-chlorite gneiss, some marble and with local serpentinite. They represent a Paleozoic-Mesozoic basement that was metamorphosed during the early Tertiary Alpine orogeny. The Austroalpine Margna and Err nappes represent largely Hercynian granite, also subjected to Alpine metamorphism and deformation. On the lower right corner of the map is the young Tertiary Bergell granite surrounded by the Forno contact zone. During the ice age, lasting until about 10,000 years BP, much of the area and particularly the valleys were covered by large glaciers, most importantly a glacier from Val Forno (southeast) that divided at Maloja into a branch that moved northeast into the Engadine, and a branch that moved southwest into Val Bregaglia and towards the current Lake of Como. Around 1500 BC and 0 AD there were warm periods, probably with minimal glaciation.



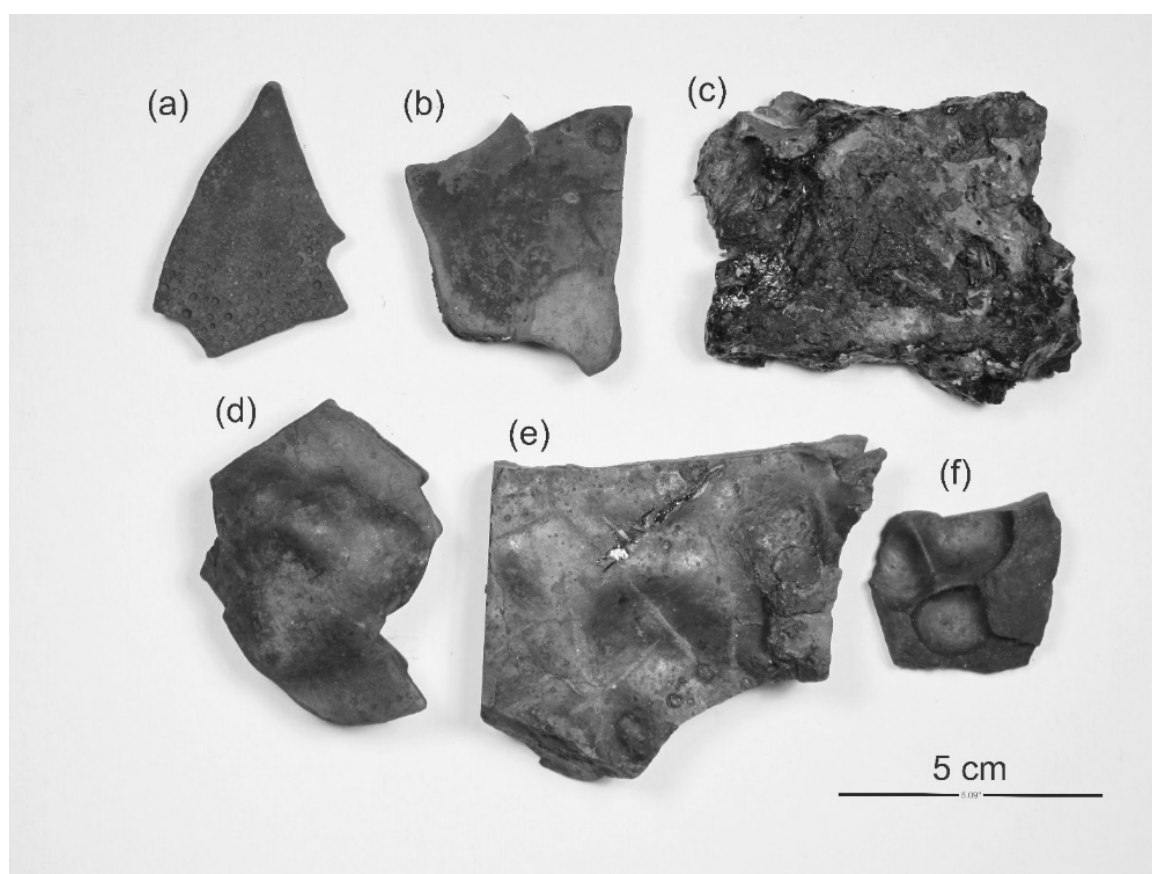
**Figure 1.** Map of upper Val Bregaglia in the Swiss Alps with tectonic units (italic). The slag locality of Mota Farun and the ore deposits at Alp Tavretga and Val Perossa are indicated by asterisk symbols. Coordinates with a square kilometer scheme are from Swiss topographic maps. Universal geographic coordinates (NS and EW) are also indicated.

Here we study samples of slag from the Casaccia site [24] in some detail with modern methods used in mineralogy to characterize microstructures, identify phases and their morphology. Apart from analyzing slags we also explore potential source material in the vicinity. This may inspire more systematic archeological studies of the Casaccia samples, to identify remains of smelting facilities, radiocarbon age determinations and locating the origin of the ore that was processed in Val Bregaglia. It also could encourage archeologists to apply these methods to explore details of microstructural features to slags from classical sites of ancient metal production. They have mainly relied on conventional geochemistry.

## 2. Sample Description and Analytical Methods

The map in Figure 1 shows the locality Mota Farun west of Casaccia where Maurizio collected slags [24]. This place is on a steep slope, 200 m above Casaccia (Swiss coordinates 140.3 km/770.6 km, 1600 m), now covered largely by Quaternary debris and forests. Here we collected new samples. The location is in the Pennine Lizun nappe of greenschist metamorphic grade with dominant muscovite-chlorite-albite gneiss.

Slags at the Mota Farun locality occur in various sizes, the largest about 20 cm. They have mainly been found in places of recent erosion (e.g., in connection with lumbering) or excavations (for an adjacent electric power line). No evidence for mining activities could be identified nor could relics of smelters be found. Figure 2 is an image of various slags. Some are homogeneous, others have inclusions of host rock (Figure 2c). Some slags, particularly those with platelet morphology, are strongly magnetic (Figure 2a,b). Most do not display significant magnetism.



**Figure 2.** Photograph of Casaccia slags. (a,b) Plate-shaped magnetic slags; (c) slag with inclusions of host rock and (d–f) non-magnetic slags with bulges.

From samples chosen for this study polished 30  $\mu\text{m}$  thin sections were prepared and viewed with optical microscopy to identify areas of interest. These were then analyzed with a Zeiss-Evo scanning electron microscope (SEM) at UC Berkeley. The SEM was operated at 20 kV. For imaging backscatter electrons (BSE) were used to highlight variations in atomic weight. Samples were studied both at low vacuum (requiring no carbon coating) and at high vacuum (with carbon coating). High vacuum microscopy provides higher resolution for BSE images. The chemical composition was assessed with energy-dispersive spectroscopy in the SEM, using an EDAX detector and data processing software. At low vacuum and without carbon coating, low atomic number elements such as carbon and oxygen can be detected. Due to the small grain size of many crystallites, and corresponding averaging in the electron beam, volume fractions of elements are qualitative estimates, particularly for oxygen.

In addition the bulk mineralogical composition of the slags was determined with X-ray powder diffraction (XRD), using an X'Pert Malvern Panalytical system with monochromatic  $\text{Co K}\alpha$  radiation (wavelength 1.7902 Å). The X-ray diffraction patterns were analyzed with the Rietveld software MAUD [33].

Two samples were also investigated with synchrotron X-ray micro-diffraction at beamline 12.3.2 of the advanced light source, Lawrence Berkeley National Laboratory, to identify local phases by X-ray diffraction at the micron scale. The instrument used a  $5 \times 2 \mu\text{m}^2$  monochromatic beam of 1.23986 Å wavelength. X-ray diffraction images were collected in transmission geometry with a DECTRIS Pilatus 1M area detector (DECTRIS, Baden, Switzerland) positioned at a  $\sim 40^\circ$  angle with respect to the incident X-ray beam and at a distance of approximately 185 mm from the sample. For these experiments thin sections of the samples were removed from glass slides and mounted on an aluminum frame. The 2D diffraction images were then analyzed using the XMAS software [34] to identify phases present in local regions.

### 3. Results

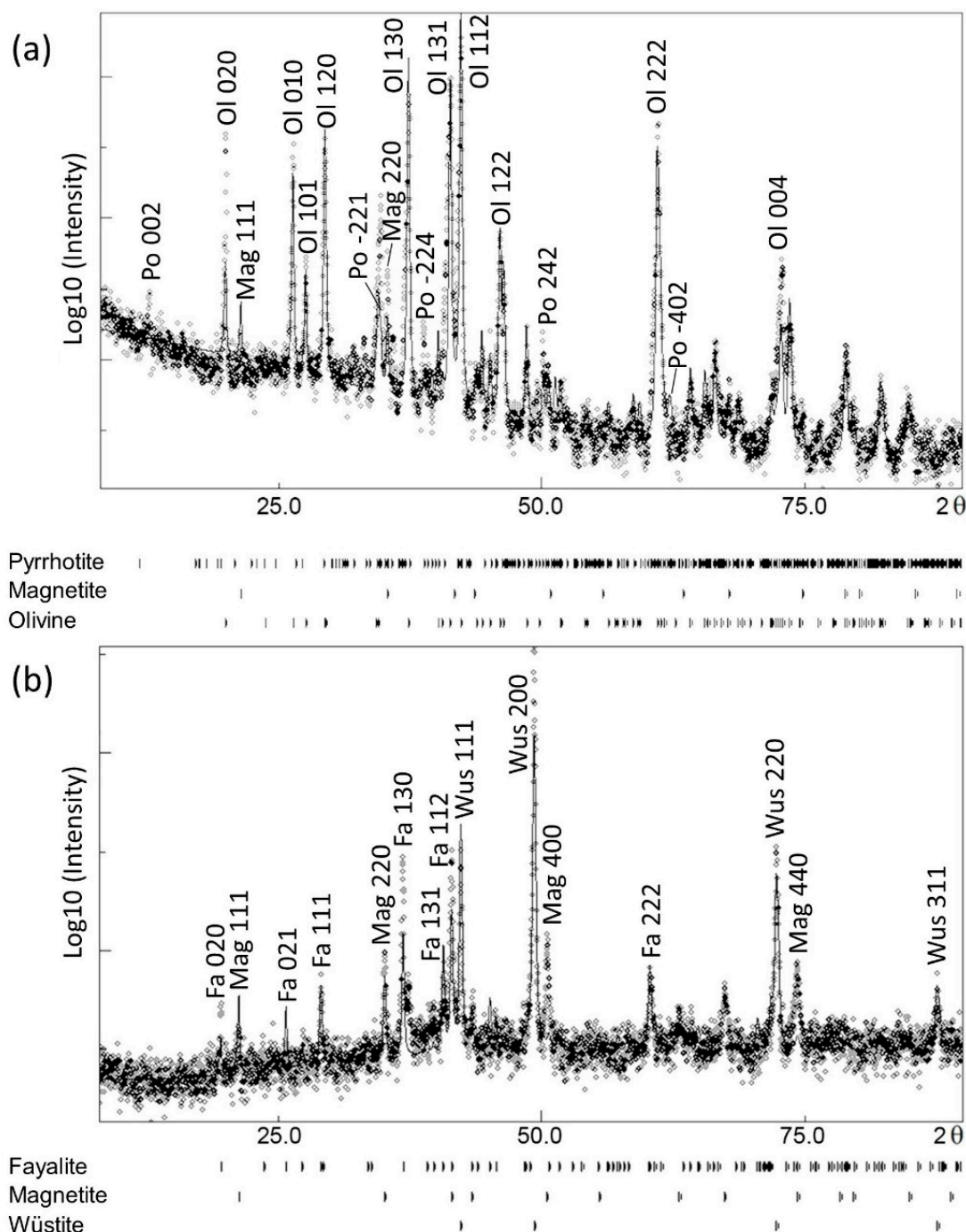
XRD on powders provided some information about the bulk mineralogical composition with olivine (volume fraction  $\sim 95\%$ , Ol), pyrrhotite ( $\sim 4\%$ , Po) and some magnetite ( $<1\%$ , Mag) for non-magnetic slags (Figure 3a), and fayalite ( $\sim 55\%$ , Fa), wüstite ( $\sim 42\%$ , Wus) and magnetite ( $\sim 3\%$ , Mag) for magnetic slags (Figure 3b). Volume fractions of phases were obtained from the MAUD Rietveld refinement [34]. Dots in the spectra represent measured intensities and the line is the corresponding Rietveld fit. For some peaks diffraction indices are shown. The relatively high background between  $25^\circ$  and  $50^\circ$   $2\theta$  in Figure 3a was probably due to an amorphous phase.

SEM-BSE images display complex microstructures. In one sample (Figure 2d) olivine crystals of various morphologies in an amorphous matrix dominate (Figure 4a). Some regions were enriched in metallic globules (bright areas in Figure 4b). Figure 4c–f display a region with a metallic nodule at higher magnification. Figure 4c,e, at higher brightness, emphasized olivine microstructures ranging from euhedral to acicular and dendritic. Particularly Figure 4e illustrates large olivine crystals with zoning, expressed by changes in brightness. The outermost zone was brightest, indicative of high iron content. Figure 4d,f is at low brightness to illustrate microstructures in metallic nodules, divided into regions with brighter and darker grey shades.

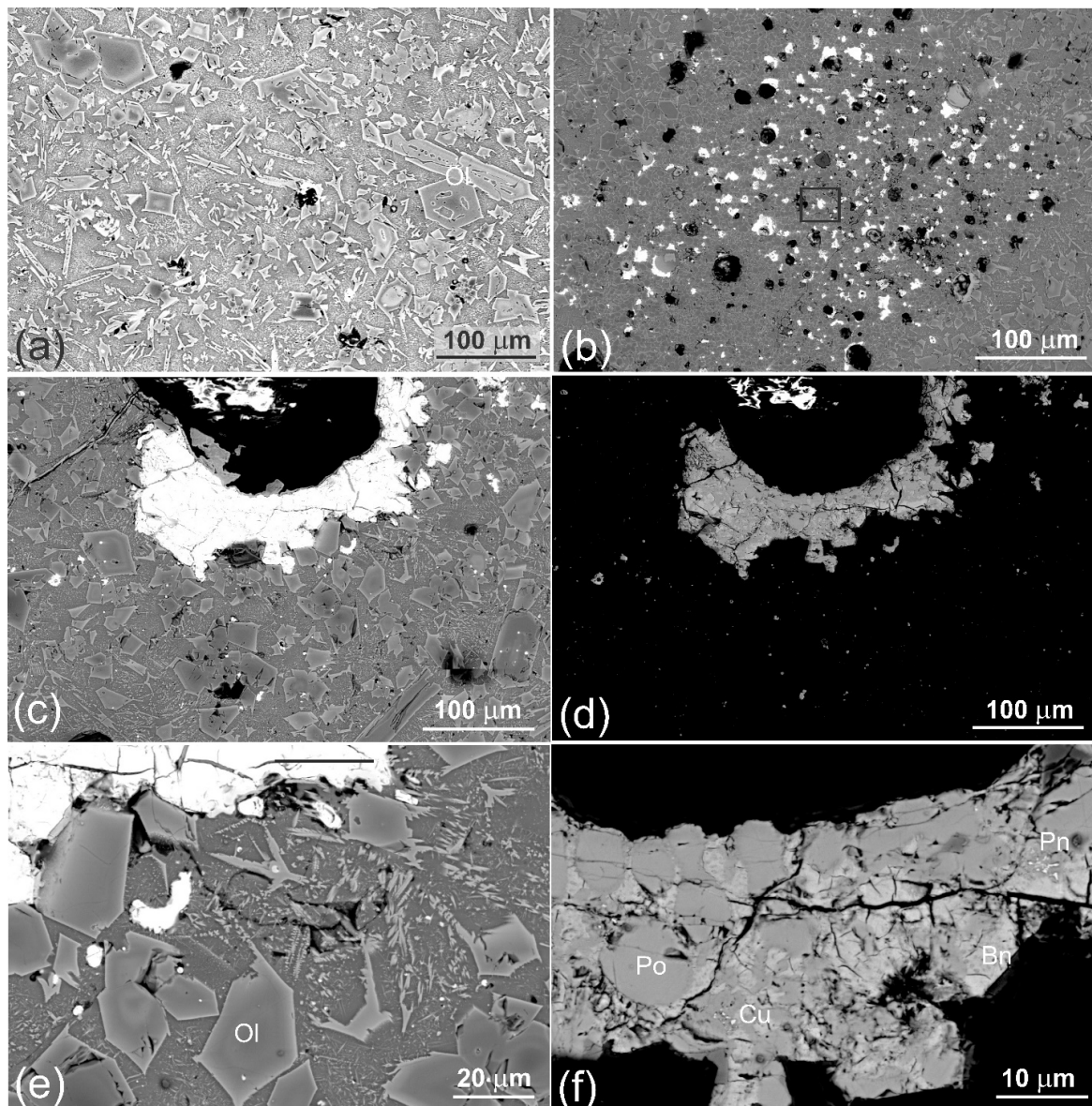
To get more information about mineral compositions elemental maps were recorded with energy dispersive spectroscopy (EDS, Figure 5). Results for a region indicated by a square in Figure 4b display olivine with variable Fe and Mg content (Mg, Si, Fe) in an amorphous matrix composed of Al, Mg, Si and Ca. The metal-rich area was composed of Fe-sulfide (darker in Figure 4f and identified as pyrrhotite Po) and Cu-Fe-sulfide (brighter in Figure 4f, identified as bornite Bn). There were some bright spots in Figure 4f attributed to native copper (Cu), as well as in EDS scans (Figure 5), and also of Fe-Ni-sulfide (pentlandite, Pn).

Figure 6 highlights another complex region of a non-magnetic slag (sample in Figure 2e). To display the microstructure with zoned prismatic olivines and olivine dendrites in a darker matrix, relatively high brightness has to be used which makes it difficult to display complexities of sulfide and metallic

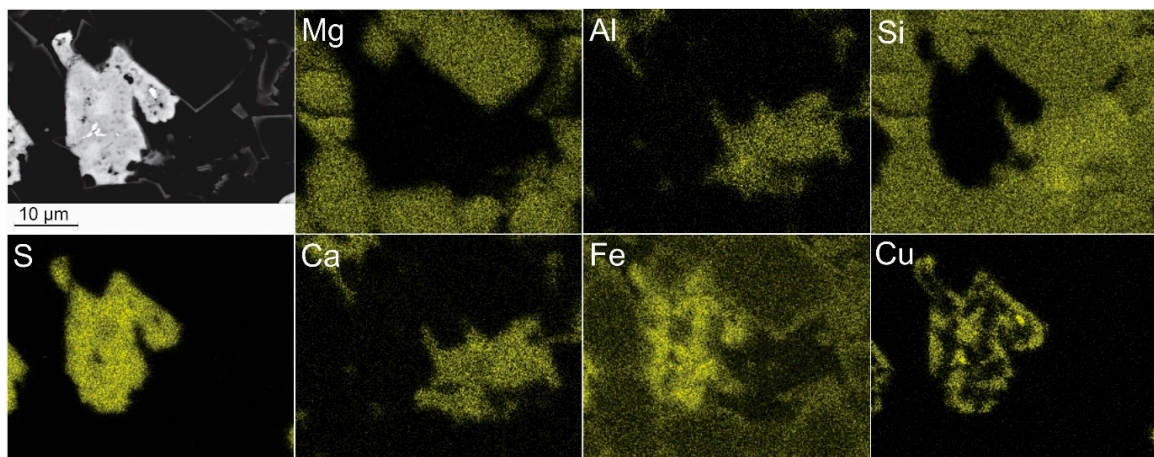
phases (Figure 6a). This sample has a higher proportion of metal sulfides in nodules (bornite, Bn and pyrrhotite Po) and metallic copper, which are best visible at lower brightness (Figure 6b). Compositional variations are again displayed in EDS maps (Figure 7) which highlight a matrix high in Al and Ca, as well as a higher concentration of Si than olivine. It also shows a zone of elemental copper (Cu in Figure 6b).



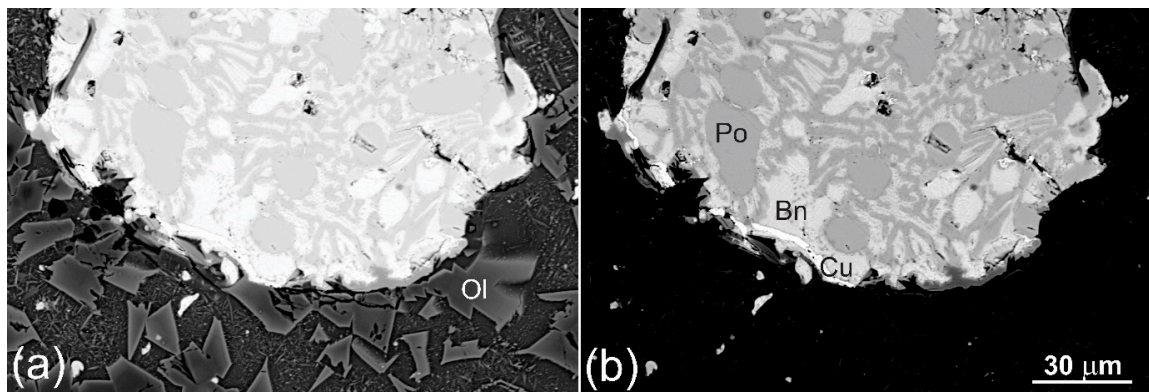
**Figure 3.** XRD patterns of Casaccia slags plotting intensity (logarithmic scale) as function of 2θ; Co-Kα-radiation. (a) Non-magnetic; (b) magnetic. Dots are measured data and line is Rietveld fit. Some peaks are identified. Phase abbreviations refer to the IUGS convention [35].



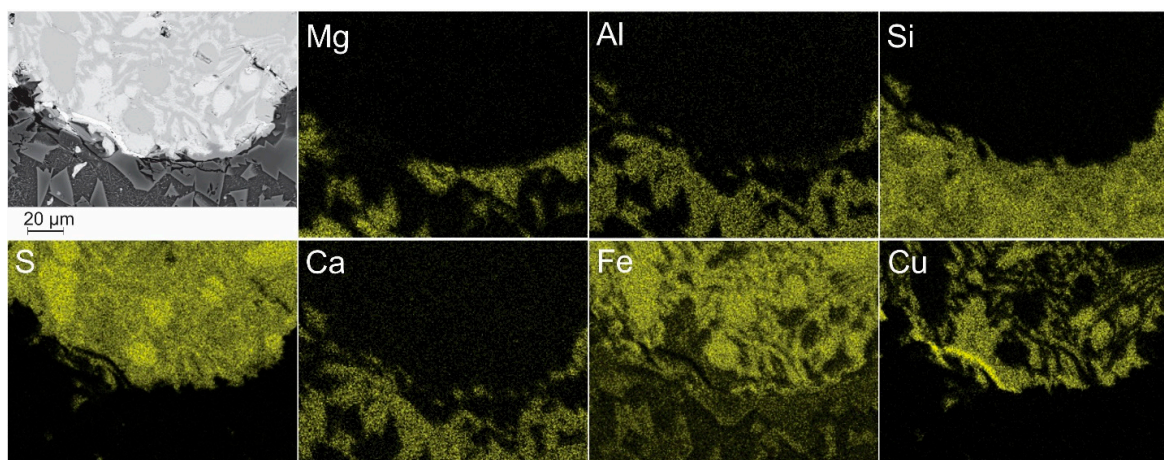
**Figure 4.** SEM-backscatter electron (SEM-BSE) images of a sample of non-magnetic slag (Figure 2d). (a) Zoned prismatic olivine (Ol) crystals, Fe-rich at the rim, in a matrix with skeletal olivine and olivine dendrites. (b) Region with a concentration of Cu-Fe rich sulfide nodules. The rectangle in the center is the area on which a SEM-energy dispersive spectroscopy (SEM-EDS) scan was performed (Figure 5). (c,d) Region rich in Cu-Fe sulfides (top) in a matrix of olivine (bottom). (c) High brightness to emphasize the olivine matrix, (d) Low brightness to emphasize sulfides. (e) Enlarged area of (c) illustrating euhedral zoned olivine and skeletal olivine in the matrix. (f) Enlarged area of (d) with pyrrhotite (Po), bornite (Bn), copper (Cu, white dots) and pentlandite (Pn, white dots). Abbreviations for minerals here and in other figures refer to IUGS convention [35].



**Figure 5.** SEM-EDS maps displaying the elemental abundance in a small area highlighted in Figure 4b. First image is SEM-BSE. Areas rich in Al, Ca and Si correspond to the amorphous matrix. High brightness in Cu is elemental copper.



**Figure 6.** SEM-BSE images of a sample of non-magnetic slag (Figure 2e). Cu-Fe sulfide nodule (bright) composed of pyrrhotite (Po), bornite (Bn) and elemental copper (Cu, white line) in a matrix of zoned prismatic olivine (Ol) crystals. Both images are of the same area and the same magnification (scale in (b) applies to both figures) but (a) is at high brightness to emphasize olivine microstructure and (b) at lower brightness to display complex intergrowth structures of sulfides.

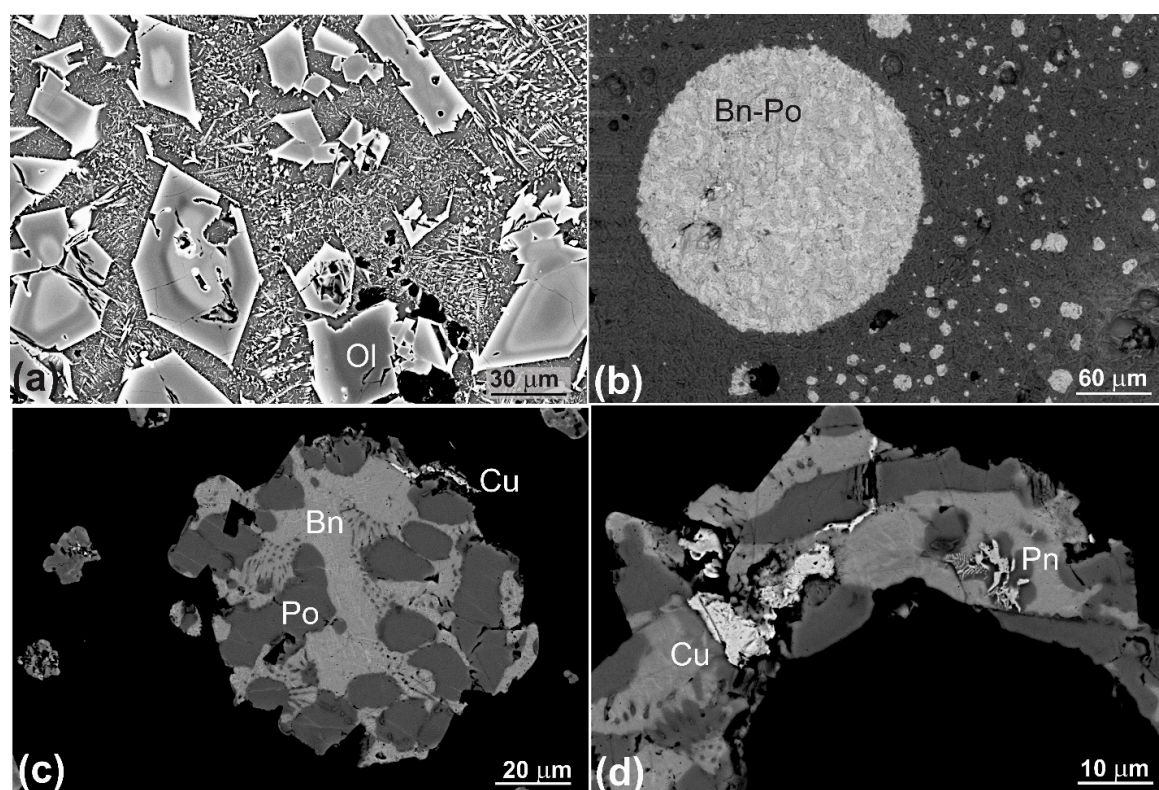


**Figure 7.** SEM-EDS maps displaying the elemental abundance in the area displayed in Figure 6. First image is SEM-BSE. Areas rich in Al, Ca and Si correspond to the amorphous matrix. High brightness in Cu map is elemental copper and medium brightness is bornite.

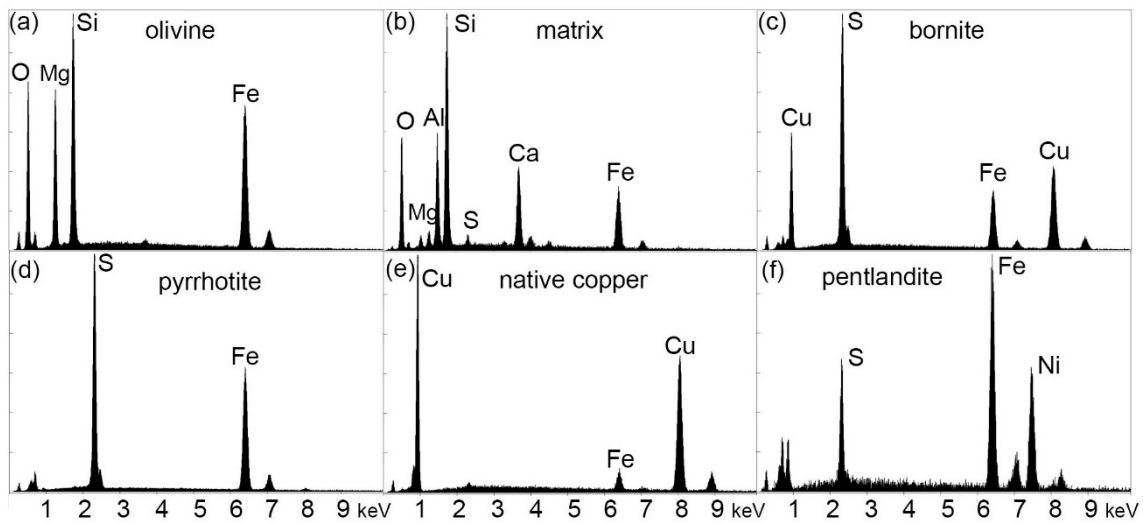
A third sample (Figure 2f) was analyzed in some detail (Figure 8). Again SEM-BSE images illustrated a microstructure with euhedral prismatic crystals of olivine with zoning expressed by changes in brightness (Figure 8a). The iron content was highest at the surface and intermediate at the core. An EDS spectrum for the core is shown in Figure 9a. The olivine composition of the core was about  $(Mg_{0.75}Fe_{0.25})SiO_4$ , at the surface it was  $(Mg_{0.5}Fe_{0.5})SiO_4$ . The dark glassy matrix, which accounted for about 20% of the volume, was composed of Fe-Al-Mg-Ca-Si-O (Figure 9b), with dendrites of olivine rich in Fe (Figure 8a). Regions of metal-rich nodules occurred in clusters (Figure 8b,c). The bulk is of bornite composition  $(Cu_{3.5}Fe_{1.5})S_4$  (Figure 9c) with regions of Fe-S corresponding to pyrrhotite FeS (Figure 9d). Locally there was elemental copper (Figure 8c,d and Figure 9e). Also, again in some areas FeNiS were documented (Figure 9f) with dendritic morphology (Figure 8d). The composition suggests pentlandite  $(Fe,Ni)_9S_8$ .

While the three non-magnetic slags, which were analyzed (Figure 2d–f), had similar microstructures (Figures 4, 6 and 8), the platy magnetic slags (Figure 2a,b) were entirely different. Figure 10 (corresponding to Figure 2a) displays grey skeletal crystals in a matrix of dark prismatic crystals and occasional bright globules. At higher magnification (Figure 10b) it becomes obvious that the grey crystals were composed of two different phases (brighter and darker grey shades) and also the bright globules were not homogeneous.

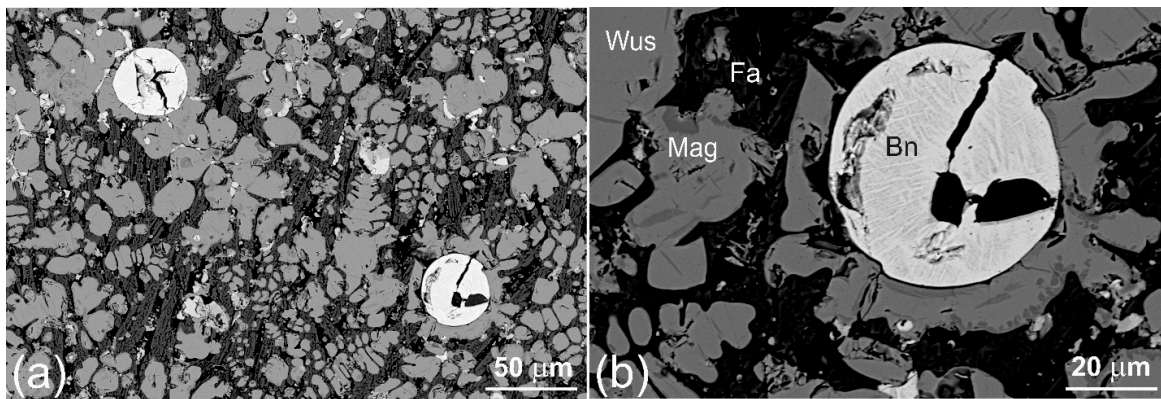
With EDS maps (Figure 11) the dark prismatic crystals could be identified as fayalite  $(Fe_2SiO_4)$ , grey skeletal crystals as iron oxides wüstite  $(FeO)$  and magnetite  $(Fe_3O_4)$  and the bright globules as copper-iron-sulfide (bornite). The very dark matrix (Figure 10a) was dominantly composed of Al, Si and Ca (Figure 11).



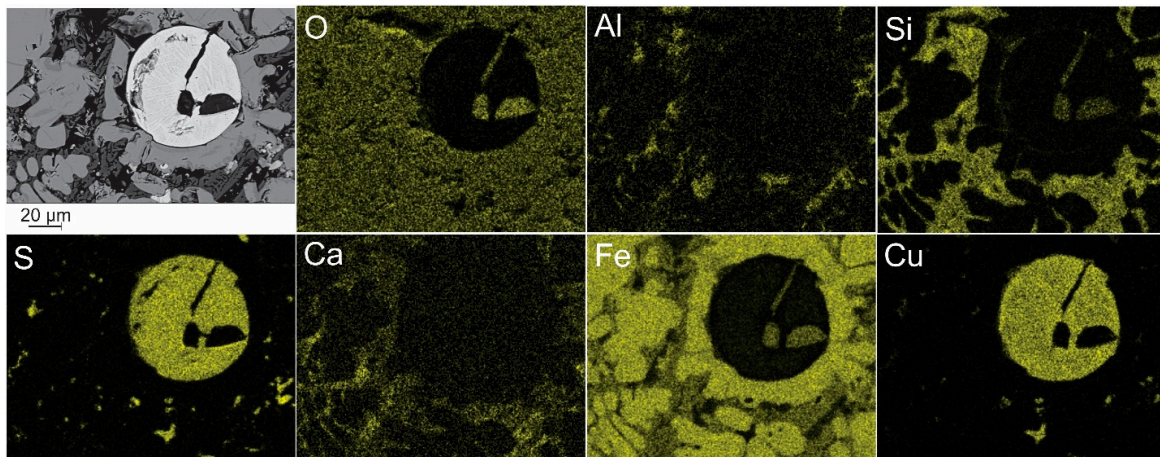
**Figure 8.** SEM-BSE images of a non-magnetic slag (Figure 2f). (a) Zoned prismatic olivine (Ol) crystals, Fe-rich at the rim, in a matrix with olivine dendrites. (b) Spherical nodule with bornite (Bn, bright) and pyrrhotite (Po, grey). (c) Metallic nodules with pyrrhotite (dark), bornite (grey) and metallic copper (Cu, white). (d) Bornite-pyrrhotite nodule with metallic copper (white on left side) and dendritic pentlandite (Pn, FeNiS) on right side.



**Figure 9.** Selected SEM-EDS spectra illustrating composition of non-magnetic Casaccia slag; (a) olivine core (from Figure 8a); (b) amorphous matrix (from Figure 8a); (c) bornite (from Figure 8c); (d) pyrrhotite (from Figure 8c); (e) native copper (from Figure 8d); (f) pentlandite (from Figure 8d). Only K $\alpha$  and L $\alpha$  peaks are labeled; vertical axis is count intensity.

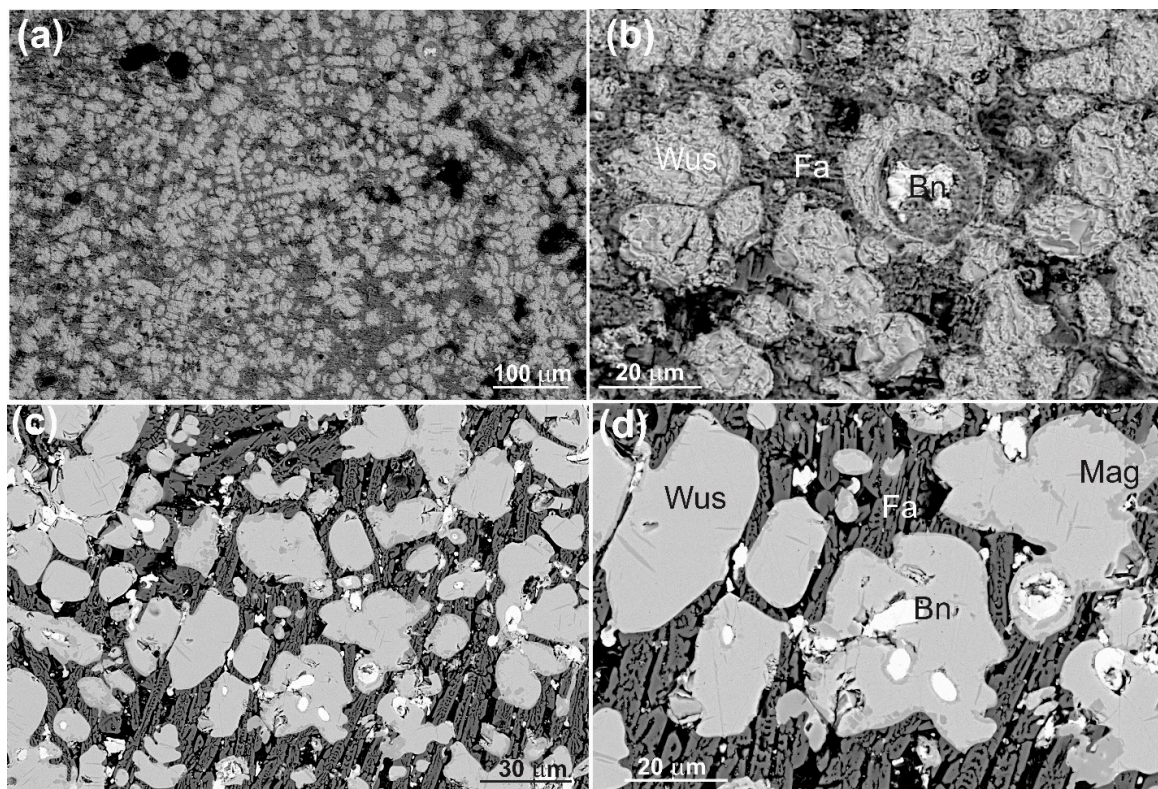


**Figure 10.** SEM-BSE images of a sample of magnetic slag (Figure 2a). (a) Overview and (b) enlarged area. Cu-Fe sulfide nodule (bright) composed largely of bornite (Bn). Skeletal crystals are Fe-oxides, mainly wüstite (Wus, brighter grey) and some magnetite (darker grey). Matrix is prismatic fayalite (Fe-olivine, Fa).

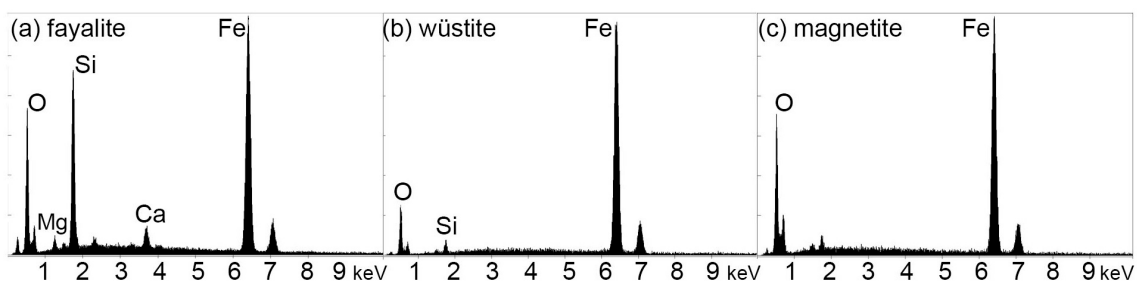


**Figure 11.** SEM-EDS maps of magnetic slag, of the area displayed in Figure 10b. First image is SEM-BSE.

A second magnetic sample (Figure 2b) was also dominantly composed of skeletal iron-oxides (bright phases in Figure 12a,b), in a matrix of prismatic fayalite (darker in Figure 12a,b). The SEM identification of phases was based on EDS spectra (Figure 13). The dark matrix, composed of Fe, Si and O is fayalite (Figure 13a). The bright nodules (Figure 12c,d, corresponding to the skeletal crystals in Figures 10a and 12a) have been identified as brighter wüstite with a high Fe-O ratio (Figure 13b) and darker magnetite with a lower Fe-O ratio (Figure 13c). Magnetite is concentrated on the periphery and along fractures of wüstite (Figure 12d). These minerals confirm the XRD analyses on bulk samples (Figure 3b). Occasionally, also in this sample, there were inclusions of bornite (very bright regions in Figure 12b,d).

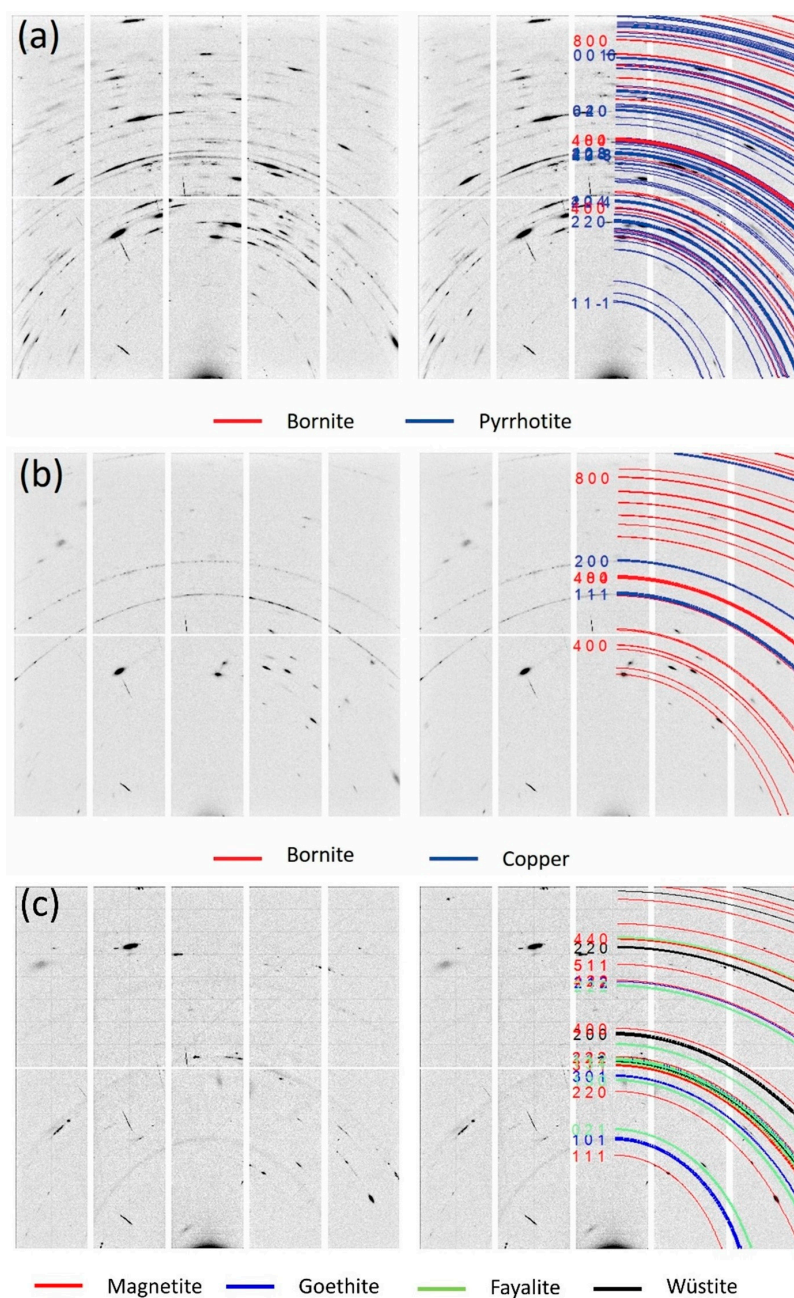


**Figure 12.** SEM-BSE images of magnetic slag. (a) Aggregations of wüstite (bright) in a fayalite matrix (dark). (b) Enlarged view of a region with wüstite (Wus) and fayalite (Fa) and some bornite (Bn) surrounded by fayalite. (c) Region with rounded wüstite/magnetite crystals (grey) and a skeletal fayalite matrix (dark). (d) Enlarged area of (c) with wüstite (Wus, brighter), magnetite (Mag, darker), some crystals with local bornite (Bn, white). Black is porosity. Images (a,b) were taken at variable vacuum, no carbon coat; (c,d) at high vacuum with carbon coat.



**Figure 13.** Selected SEM-EDS spectra from Figure 12d illustrating composition of magnetic Casaccia slag. (a) fayalite, (b) wüstite (high Fe/O ratio); (c) magnetite (lower Fe/O ratio). Only K $\alpha$  and L $\alpha$  peaks are labeled; vertical axis is count intensity.

To ascertain the phase identification of crystals at the micrometer scale microbeam synchrotron X-ray diffraction was used on two samples (Figure 2b,e). The beamsize was comparable to the particle sizes and diffractions occurred as fairly sharp spots on Debye rings, rather than continuous rings (left side of Figure 14), except for fine-grained copper (Figure 14b) and goethite (Figure 14c). On the right side of Figure 14 identified phases are highlighted with color circles. Bornite and pyrrhotite were confirmed in regions with metal-rich clusters of the non-magnetic sample (Figure 14a). Bornite and fine-grained elemental copper (fcc) occurred locally (Figure 14b). In the magnetic sample wüstite, magnetite and fayalite could be documented (Figure 14c). In addition there is a minor fraction of fine-grained goethite, probably formed as alteration of iron oxides.



**Figure 14.** Microfocus synchrotron X-ray diffraction images of (a,b) non-magnetic and (c) magnetic slag. On the left side is the diffraction image, on the right side mineral phases are superposed and identified with colors; (a) corresponds to the circular region in Figure 8b, (b) to left side of Figure 8d and (c) to Figure 12d.

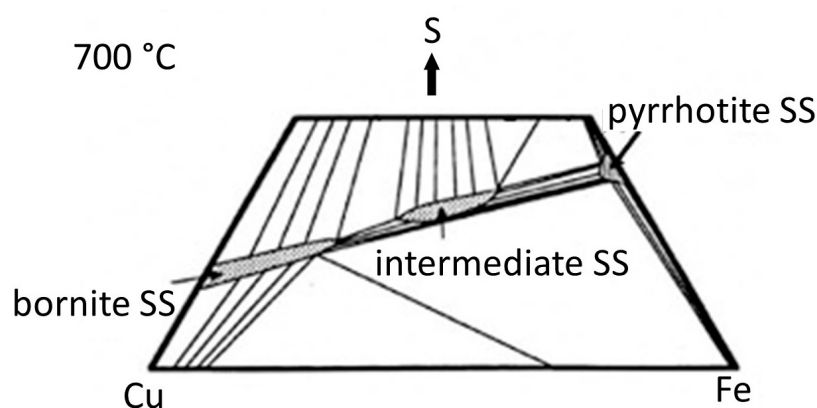
## 4. Discussion

### 4.1. Geochemistry of Copper Slags

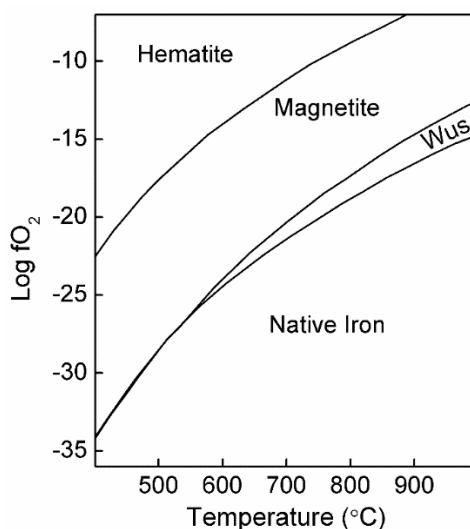
Copper ores were processed most likely in small bloomery furnaces [36–40] at temperatures 1200–1400 °C [41]. Charcoal used in the furnaces was produced locally in heaps by pyrolysis of fir wood.

The geochemistry of copper slags has been explored in detail, both experimentally and based on thermodynamics [42,43]. Figure 15 displays a Fe-Cu-S phase diagram [43–45] with pyrrhotite and bornite coexisting at 700 °C. At higher temperature melting occurs [45]. The temperature of the Mg-rich core of olivine crystallizing from a melt is about 1200 °C [46]. The prismatic euhedral morphologies of olivine transforming to an acicular/dendritic pattern (Figures 4a and 8a) suggest initially relatively slow cooling rates at equilibrium conditions changing to a higher degree of undercooling as documented experimentally and with models for olivine crystallizing from melt [47–50]. Such microstructures were also described in modern copper slags [51].

The log  $f_{O_2}$ -temperature phase diagram (Figure 16) illustrates a likely fugacity of  $-15$  at temperatures of  $\sim 1000$  °C for the magnetic slag [52,53] to account for the prevalence of wüstite relative to magnetite. Some goethite documented with X-ray microdiffraction (Figure 14c) may be due to secondary oxidation.



**Figure 15.** 700 °C isothermal section of Fe-Cu-S phase diagram. SS solid solution, based on Yund and Kullerud [44].



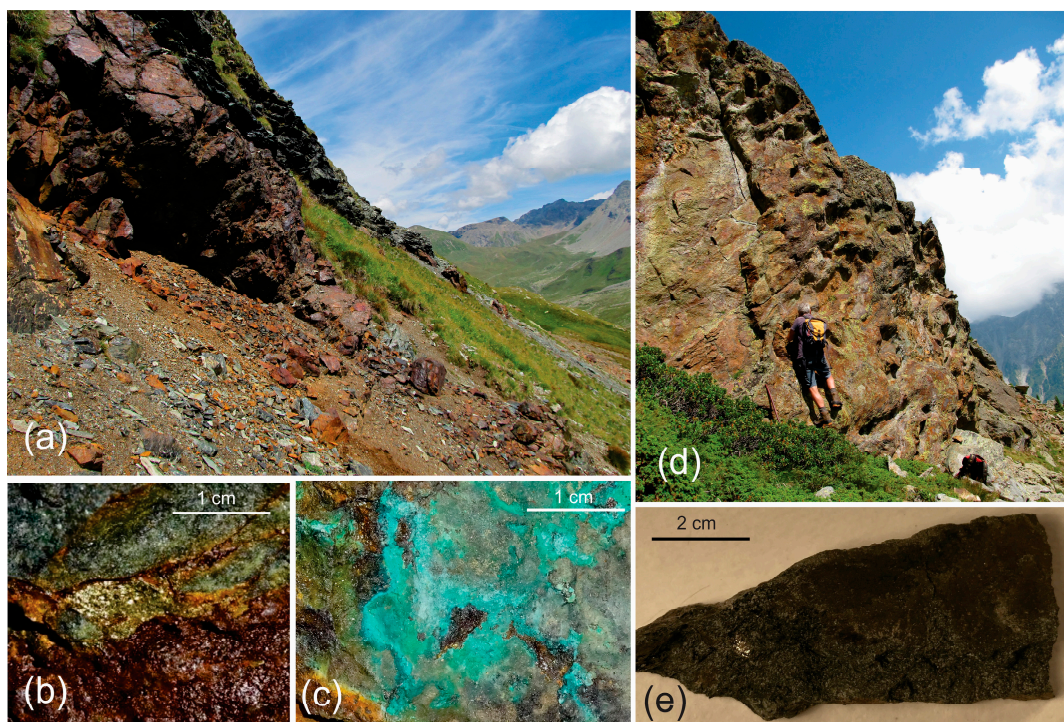
**Figure 16.** Log  $f_{O_2}$ -temperature phase diagram for Fe-O; Wus is wüstite. Modified from Miyashiro [52].

#### 4.2. Ore Deposits

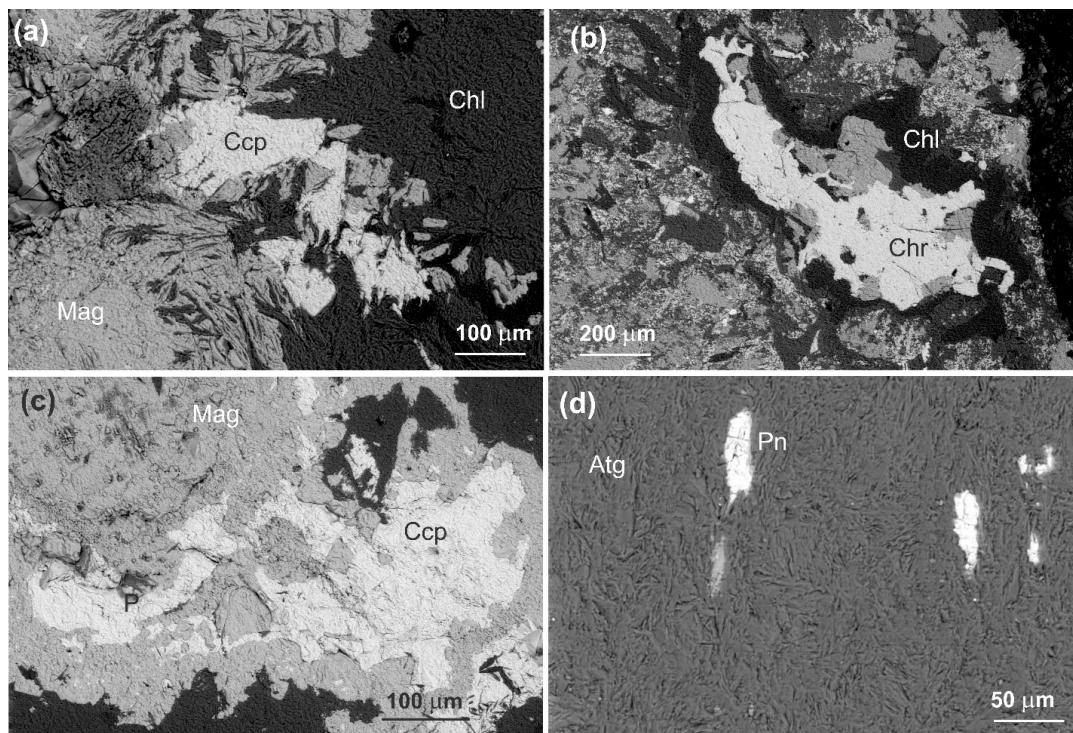
Metal ore deposits in Graubünden (E-Switzerland) have been explored by Schmidt [54] and then in more detail by Escher [28], Grünenfelder [29] and Dietrich [30]. These studies focus on mining activities in the 19th century, most of which were soon abandoned because they were not profitable. The main copper ore is chalcopyrite. Minor bornite has been described in the Suretta nappe at Alp Ursera near Andeer [28], at Piz Grisch [29] and the East-Alpine Silvretta nappe at Sertig and Lavin [28].

More closely related to Casaccia are historic and prehistoric Cu-Fe mines in the Oberhalbstein, associated with ophiolites and serpentinites of the Pennine Platta nappe such as Colm da Bovs (Tinzen), Marmorera, Crap Fess and Alp Tgavretga S of Bivio [30]. Close to the Mota Farun locality in Val Bregaglia, chalcopyrite has been described in prasinites near Piz Lizun [55] and Val Perossa [56]. The most likely source of the copper ore is chalcopyrite in metasedimentary layers of the Lizun nappe, the southern Platta nappe, probably associated with serpentinites, where pentlandite (Ni-S) has been identified [30].

We have a closer look at two localities. First an ore deposit in the vicinity of Alp Tgavretga near Septimer Pass (Swiss coordinates 768.96/144.27) at the contact of greenschists with serpentinites in the Platta nappe (samples Brg1828, 1829). This ore was exploited more recently, in the 19th century, but without much success [27]. Figure 17a shows a red layer very rich in sulfides and with a very high density. In hand specimens chalcopyrite (Figure 17b) and a malachite/azurite alteration (Figure 17c) can be observed. SEM-BSE images document abundant chalcopyrite (Figure 18a,c) with transformation to magnetite, and in a matrix of chlorite. Locally chromium spinel has been identified (Figure 18b). Other ore minerals are pyrite, pyrrhotite and ilvaite [30]. It is conceivable that material from Alp Tgavretga was transported across the Septimer Pass, southwards, because the forests above Casaccia are the closest providers of fuel for processing.



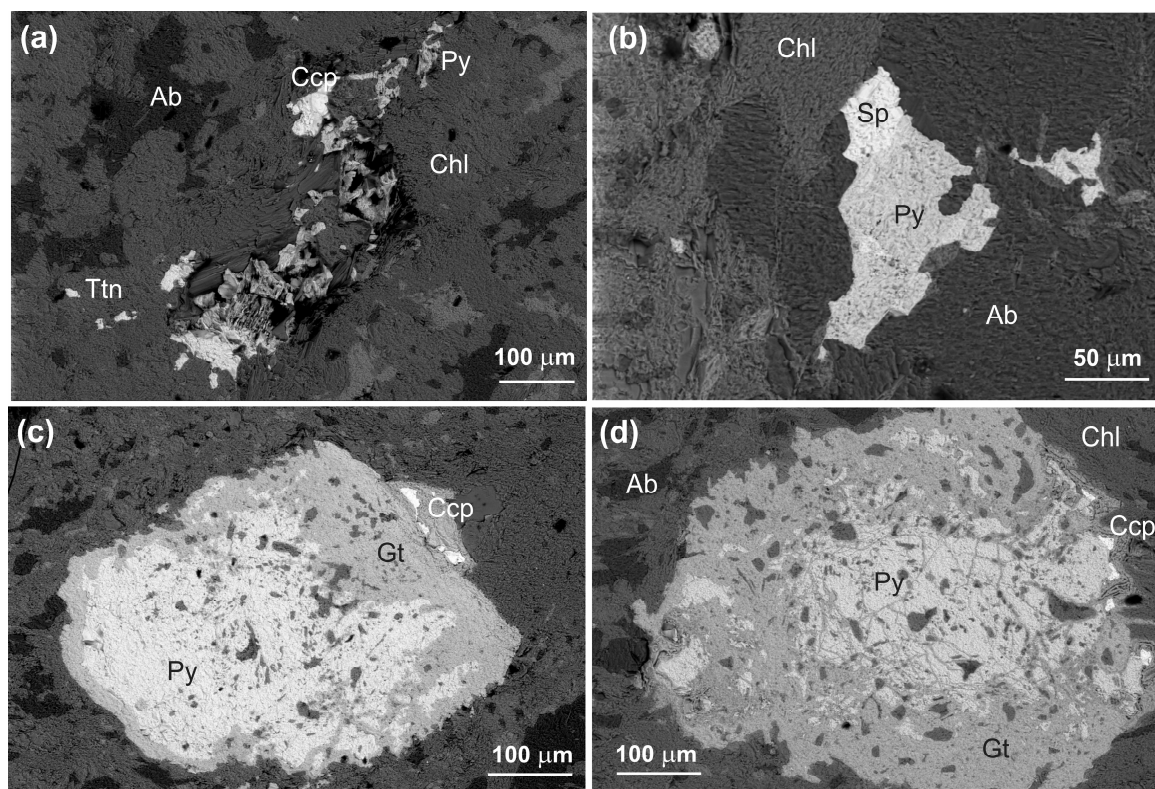
**Figure 17.** Images of ore deposits. (a–c) Alp Tavretga; (a) outcrop with red ore concentration; (b) hand specimen with chalcopyrite and magnetite; (c) copper ore altered to malachite. (d,e) Val Perossa; (d) outcrop with ore-rich layers; (e) hand specimen with pyrite in schist.



**Figure 18.** Microstructures in ore sample Brg1828 from Alp Tgavretga (a–c). SEM-BSE images. (a) chalcopyrite (Ccp, bright), magnetite (Mag, grey) and chlorite (Chl, dark). (b) Chromite (Chr) surrounded by chlorite (Chl). (c) chalcopyrite (Ccp, bright) and pyrite (P) transforming to magnetite (Mag, grey). (d) Serpentinite Brg1800 from Blaunca/Plaun dal Sel with pentlandite (Pn) in a matrix of antigorite (Atg).

Another locality is Val Perossa (formerly Val Parossa, Swiss coordinates 769.5/138.5, samples Brg1821, 1822), which contains a red zone of ore-rich greenschists (hence the name “rossa”) that was explored for ore around 1600 under the direction of the Vertemate family in Piuro [24,56] (Figure 17d). Most of the ore is pyrite (Figure 17e) but SEM observations document local concentrations of chalcopyrite associated with pyrite (Figure 19). Here the sulfides also oxidized, producing red iron hydroxides (goethite-lepidocrosite) responsible for the red color. Locally sphalerite (ZnS) was observed (Figure 19b). The matrix is composed of chlorite, muscovite, clinozoisite, albite, with inclusions of apatite and titanite. The same zone could continue towards Casaccia but may be covered by moraines, Quaternary debris, soils and forests.

Small amounts of pentlandite were observed in the Mota Farun slags (e.g., Figures 4f and 8d). Nickel is mainly observed in ultramafic rocks such as serpentinites in the western Alps [57] and serpentinitized ultramafics in Western Australia [58]. In a serpentinite from the Platta nappe at Blaunca near Grevasalvas, pentlandite has been documented (Figure 18d) and it is likely that minerals from serpentinites were added to ore processing, with slag compositions rich in magnesium and iron. This does not imply that pentlandite was significant for the ore production.



**Figure 19.** Microstructures in ore samples from Val Perossa (Brg1822). SEM-BSE images. (a) Pyrite (Py, grey), chalcopyrite (Ccp), titanite (bright spots on lower left, Ttn) and albite (Ab, black) in a matrix of chlorite (Chl); (b) Pyrite (Py) with sphalerite (Sp). (c,d) Pyrite (Py) altered to goethite (Gt) with regions of chalcopyrite (Ccp, bright spots on right side).

#### 4.3. Prehistoric Copper Mining in the Eastern Alps

Significant prehistoric copper mining occurred in the Oberhalbstein, north of the Casaccia locality [12,26,59–61], in the Inn valley and Silvretta region [14–16,18,62], and around Luserna in Trentino-Italy [19–21]. The Bronze Ages are based on radiocarbon dating of wood inclusions in slags and go back to ~3000–2000 BC [22]. The microstructures and composition of slags from Luserna [20] show many similarities with the two Casaccia copper slags described here. It is likely that they are also Prehistoric, though no age determinations have been performed and there is no proof of that assumption. Contrary to the Oberhalbstein or Luserna the copper production at Casaccia was also on a much smaller scale. The bulk chemical composition of the Casaccia slags, rich in Fe, Si, with significant Mg, but poor in Ca and alkalis corresponds to other Alpine slags resulting from copper production [22]. The main phases in the two Casaccia slags are olivine-fayalite, wüstite, pyrrhotite, bornite, magnetite and copper. No quartz or feldspars were identified, which are major phases in the surrounding rocks of the Lizun nappe.

#### 4.4. A Discussion of Analytical Methods

Scanning electron microscopy, particularly with backscatter imaging revealed complex microstructures in these Alpine slags. With EDS spectra it was possible to identify crystallites which are often at the submicron scale. Particularly important has been synchrotron microfocus synchrotron X-ray diffraction for unambiguous identifications of crystallites in extremely fine-grained materials. Similar methods have been applied to characterize other archeological materials such as Roman concrete [63] and Anthropocene products such as debris from nuclear explosions [64].

## 5. Conclusions

The Mota Farun slags are the first evidence for copper production in the Bergell Alps. In this study we explore compositions and microstructures of phases with modern methods used in materials science and mineralogy. Microstructures observed with scanning electron microscopy reveal complex conditions of formation such as olivine transforming from a euhedral to a dendritic morphology and intergrowth of pyrrhotite and bornite in globules. Magnetic slags display intricate intergrowths of wüstite and magnetite in a matrix largely composed of fayalite. Interestingly several slag samples from the same locality display very similar microstructures. The investigation may inspire others to apply similar methods to characterize different types of ancient slags to establish a data base to explore variations due to different ore compositions and production details.

**Author Contributions:** H.-R.W. initiated this study and prepared a draft of the manuscript. R.Y. was involved in all experiments and data analysis. N.T. conducted synchrotron experiments at the Advanced Light Source. D.B. and W.H. made critical contributions to sample collection.

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