Compositional zoning in pyrite as a tool for reconstructing the ore ore-forming processes: an example from the abandoned Fe-Cu sulfide mine of Herin (Aosta Valley, Italy)

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The Herin abandoned mine (Champdepraz, Aosta, Italy) was exploited for at least 250 years for its Cu-Fe sulphide ore. It is located at the orographic right of the Aosta Valley, approximately between 1600 and 1800 m a.s.l.. Host rocks belong to a metaophiolitic domain of the Western Alps that underwent high pressure metamorphism, and re-equilibrated under blueschist to greenschist facies conditions (Martin *et al*., 2004; Dal Piaz *et al*., 2010). Ore association is mostly composed of pyrite and chalcopyrite, with minor other sulfides (pyrrhotite, sphalerite, cubanite, digenite) and oxides (magnetite, rutile, ilmenite). The sulfide ore occurs with zoned textural patterns, from massive to disseminated. The deposit consists of lenticular massive bodies and thin layers hosted in various greenschist facies metamorphosed lithotypes. Some preserved slug dumps and mining structures document an intense exploitation. Thus, the interest for this site is aroused mainly by the lack of modern studies on the mineralisation, but also by the potential of an environmental recovery and cultural evaluation of the site.

The aim of our work is to document the overall state of the mine and to give interpretation of the ore genetic processes. We gathered historical information about the exploitation and mapped the underground works with speleological tools. Moreover, we collected data on mineralogy, mineral chemistry, petrography on mineralized samples. The mineralogical and textural study was conducted by optical transmitted and reflected light microscopy. We undertook electron microprobe spot analyses (EMPA) on single grains of the ore minerals, as well as of the gangue and the host rock minerals. Besides, we performed elemental mapping on single grains or pyrite, representative of its various textures. On the basis of previous works and our results, we identified two parameters as the driving criteria for a comprehension of the multistage process that led to the actual configuration of the ore: (a) the textural characters of pyrite and (b) the distribution of trace elements in sulfides, with specific focus on cobalt and nickel in pyrite.

Because of its refractory nature, pyrite is in fact known to preserve changes that occurred during its growth history, such as multiple episodes of metamorphic/hydrothermal activity, or the chemical evolution of the fluid during a single episode (Craig *et al.,* 1998). In particular, the concentration of cobalt and nickel and the Co/Ni ratio in pyrite have extensively been used as indicators of primary genesis and tools for reconstructing the ore forming systems (Bralia *et al., 1979*; Campbell & Ethier, 1984; Agangi *et al.,* 2013).

The coupled use of spot analysis and atomic maps (Fig. 1) provides an integration of the textural and geochemical sets of data. The concentration data show a zoned distribution of cobalt in pyrite that can be related to typical recrystallization textures. We determined a critical concentration value for cobalt of 3160 ppm, as a discrimination point between two generations of pyrite. This led to outline a series of dissolution and crystallization events that describes the metamorphic history of the sulfide ore at the sample-scale. Moreover, on the basis of the Co/Ni ratio we propose a volcanogenic-hydrothermal origin for the first generation of pyrite, thus for the primary deposition of the Herin ore deposit.

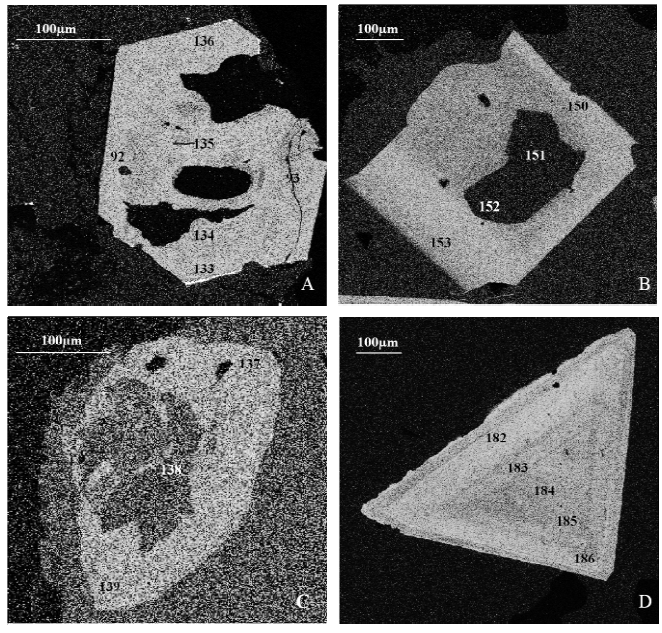

Figure 1.: Atomic EMP maps of Co. Some recrystallization textures of pyrite are represented. The numbers refer to the punctual analysis series.

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