Title: Crystal chemistry and origin of copper minerals of Somma-Vesuvio

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Research program

Copper is a base metal, pivotal for mankind nowadays as in the past, mainly concentrated in endogenous geological formations in the form of oxygen-free chalcogenide minerals, most typically in sulfides and sulfosalts. Despite this, the number of oxygen- and halogen-free minerals is lesser than the O-bearing copper mineral species, such as oxides, oxysalts, halides, sulfates, carbonates, silicates, etc. The bulk of oxygen- and halogen-bearing Cu minerals mainly occur in the oxidation

zones of chalcogenide ores and are formed under supergene conditions; they are also found in fumarolic environment of volcanic areas (Balic-Žunic et al., 2016; Pekov et al., 2018). A crystal-chemical review on copper minerals from volcanic exhalations was recently carried out by Pekov et al. (2018), and shows that Cu-bearing compounds have very specific crystal-chemical features, of interest both for the systematic mineralogy and the surveys and explorations on base metal ore deposits. The majority of these minerals were discovered between 1980 and today, and only a few of their synthetic analogues are known thus far. Somma-Vesuvius is worldwide one of the most important areas of various families of copper minerals, primarily associated with fumarolic products of historical eruptive activity. Only few species are detected in ejecta from plinian eruptions (i.e. Pompei, Avellino). A first, very recent, review study of Cu minerals from volcanic exhalations of Vesuvius (Balassone et al., 2019) was conducted on samples of the Mineralogical Museum of Naples University Federico II (MMN), where more than 1000 copper-bearing samples belonging to the prestigious "Vesuvian Collection" are preserved. This research showed a wide compositional range and structural diversity in oxides, halides, oxy-halides, carbonates, sulfates, vanadates, arseniates, molibdates and silicates; unusual and rare (Cu-bearing and - free) phases are also found, some of which representing first recorded occurrences at Somma-Vesuvius (Balassone et al., 2019). Ongoing researches on minerals from new sets of MMN Cu-bearing samples are revealing further interesting crystal-chemical features, confirming that their mineralogical characterization (and their minerogenesis) is far from the complete accomplishment. The requirement of studying samples from the museums is due to the unavailability of most of the outcrops at Vesuvius and to intensive sampling, also by mineral collectors, over centuries; hence, it is almost impossible to find these types of samples at the volcano today, and most of the samples of interest are currently housed in the mineralogical museums collections, also as concerns the Cu-bearing minerals. A granted project is in progress for the study of copper minerals from Vesuvius in samples preserved in the National History Museum (NHM) of London (UK), very similar to those of the MMN (project SYNTHESYS 2020, # GB-TAF-2394, leader N. Mondillo, participant G. Balassone). Indeed, in the NHM there is a significant set of Vesuvian samples, the Teodoro Monticelli collection, introduced in 1808, most of them never studied before. This study is aimed to shed light on copper enrichment/minerogenesis in hydrothermal systems of volcanic active areas (porphyry copper-like) and is carried out concomitantly with the investigations on MMN Cu-samples. On that basis, very detailed researches on historical Cu-bearing samples from MMN

are needed and focused on: (1) the crystal-chemical characterization of copper minerals and associated phase, also aimed at enhancing the mineralogical database of Vesuvius and not only; (2) a comparison between crystal chemistry of copper minerals from volcanic exhalations and supergene zones of sulfide ores; (3) giving a contribution in understanding the Cu concentration mechanisms in hydrothermal systems of volcanic areas.

Proposal for a PhD position

The PhD proposal plans to carry out a systematic mineralogical investigation of products of historical activity of Vesuvius (starting from 1631 lavas) collected in the MMN, according to the three points exposed above. volcanoes. In the first phase of the research the PhD student will carry out a detailed survey of all the Cu-bearing samples potentially interesting for the proposed topic, in collaboration with a Museum expert (Dr. Carmela Petti). The sample examination will be devoted at a careful selection of fumarolic products, as encrustations, cavity fillings and other mineralizations occurring in various lava rocks, which are most promising with regards to peculiar mineral associations. Xenoliths will be also investigated, if any. Then, after a sample/crystal selection work, combined analytical methodologies (optical microscopy, X-ray powder diffraction XRPD, single-crystal X-ray diffraction SC-XRD, EDS and WDS microanalysis, infrared spettroscopy FTIR, thermal analyses TGA-DTA-DSC) will be used to fully identify all the copper mineral components and the associated phases. For some specific minerals and/or paragenesis needed to be investigated down to the nanoscale (micro-to-nanosized minerals, particular sulfates, oxy-halides, etc.), high-resolution transmission electron microscopy (HRTEM) with microanalysis (AEM) and electron diffraction (SAED) will be performed by the PhD student. The results obtained will be integrated and interpreted to give a minerogenetic model related to the Cu enrichment processes in active volcanic areas, for which Somma-Vesuvius represents a remarkable case-study. The PhD candidate will follow a work schedule articulated as follows:

1st year - Bibliographic research. Sample selection and preparation. Basic mineralogical analyses. PhD courses.

2nd year - Detailed mineralogical analyses, with at least 3-month external stay in research laboratories. PhD courses. Crystal-chemical and structural data elaboration. Results presentation at international conferences. Papers preparation to be submitted to peer-reviewed journals.

3rd year - Minerogenetic modelling. Results presentation at international conferences. Papers preparation to be submitted to peer-reviewed journals. Thesis writing.

The PhD candidate should have a good knowledge of Mineralogy, as well as of the techniques of mineralogical analysis, and geochemical-petrographic ones. He/she must be fluent in both spoken and written English.