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Major and trace element geochemistry of a distal Fe skarn - Torre di Rio, Elba Island (Italy): Insights from hedenbergite, epidote and ilvaite LA-ICP-MS analyses.

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Distal skarns are calc-silicate rocks formed by the interaction between magmatic fluids and carbonate hosts without direct link with a causative intrusion. In the present study we use trace element patterns in main skarn silicates from a classical type locality in Tuscany to trace the genetic link with the Miocene magmas. The Torre di Rio distal Fe skarn is located south of the Rio Marina village, Elba Island (Italy). It is hosted by calc-schists belonging to the Acquadolce Unit (Bortolotti et al., 2001), with a strong foliation dipping to the NW that is preserved in most parts of the skarn. The skarn body presents a spectacular mineral zonation, with hedenbergite, ilvaite and epidote domains.While hedenbergite and ilvaite zones are developed in carbonate-dominated host (marbles ans calc-schists), the epidote zone is formed by selective replacement of silicate rocks (mica-schists).

Clinopyroxene forms up to 40 cm in diameter spherical agregates from fibrous crystals in the main pyroxene zone, mixed patchy texture with epidote at the transition to the epidote zone, and layered "zebra-like" texture together with ilvaite, towards the contact with the ilvaite zone. The clinopyroxene occuring in the skarn has an Fe-rich composition corresponding to the hedenbergite end-member. Slight compositional variation is recorded at the crystal tips, where Mg is fully replaced by Fe and, therefore, clinopyroxene becomes even more hedenbergitic in composition. Trace element composition of hedenbergite does not show important variations along single crystals. Copper, Cr and Rb are bellow their limit of detection by LA-ICP-MS, while Zn content is up to 60 ppm. Nickel (up to 40 ppm) and Co (up to 12 ppm) seem to be enriched in the crystal cores, while being below detection at the rim. Anomalous B and Sn contents (100s ppm) are also observed. REE_{total} content is as low as 2-4 ppm. REE pattern of hedenbergite is characterized by low LREEs and high HREEs, and important variations have been observed only for some heavy REEs.

Ilvaite is a hydrated sorosilicate $(CaFe^{+3}(Fe^{+2})_2O(Si_2O_7)(OH))$ mainly consituted by Fe (39%), Ca (10%) and Si (13%), with minor amounts of Mn, Al and Mg.
The first LA-ICP-MS analyses of ilvaite reveal anomalous conents on different trace elements. Boron content in ilvaite is up to 170 ppm, Zn up to 70 ppm, Ga up to 40 ppm, Ge up to 60 ppm, As up to 300 ppm, Sn up to 0.45% and REE_{total} up to 400 ppm. On the contrary, Ni and Cu are below detection limit, while Th and U present concentrations of <1 ppm. The REE pattern of ilvaite is similar to the one of hedenbergite.

Epidote has a complex patchy zoning revealed by BSE imaging, mainly produced by Fe-Al substitution. Trace element geochemistry of epidote is characterized by high Sn (up to 990 ppm) and Ga (up to 130 ppm) content and low Pb (up to 6 ppm). Cobalt, Ni, Cu and Zn are at or below their limit of detection by LA-ICP-MS, while Th and U contents are <1 ppm. Furthermore, REE contents are usually <100 ppm, but some analysis show REE_{total} contents up to 690 ppm. The REE pattern of epidote differs significantly from those of hedenbergite and ilvaite – with enrichment of LREEs and depletion of HREEs. In some cases negative Eu anomaly has been observed.

The significant B and Sn anomaly detected in the skarn minerals at Torre di Rio is a common characteristic of the magmatic rocks occuring on Elba Island (but also along the Tuscan Magmatic Province) and the Fe-ores of Rio Marina. The magmatic rocks (granites, rhyolites and pegmatites) have a B content ranging from 20 to 1500 ppm, with tourmaline occuring as a common mineral (Dini *et al.*, 2005). It is, therefore, believed that part of this magmatic boron was introduced into the hydrothermal system and incorporated into the skarn minerals. On the other hand, Fe-ores (hematite) from the Rio Marina deposit (1km north of the Torre di Rio skarn) are significantly enriched in Sn (190-8400 ppm), but also in W (87-4950 ppm) as reported by Benvenuti et al. (2013).
This characteristic geochemical signature of the rocks in Elba Island, and in the Tuscan Magmatic Province, is a direct evidence of the complex tectonic, magmatic and hydrothermal evolution of the region.

REFERENCES

Benvenuti, M., Dini, A., D'Orazio, M., Chiarantini, L., Corretti, A., & Costagliola, P. 2013: The tungsten and tin signature of
    iron ores from Elba Island (Italy): A tool for provenance studies of iron productionin the Mediterranean region,

Archaeometry, 55, 479-506.

Bortolotti, V., Fazzuoli, M., Pandeli, E., Principi, G., Babbini, A., & Corti, S. 2001: Geology of central and eastern Elba Island, Italy, Ofioliti, 26 (2a), 97-150.

Dini, A., Gianelli, G., Puxeddu, M., & Ruggieri, G. 2005: Origin and evolution of Pliocene-Pleistocene granites from Larderello geothermal field (Tuscan Magmatic Province, Italy), Lithos, 81, 1-31.

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Shallow porphyry stockwork veining at Cerro de Pasco: constrains from fluid inclusions, in-situ oxygen isotope and trace element analysis by SIMS and LA-ICP-MS

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The Miocene epithermal base metal deposit of Cerro de Pasco in central Peru located along the eastern margin of a large diatreme-dome complex (Baumgartner et al., 2008) is the second largest known epithermal base metal ("Cordilleran") deposit after Butte in Montana, USA. Recently, multiple porphyry events at Cerro de Pasco have been reported (Rottier et al., 2014). Two types of porphyry mineralization have been found: (i) magmatic and hornfels clasts with typical A- and B-type quartz-molybdenite veins incorporated in the diatreme-breccia and also in E-W trending quartz-monzonite porphyry dykes; and (ii) a porphyritic andesitic plug crosscut by a stockwork of quartz-magnetite-chalcopyrite-pyrite veins, cropping out in the central part of the diatreme. This contribution is focused on results obtained on the second type of porphyry mineralization.

The andesitic plug crops out at the same elevation as the epithermal mineralization in the district. No important erosion pre- or post-dating the epithermal stage of ore formation has been recognized at Cerro de Pasco. The plug is affected by pervasive chlorite-epidote-magnetite alteration spatially associated with a network of up to 2 cm-thick quartz-magnetite-chalcopyrite-pyrite porphyry style veinlets (Fig. 1A). Microscopic observations reveal high chalcopyrite/pyrite ratios in the veins, with up to 5% chalcopyrite in some samples, both sulfides being affected by supergene oxidation. Quartz veins are banded in places (Fig. 1B) and SEM-CL imaging reveals two different quartz generations: 1) high-luminescence euhedral and in places fine-grained sulfide-free quartz (Qz1); 2) late low-luminescence euhedral quartz (Qz2) crosscutting and overgrowing Qz1 and commonly intergrown with sulfides (Fig. 1C).

Qz1 presents assemblages of vapor inclusions and hydrous salt melt inclusions (HSMI). The HSMIs contain several transparent crystals (halite, sylvite, anhydrite, and an unknown phase), hematite flakes, unknown opaque phase, and vapor bubbles; no liquid is optically distinguishable (Fig. 1D). Final halite melting occurs between 580° and 600°C corresponding to a salinity of >70% NaCl eq. (Sterner et al., 1988). The total homogenization temperature (Th) is > 600°C. The association of vapor inclusions and HSMIs indicates pressure of entrapment of < 1kbar (Dreisner and Heinrich 2007). Qz1 has a high Ti content (100 to 356 ppm; based on 18 LA-ICP-MS analyses and 6 SIMS analyses) indicating a high formation temperature (>600°C based on Ti-in-quartz geothermometer; Huang and Audétat, 2012). Qz2 is spatially associated with sulfides and hosts only L-V inclusions with Th from 270° to 330°C and salinity from 0.2 to 25 wt% NaCl. This large range of salinity might result from a late stage mixing of a low-salinity fluid with some residual hydrous salt melt. The Ti content of Qz2 is low, from 2.4 to 7.6 ppm (SIMS analyses n=5). In-situ SIMS oxygen isotope analyses on the two quartz generations provide distinctly different results: $\delta^{18}O_{Qz1}$=10.2‰ (n=31, 2σ=0.5) and $\delta^{18}O_{Qz2}$=13.1‰ (n=9, 2σ=0.9). The calculated $\delta^{18}O$ of water in equilibrium with quartz yields for Qz1 $\delta^{18}O_{fluid}$=8.9‰ at 650°C and for Qz2 $\delta^{18}O_{fluid}$=7.2‰ at 330°C (Matsuhisa et al., 1979). These values indicate a strong magmatic signature of the fluid. The difference of 1.9 ‰ between the two quartz generations could be due to a minor meteoric water input (<10%) or to a change of $\delta^{18}O$ of the magmatic fluid with time.

Our results indicate a two step-formation of the banded porphyry quartz veins. Hot hydrous silica-rich andesitic magma is emplaced in a shallow subvolcanic environment leading to direct exsolution of vapor and a hydrous salt melt. Qz1 precipitated from such fluids at high temperature (>600°C).The formation Qz2 and the sulfides at lower temperature (270-330°C) could result from (i) input of a second predominantly magmatic lower-temperature fluid resulting in cooling of the system, or (ii) incursion of meteoric water (partly equilibrated) that mix with magmatic fluids