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The Quenamari prospect, San Rafael tin district, southern Peru: geology, mineral assemblages, fluid inclusion microthermometry, and stable isotope compositions.

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The San Rafael tin district, comprising the underground San Rafael deposit, the Quenamari, and other prospects, is located in southern Peru, and represents the northernmost expression of the Andean tin belt. The ore mostly occurs as between 45° and 75°E dipping and NW-SE trending veins, mainly hosted by Late Oligocene cordierite-bearing granite (24.6 ± 0.2 Ma at San Rafael; Kontak and Clark, 2002) and Late Ordovician shale and quartzite.

Three of the four mineralization stages defined previously (e.g. Mlynarczyk et al., 2003) at San Rafael have been recognized at surface in the Quenamari prospect (2 km NE of San Rafael, >4700 m a.s.l.) during the present work (Corthay, 2014). Stage I is observable as small veins (< 3 cm wide) of fine-grained quartz and tourmaline in the Ordovician host rock. The main cassiterite stage II, also containing abundant quartz, muscovite, and chlorite at San Rafael, does not crop out at Quenamari (at San Rafael, cassiterite is mainly present below 4500 m whereas polymetallic veins are mostly found higher than 4500 m). The mineral association of polymetallic stage III consists of chalcopyrite, sphalerite, needle-tin cassiterite, galena, pyrite, marcasite, pyrrhotite, rhodonite, rhodochrosite and sulfosalts (including kobellite $(Cu,Fe)_2Pb_{11}(Bi,Sb)_{15}S_{35}$, tetrahedrite-freibergite $Cu_6[Cu_4(Fe, Zn)_2]Sb_4S_{13}$ - $Ag_6[Cu_4Fe_2]Sb_4S_{13-x}$, and canfieldite Ag_8SnS_6). The late stage IV is characterized by narrow (< 20 cm wide) barren quartz dominant veins.

Mapping at a scale 1:2000 at Quenamari has revealed generally NW-SE trending mineralized steeply dipping veins showing good continuity (> 1 km the Quenamari vein, > 3 km the parallel Nazareth vein) and considerable width emplaced in faults with normal and sinistral strike-slip displacement.

Tourmaline of stage I and within granite dykes shows a color and compositional evolution from orange-brown (intermediate composition between dravite and schorl) to blue tourmaline (schorl pole, 0.03 Mg apfu and 2.36 Fe apfu), similar to that described at San Rafael, and indicating a decrease of temperature. A colorless tourmaline vein (dravite pole, 1.9 Mg apfu and 0.19 Fe apfu), seems to be post orange-brown tourmaline which, if confirmed, would imply a hotter pulse. Microprobe analysis of sphalerite indicates a strong correlation between color and iron content. Opaque sphalerite has up to 11.4 wt. % Fe and orange-yellow sphalerite under microscope down to 3.3 wt. %.

At Quenamari, microthermometric analyses performed on liquid-vapor fluid inclusions occurring in quartz interpreted to be slightly later than sphalerite and in quartz intergrown with chalcopyrite of stage III, and in liquid-vapor fluid inclusions in quartz of stage IV, have salinity and homogenization temperatures for stage III ranging from 1.2 to 9.4 wt% NaCl eq. and 248 to 324 ℃ respectively (with values from 7.3 to 9.5 wt% NaCl eq. and 248 to 295 °C for sphalerite, 4.6 to 7.9 wt% NaCl eq. and 253 to 283 °C for quartz syn- to post sphalerite, and 1.3 and 5.8 wt% NaCl eq. and 283 to 324 °C for quartz intergrown with chalcopyrite). Salinities for stage IV quartz-hosted fluid inclusions are between 0.7 and 0.9 wt% NaCl eq. and homogenization temperatures between 170°C and 217°C. The minimum pressure of entrapment for stage III is 103 bar and for stage IV 16 bar.

At Quenamari, $d^{18}O_{V-SMOW}$ values have a range from 11.3 to 12.0 ‰ in tourmaline (stage I), 10.6 to 17.8 ‰ in stage III quartz, and 8.6 to 9.8 ‰ in stage IV quartz. For chlorite, the range is from 4.8 to 6.2‰ for stage III and 0.7‰ for stage IV. δD_{V-SMOW} values range from -79.6 to -70.4 ‰ for tourmaline and from -76 to -59.2 ‰ and -90.1‰ for chlorite, from stage III and IV, respectively. Tourmaline (stage I) values are clearly magmatic; stage III but also stage IV chlorite values are close to the magmatic range and those of stage III suggest boiling and variable fluid $d^{18}O$ values. Quartz $d^{18}O_{V-SMOW}$ values decrease with time. Two quartz-chlorite pairs from Quenamari give temperatures for stage III of 270 °C and 290°C.

The results for Quenamari are comparable with previous findings at the San Rafael deposit (e.g. Wagner et al., 2009), suggesting that the Quenamari prospect is the upper part of a steep system similar to the one that formed the San Rafael tin deposit. Stable isotope data are indicative of magmatic fluids during stage I mineralization. Precipitation during stage III is accompanied by mixing between a, possibly magmatic, fluid (≥ 9.5 wt.% NaCl eq. and ≤ 250°C) and a low-salinity fluid of higher temperature (≤ 2 wt.% NaCl eq. and ≥340°C). Taking into account the stable isotope results, this second fluid could correspond to condensed magmatic vapor or, less likely, to isotopically exchanged, extraneous fluids. Stable isotope

and fluid inclusion data indicate that in stage IV ingression of meteoric fluids was important.

The fact that at comparable altitude above sea level, similar mineral paragenesis, fluid inclusion characteristics, and stable isotope ratios are found, suggests that the magmatic roots of the mineralizing system at Quenamari are located at a similar depth compared to San Rafael. This, together with the lateral extension and width of the mineralized veins revealed by the detailed surface mapping of the present work, points to an important potential at depth for Sn mineralization at the Quenamari prospect.

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The hydrothermal sericites of copper- molybdenum porphyry ore-magmatic systems of the Zangezur ore district (Southern Armenia, Lesser Caucasus)

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The main mineral district is situated in the southern part of Tsaghkounk-Zanghezour metallogenic belt of the South-Armenian terrane and is represented by the giant Kajaran deposit, the smaller deposits of Agarak, Lichk, Dastakert and epithermal gold-ore deposits of Tey-Lichkvaz as well. Subduction and subsequent continental collision caused extensive calc-alkaline volcanic and plutonic igneous activity, including intrusion of Meghri pluton and small massives of Bargushat. The Meghri pluton is characterized by the abundant manifestation of polyphase collisional magmatism. According to Rb-Sr and U-Pb isotopic age determinations (Melkonyan et al., 2013) in the composition of the pluton Upper Eocene gabbro-monzonite syenogranite complex (41- 37Ma) and early Oligocene monzonite-syenite (31-28Ma) are distinguished, and in Lower Miocene (Tayan, 1998) the formation of pluton was completed by three-phase intrusive complex of porphyry granite-granodiorite (24 - 21Ma). Each stage was accompanied with the hydrothermal activity.

Early hydrothermal alteration produced propylitic assemblage (biotite and epidote-chlorite). Epidote-chlorite propylitic alteration was accomplished by the formation of secondary quartzites of mono-quartzite and quartz-sericite facies. The potassic alteration (orthoclase-biotite) occurred contemporaneously with the biotite propylitic alteration. Phyllic and argillic alterations occurred later, overprinting the earlier alteration. Phyllic alteration, consisting of quartz, sericite ± chlorite, accompanied the quartz-molybdenite, quartz-molybdenite-chalcopyrite, quartz-chalcopyrite mineralization stages. The sericite, kaolinite, quartz ± chlorite accompanied the quartz-pyrite, quartz-sphalerite-galena and other mineralization stages.

The crystal chemistry of the mica of quartz-sericite metasomatites in different formations of Agarak, Lichk, Kajaran and Dastakert ore fields in the Zangezur ore district was studied.

1. High- temperature (500-520^{0}C) polytype 2M$_1$ (Karamyan et al., 1987) siliceous illites (Si –3,6-3,75pfu) with potassium deficit (interlayer K ≈0,4pfu), low content of Al^{IV} 0,19–0,37pfu (Al^{IV} – 1,50-1,70pfu), with hydration degrees ≈ 4,5 wt. %, are characteristic for hydrothermal secondary quartzites. The siliceous illites are characterized by low ferruginosity κ_{Fe3+} = 0,05-0,1 (κ_{Fe3+}= Fe^3+/ Fe $^{3+}$ + Al^{IV}), they are low-charge, with 0,50-0,63; values for general-layered charge providing even distribution by tetrahedral and octahedral grids. The contents of phengite component varies from 0,13 to 0,30.