Proceedings Chapter

Early hydrothermal alteration stages at the giant San Rafael tin deposit, Peru

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Abstract

At the giant tin deposit of San Rafael, Peru, the early hydrothermal stages, preceding the economic tin mineralization, include successively: 1) potassic alteration represented by hydrothermal K-feldspar altering magmatic plagioclase; 2) sericite replacing magmatic plagioclase in the ground mass and hydrothermal K-feldspar, with greisen formation in the apical part of the intrusion; 3) widespread albitic alteration, both disseminated and as intense replacement along fractures, overprinting and obliterating the previous stages; 4) quartz-tourmaline veins rimmed by albitic alteration halos. In this contribution, the greisen-style alteration and sodic alteration, are studied in depth. Trace element analysis of hydrothermal albite reveals a marked enrichment in incompatible elements (B, Rb, Cs) compared to magmatic plagioclase, suggesting albitization was triggered by magmatic fluids exsolved from an evolved silicate melt.

Reference

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Early hydrothermal alteration stages at the giant San Rafael tin deposit, Peru

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Abstract. At the giant tin deposit of San Rafael, Peru, the early hydrothermal stages, preceding the economic tin mineralization, include successively: 1) potassic alteration represented by hydrothermal K-feldspar altering magmatic plagioclase; 2) sericite replacing magmatic plagioclase in the ground mass and hydrothermal K-feldspar, with greisen formation in the apical part of the intrusion; 3) widespread albitic alteration, both disseminated and as intense replacement along fractures, overprinting and obliterating the previous stages; 4) quartz-tourmaline veins rimmed by albitic alteration halos. In this contribution, the greisen-style alteration and sodic alteration, are studied in depth. Trace element analysis of hydrothermal albite reveals a marked enrichment in incompatible elements (B, Rb, Cs) compared to magmatic plagioclase, suggesting albitization was triggered by magmatic fluids exsolved from an evolved silicate melt.

1 Introduction

Early alteration taking place during magmatic-hydrothermal transition of granites hosting Sn-W mineralization, has been widely described. A typical feature of Sn-W deposits is the presence of early greisenization and albitization (Černý et al. 2005; Pirajno 2009). In the present contribution we focus on the hydrothermal alteration stages preceding Sn mineralization in the giant San Rafael Sn deposit (Central Andean Tin Belt, Peru; Kontak and Clark 2002; Mlynarczyk et al. 2003; Gialli et al., 2017). We report, in addition to the previously described potassic and sericitic alteration stages, development of greisen-style alteration in the apical part of the main intrusion. We have also found that albitization, already mentioned by Kontak and Clark (2002) is widespread and intense at San Rafael. This alteration feature, albeit commonly associated with many different deposit styles and settings, has received limited attention in the literature (Boulvais et al. 2007 and references therein). Combining optical microscopy, QEMSCAN, optical cathodoluminescence, EPMA and LA-ICP-MS analyses on samples representative of different pre-ore alteration styles, we present here a revised sequence of the early alteration stages at San Rafael and we discuss implications for fluid evolution at the magmatic-hydrothermal transition.

2 Geological setting

The San Rafael mining district is located in the Eastern Cordillera of southern Peru and is the largest and richest underground tin mine in the world, with resources of 11.2 million tons of ore at 1.99% Sn (Minsur corporate presentation 2018). The ore occurs as quartz-cassiterite-sulfide veins mainly hosted by a shallow peraluminous composite granitic intrusion (Kontak and Clark 2002; Mlynarczyk 2005) dated at 24.6±0.2 Ma (U-Pb zircon, Clark et al. 2000) and, subordinate, by surrounding Ordovician slates of the Sandia Formation. Main magmatic facies are biotite-cordierite megacrystic granite, volumetrically less important microgranite, in part as dismembered dikes, and late alkali granite. Lamprophyre dikes crosscut the granitic complex. The vein system formation is controlled by sinistral normal faults striking NNW-SSE and dipping at high angle towards the NE (Gialli et al. 2017; Fig. 1). We distinguish three main alteration and mineralization stages (Fig. 2): i) early pre-ore alteration stage with, from early to late, K-feldspar alteration, sericitic alteration, greisen formation, albitic alteration and tourmaline veining (Tur 2) with albitic halo (Fig. 3); ii) syn-ore stage in veins/breccias including Tur 3 and the main quartz-chlorite-cassiterite ± subsequent sulfide mineralization; and iii) post-ore stage consisting of late quartz ± carbonates ± fluorite ± adularia veins, which cut and overprint the earlier mineralization and alteration stages.

3 Results

The early pre-ore hydrothermal stage includes the following four major events (Fig. 2):

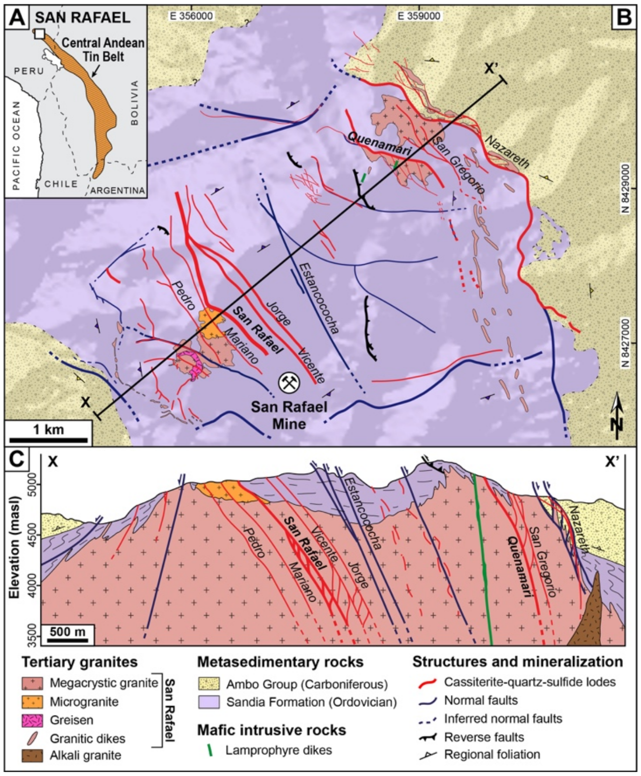

Figure 1. Geological map and cross-section of the San Rafael district, Southeast Peru. **a)** Location of the San Rafael deposit in the Central Andean Tin Belt (modified after Mlynarczyk et al. 2003); **b)** Geological map of the San Rafael district compiled from new mapping campaigns (Gialli et al. 2017, MINSUR S.A. unpublished data) and integrating older data (Arenas 1980, Palma 1981, Kontak and Clark 2002, Corthay 2014); **c)** Longitudinal cross-section of the San Rafael lode system from Gialli et al. 2017; modified after MINSUR S.A. unpublished data.

A) Potassic alteration. Pervasive potassic alteration is the earliest event of the pre-ore stage and consists of discrete patches of hydrothermal K-feldspar partially replacing magmatic plagioclase in the granitic rocks (Fig. 4A and D). This alteration is volumetrically restricted.

B) Sericitic alteration and greisen formation. Sericite commonly replaces magmatic plagioclase and hydrothermal K-feldspar (Fig. 4D). The intensity of the pervasive sericitic alteration increases progressively towards the upper part of the granitic intrusion where, in patchy areas, least altered granite grades toward intensely sericitized and albitized rocks (Fig. 4E-F). In the apical part of the pluton, cropping out in the south-eastern part of the studied area (Fig. 1B), an elongated area of intense greisenization extending for a few hundred meters in NNW-SSE direction has been recognized for the first time. The greisen mineral composition consists of quartz (~60%), muscovite (~35%), with minor amounts of tourmaline and dumortierite (<5%) (Fig. 4G).

C) Albitic alteration. Sodic alteration occurs as partial to almost complete replacement of magmatic plagioclase, hydrothermal K-feldspar as well as previous alteration

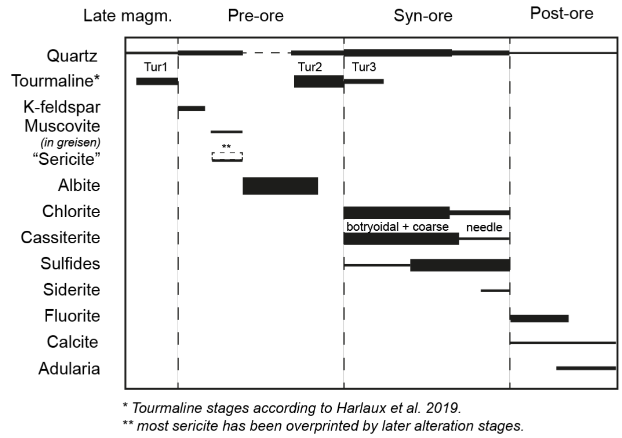

Figure 2. Simplified paragenetic sequence of the San Rafael tin deposit detailing the revised paragenesis of the early hydrothermal alteration stages.

minerals by albite (Fig. 4E). This pre-ore hydrothermal alteration episode is the most widespread and volumetrically important alteration event at San Rafael, affecting the intrusion as a whole, with variable degrees of intensity. Albitic alteration affects most of the samples that should be characterized as "fresh" by naked eye observation, from the bottom level of underground mining operations, till the surface outcrops of the granitic apophyses, with a vertical span of around 1500 meters. Hydrothermal albite occurs disseminated in the whole granitic intrusion, with alteration intensity varying from subtle to intense (Fig. 4E). Mass-balance calculations for albitized granite samples indicate a strong increase in Na and Si, relative increase in Al, and depletion in all other elements, in particular Ba, Y and LREE, leading to LREE-depleted patterns typical of strong albitic alteration (e.g. Boulvais et al. 2007). EPMA followed by LA-ICP-MS analyses were performed on hydrothermal albite and unaltered magmatic plagioclase, ranging in composition from andesine to oligoclase. In Figure 5, where highly incompatible elements (B, Cs, and Rb) are plotted vs. Ca/Na ratio, hydrothermal albite and magmatic plagioclase cluster in clearly different fields. The Ca/Na

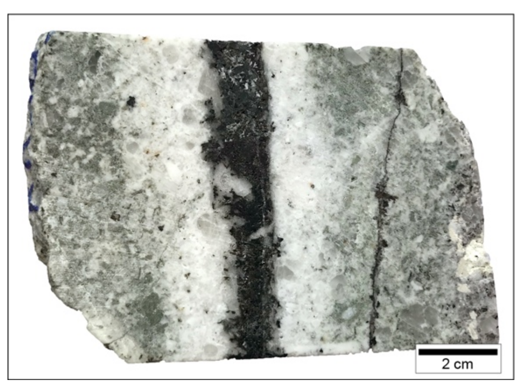

Figure 3. Intense albitic alteration along a quartz-tourmaline (Tur 2) vein in biotite-cordierite megacrystic granite (sample KK-09).

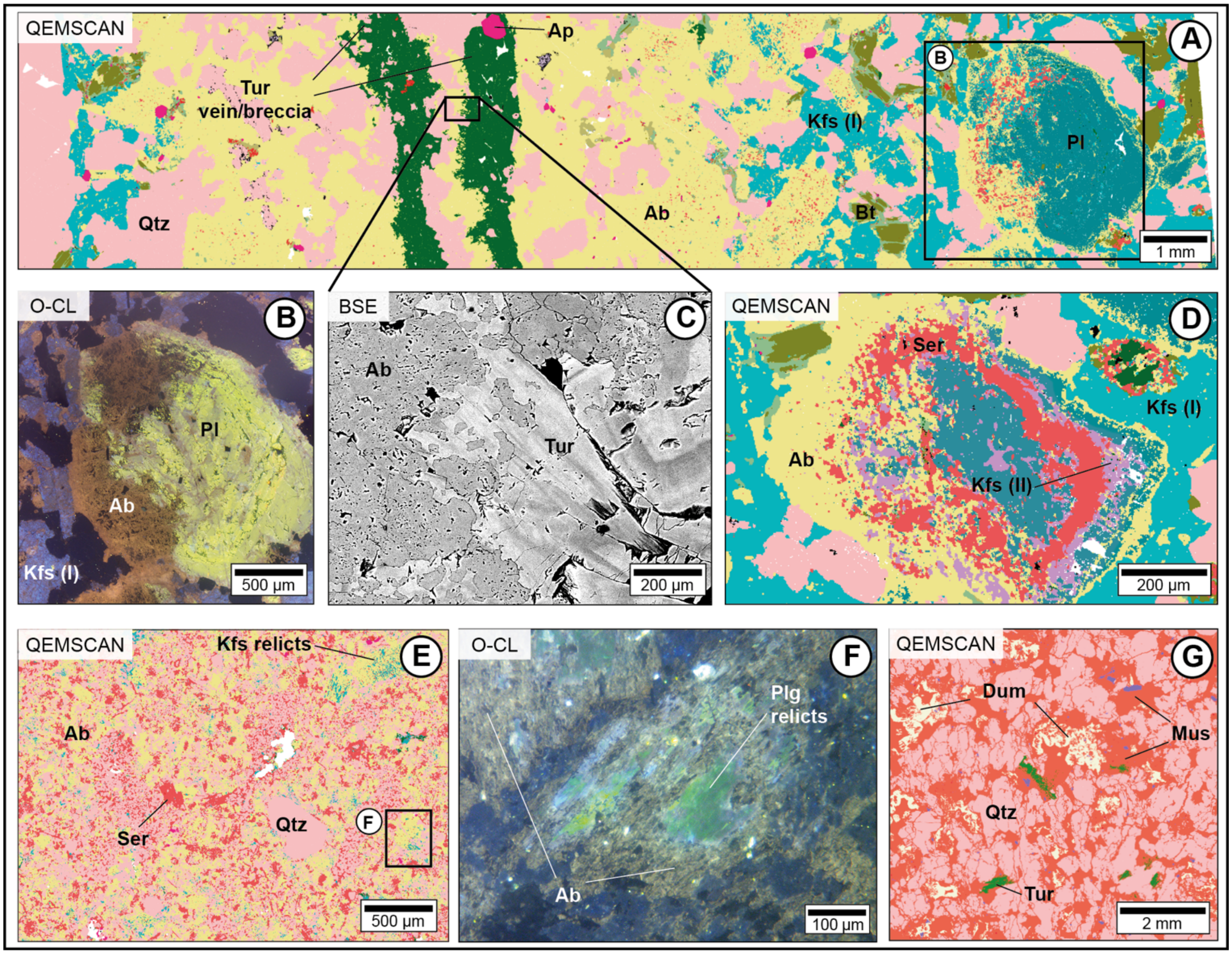

Figure 4. QEMSCAN, back scattered electron (BSE) and optical cathodoluminescence (O-CL) images, illustrating the paragenetic relationships of the early alteration stage at San Rafael. **a)** Megacrystic granite cut by tourmaline vein with albitic halo, overprinting magmatic minerals as well as earlier alteration stages (K-feldspar and sericite) (sample SRG-68); **b)** O-CL detail of magmatic plagioclase partially replaced by albite, which shows a "dusty" texture due to porosity creation during the replacement process (Hövelmann et al. 2010); **c)** BSE image showing hydrothermal albite that is replaced by hydrothermal tourmaline (Tur 2 according the terminology of Harlaux et al. 2019); **d)** Magmatic plagioclase altered to early hydrothermal K-feldspar (Kfs (II), determined by O-CL and QEMSCAN; color changed to violet), in turn replaced by sericite. Hydrothermal albite overprints the whole (sample SRG-68); **e)** Intensely sericitized granite subsequently affected by pervasive albitic alteration (sample SRG-116); **f)** Detail of relictic magmatic plagioclase almost completely replaced by hydrothermal albite; **g)** Greisen consisting mainly of quartz and muscovite with accessory dumortierite and tourmaline (sample SRG-133b). Ab-Albite, Bt-biotite, Dum-dumortierite, Kfs-Kfeldspar, Mus-muscovite, Plg-plagioclase, Qtz-Quartz, Ser-sericite, Tur-tourmaline.

ratio varies from 0.25 to 0.75 for magmatic plagioclase and from 0.05 to 0.20 for hydrothermal albite. The concentrations of B, Cs and Rb are low in magmatic plagioclase (3.9 to 20.8 ppm, 0.1 to 1.2 ppm and 1.9 to 8.4 ppm respectively). In hydrothermal albite, concentrations range from 10 to 140 ppm B, 0.1 to 25 ppm Cs, and 4 to 207 ppm Rb.

D) Tourmaline veins and breccias. Pre-ore hydrothermal tourmaline (Tur 2) in veins and breccias ranges in composition from dravite to schorl (Harlaux et al. 2019). Tur 2 veins are systematically rimmed by albitic alteration halos (Fig. 3, 4A) and cut the megacrystic granite including the greisen body cropping out at surface.

4 Discussion

After a first alteration stage forming K-feldspar from a near neutral pH hydrothermal fluid exsolving from the crystallizing magma, pervasive sericitic alteration can be interpreted in terms of a fluid becoming more acidic during cooling or by increasing volatile proportion. Concentration of hot and acidic fluids in the apical part of the intrusion would explain the formation of greisen (Černý et al. 2005).

The widespread albitic alteration, followed by tourmalinization (Tur 2), may be the result of a second hydrothermal pulse showing again an evolution path from neutral to acidic conditions.

The high concentrations of B, Cs and Rb in hydrothermal albite suggest a magmatic origin of the fluid responsible for the widespread albitization. This

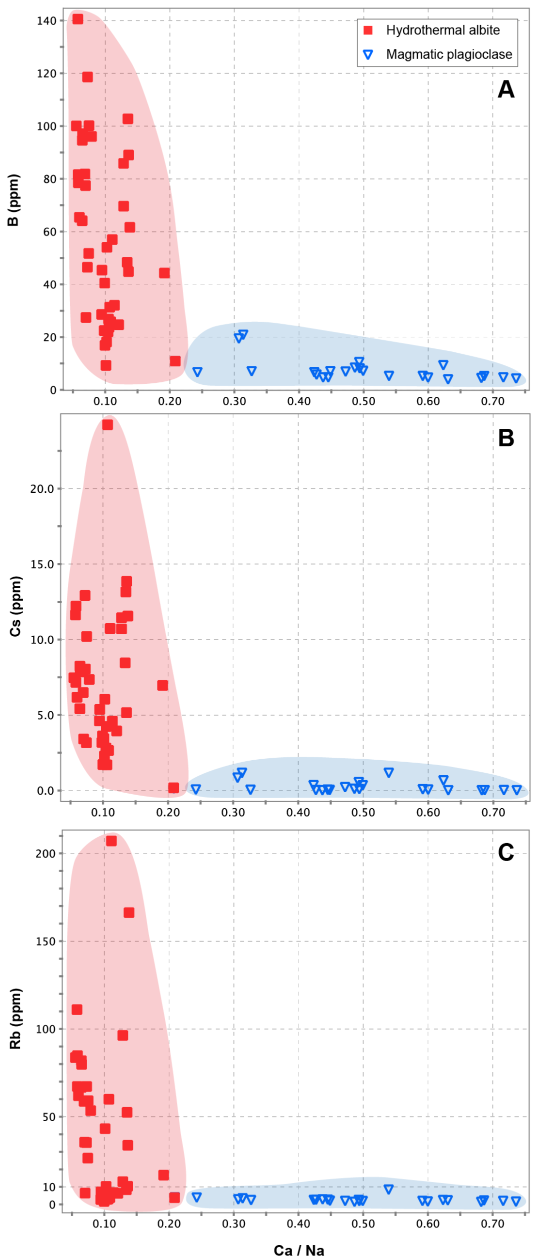

Figure 5. Plots of selected incompatible trace elements vs. Ca/Na ratio for hydrothermal albite (in red) and magmatic plagioclase (in blue). The enrichment in B, Cs, and Rb in the hydrothermal albite is indicative of a precipitation from a fluid of magmatic affinity (Audetat et al. 2000).

interpretation is also supported by the results of Harlaux et al. (2019), indicating precipitation of Tur 2 at ~500°C, from fluids with magmatic isotopic signature. Our results underline the role of magmatic-dominated fluids at the magmatic-hydrothermal transition during the pre-ore alteration stage at San Rafael.

5 Conclusions

A detailed textural study combining microscopic observations, QEMSCAN, optical cathodoluminescence, and scanning electron microscopy, has been carried out at the San Rafael tin deposit. Focus has been placed on the greisen occurring in the apical part of the composite granitic intrusion and on the importance and volumetric extension of albitic alteration. This has allowed a new interpretation of the sequence of alteration events during the early pre-ore hydrothermal stage at the San Rafael tin deposit. The paragenetic sequence combined with LA-ICP-MS analysis of trace elements in hydrothermal albite strongly support a magmatic origin for the early hydrothermal fluids and suggest the existence of two distinct fluid pulses during the pre-ore hydrothermal stage.

Acknowledgements

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