archive ouverte UNIGE

http://archive-ouverte.unige.ch

Proceedings Chapter

Cassiterite deposition triggered by fluid mixing: Evidence from in-situ δ^{18} O- δ^{11} B analysis of tourmaline from the San Rafael tin deposit, Peru

HARLAUX, Matthieu, et al.

Abstract

We present a combined study of oxygen and boron isotopes (δ 18O and δ 11B) measured in situ in tourmaline from the giant San Rafael tin deposit (Central Andean Tin Belt, Southeast Peru) to trace fluid processes during the magmatic-hydrothermal transition leading to tin mineralization. The results show that magmatic and pre-ore hydrothermal tourmaline has similar δ 18O- δ 11B values, which are consistent with crystallization in a continuously evolving magmatichydrothermal closed system. In contrast, syn-ore hydrothermal tourmaline has δ 18O- δ 11B values defining a linear array interpreted as the result of mixing with external fluids, thus indicating an opening of the hydrothermal system during the ore stage. Quantitative fluid modeling shows that a Rayleigh fractionation process in a closed system reproduces closely the δ 18O- δ 11B compositions of magmatic and pre-ore tourmaline, whereas mixing of a hot and saline (500°C, 45 wt% NaCl eq) tin-rich magmatic fluid with a heated meteoric fluid (250°C, 0 wt% NaCl eq) explains the observed δ 18O- δ 11B compositions for syn-ore tourmaline.

Reference

HARLAUX, Matthieu, *et al.* Cassiterite deposition triggered by fluid mixing: Evidence from in-situ δ^{18} O- δ^{11} B analysis of tourmaline from the San Rafael tin deposit, Peru. In: *15th Biennial SGA Meeting*. 2019.

Available at: http://archive-ouverte.unige.ch/unige:123230

Disclaimer: layout of this document may differ from the published version.



Cassiterite deposition triggered by fluid mixing: Evidence from in-situ δ^{18} O- δ^{11} B analysis of tourmaline from the San Rafael tin deposit, Peru

Matthieu Harlaux, Kalin Kouzmanov, Stefano Gialli, Lluís Fontboté Department of Earth Sciences, University of Geneva, Switzerland

Katharina Marger, Anne-Sophie Bouvier, Lukas Baumgartner

Institute of Earth Sciences, University of Lausanne, Switzerland

Andrea Dini

Istituto di Geoscienze e Georisorse, CNR Pisa, Italy

Alain Chauvet

Géosciences Montpellier, CNRS, France

Miroslav Kalinaj

MINSUR S.A., Peru

Abstract. We present a combined study of oxygen and boron isotopes ($\delta^{18}O$ and $\delta^{11}B$) measured in situ in tourmaline from the giant San Rafael tin deposit (Central Andean Tin Belt, Southeast Peru) to trace fluid processes during the magmatic-hydrothermal transition leading to tin mineralization. The results show that magmatic and pre-ore hydrothermal tourmaline has similar $\delta^{18}O-\delta^{11}B$ values, which are consistent with crystallization in a continuously evolving magmatichydrothermal closed system. In contrast, syn-ore hydrothermal tourmaline has $\delta^{18}O-\delta^{11}B$ values defining a linear array interpreted as the result of mixing with external fluids, thus indicating an opening of the hydrothermal system during the ore stage. Quantitative fluid modeling shows that a Rayleigh fractionation process in a closed system reproduces closely the δ^{18} O- δ^{11} B compositions of magmatic and pre-ore tourmaline. whereas mixing of a hot and saline (500°C, 45 wt% NaCl eq) tin-rich magmatic fluid with a heated meteoric fluid (250°C, 0 wt% NaCl eq) explains the observed δ^{18} O- δ^{11} B compositions for syn-ore tourmaline.

1 Introduction

Primary Phanerozoic tin (Sn) and/or tungsten (W) mineralization is mostly associated with reduced and highly evolved granitic magmas that were generated in orogenic belts by melting of tectonically thickened sedimentary sequences (Romer and Kroner 2016). Granite-related Sn±W deposits dominantly consist of cassiterite±wolframite-bearing quartz veins hosted by the apical part of granitic intrusions or extending into surrounding country rocks (Černý et al. 2005). The ore-bearing hydrothermal fluids and metals are generally considered to be of magmatic origin and cassiterite deposition is interpreted to result from several processes, including fluid cooling, boiling, fluid-rock interaction, and mixing with external fluids (Heinrich 1990). Here, we traced hydrothermal fluid evolution by

using the isotopic composition of tourmaline, which is a common boron-rich mineral in granite-related Sn-W deposits and a robust chemical and isotopic monitor of ore-forming processes (Slack and Trumbull 2011).



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 (Gialli et al. 2017, MINSUR S.A. unpublished data).

We present a combined study of oxygen and boron isotopes measured in situ in tourmaline from the giant San Rafael Sn deposit (Peru) to trace fluid processes occurring at the magmatic-hydrothermal transition and leading to tin mineralization.

2 Geological setting

The world-class San Rafael lode-type tin deposit (>1 Mt Sn) is located in the northern part of the Central Andean Tin Belt extending from southeast Peru to Bolivia and northern Argentina (Fig. 1A). Mineralization consists of a NW-trending guartz-cassiterite-sulfide vein system hosted by a late-Oligocene (ca. 25 Ma) peraluminous Stype granitic complex and by surrounding Ordovician shales of the Sandia Formation (Fig. 1B-C; Kontak and Clark 2002, Mlynarczyk et al. 2003, Gialli et al. 2017). Description of the early hydrothermal alteration stages is presented in Gialli et al. (2019). The deposit is characterized by volumetrically important presence of tourmaline, both of magmatic and hydrothermal origin (Mlynarczyk and Williams-Jones 2006). The following three major tourmaline generations have been distinguished (Harlaux et al. 2018): (i) Tur 1 is magmatic tourmaline found in peraluminous granites as guartztourmaline nodules and disseminations (Fig. 2A-B); it is texturally homogeneous and has dravitic composition (XMg=0.49-0.61); (ii) Tur 2 is pre-ore hydrothermal tourmaline formed during post-magmatic subsolidus alteration and veining-brecciation (Fig. 2C-D); it shows primary banding and overgrowth textures at microscopic scale and ranges in composition from dravite to schorl (XMg=0.22-0.98); (iii) Tur 3 is syn-ore hydrothermal tourmaline forming widespread microscopic veinlets and previous overgrowths, partly cross-cutting the tourmaline generations (Fig. 2E-F); it has schorl-foitite composition (XMg=0.08-0.55) and is locally intergrown with cassiterite, chlorite and quartz from the ore stage.

3 Results

We analyzed the $\delta^{18}O-\delta^{11}B$ compositions of different tourmaline generations (Tur 1 to Tur 3) in situ by secondary ion mass spectrometry (SIMS) at the SwissSIMS facility. University of Lausanne. Our results (Fig. 3A) show that Tur 1 and Tur 2 have similar δ^{18} O (10.6% to 11.6%) and $\delta^{11}B$ (-11.5‰ to -6.90‰) values. In contrast, Tur 3 has lighter δ^{18} O compositions (4.90‰ to 10.2‰) and in part heavier $\delta^{11}B$ compositions (-9.90% to -5.40%). We also measured in situ the δ^{18} O compositions of magmatic and hydrothermal quartz showing equilibrium textures with tourmaline in order to estimate crystallization temperatures (Fig. 4). Quartztourmaline oxygen isotope compositions vield equilibrium temperatures of 485-618°C for magmatic quartz-tourmaline nodules (Tur 1, average 555±44°C), and 429-487°C for pre-ore hydrothermal guartztourmaline veins (Tur 2, average 455±30°C). This indicates temperatures of ca. 450-500°C for the magmatic-hydrothermal transition, which is in agreement with previous fluid inclusion data (Kontak and Clark 2002, Wagner et al. 2009). Considering the upper values for quartz-tourmaline isotopic equilibrium, crystallization temperatures of about 600°C for Tur 1 and 500°C for Tur 2 can be estimated. No quartz was found directly intergrown with Tur 3, but previous works reported homogenization temperatures of about 350°C for primary fluid inclusions hosted in cassiterite (Wagner et al. 2009), temperature taken here as representative for the crystallization of Tur 3.



Figure 2. Mineralogical and textural features of tourmaline from the San Rafael tin deposit. A) Magmatic quartz-tourmaline nodule (Tur 1) in microgranite. B) Disseminated magmatic tourmaline (Tur 1) in microgranite. C) Subsolidus hydrothermal tourmaline (Tur 2) replacing a K-feldspar phenocryst in megacrystic granite. D) Typical quartz-tourmaline hydrothermal vein (Tur 2) surrounded by hydrothermal albite halo cross-cutting chloritized megacrystic granite. E) Blue tourmaline veinlets and overgrowths (Tur 3) overprinting a quartz-tourmaline vein (Tur 2). F) Cassiterite intergrown with green tourmaline needles (Tur 3). Abbreviations: Ab=albite, Bt=biotite, Chl=chlorite, Cst=cassiterite, Kfs=K-feldspar, Plg=plagioclase, Qtz=quartz, Tur=tourmaline.

4 Discussion

4.1 Origin of the B-rich fluids

Assuming temperatures of 600°C for Tur 1, 500°C for Tur 2 and 350°C for Tur 3, we calculated the δ^{18} O and δ^{11} B composition of water in equilibrium with tourmaline (Fig. 3B), based on the oxygen and boron isotope fractionation of the tourmaline-water system (Zheng 1993, Meyer et al. 2008). The isotopic composition of water equilibrated with Tur 1 and Tur 2 hosted in granites overlaps over a range of δ^{18} O=10.5‰ to 12.0‰ and δ^{11} B=-9.8‰ to -5.0‰. These oxygen isotope compositions are similar to the bulk δ^{18} O values (9.7‰

to 12‰) of guartz and tourmaline from the pre-ore stage equilibrated with water at the same temperatures. The lowest values of δ^{18} O=11.5‰ and δ^{11} B=-9.5‰ point to a single fluid end-member ("fluid A" in Fig. 3B) that fits the typical isotopic compositional range of a magmatichydrothermal fluid derived from a S-type magma. The magmatic origin of this fluid is also supported by the high salinity (40-55 wt% NaCl eq) and high temperatures (350-500°C) of primary fluid inclusions hosted in the early quartz-tourmaline veins (Kontak and Clark 2002, Wagner et al. 2009). The isotopic composition of water equilibrated with Tur 2 hosted in the enclosing shales has different $\delta^{18}O-\delta^{11}B$ values, pointing to a fluid end-member having $\delta^{18}O=14\%$ and $\delta^{11}B=-6\%$. Such a fluid composition may correspond to a contact-metamorphic fluid equilibrated with the shales or a magmatic-hydrothermal fluid that interacted with the metamorphic host-rocks. Isotopic composition of water in equilibrium with Tur 3 plots along a well-delineated array ranging from $\delta^{18}O{=}8.4\%$ and $\delta^{11}B{=}{-}6.7\%$ to δ^{18} O=3.2‰ and δ^{11} B=-2.1‰. These oxygen isotopic compositions are also consistent with the bulk $\delta^{18}O$ values (3.3% to 8.1%) of quartz, cassiterite, and chlorite from the main ore stage equilibrated with water at 350°C. This linear δ^{18} O- δ^{11} B array can be interpreted as a mixing line between a magmatic-hydrothermal fluid end-member having δ^{18} O=11.5‰ and δ^{11} B=-9.5‰ ("fluid A") and another fluid end-member having $\delta^{18}O=0$ and $\delta^{11}B=0\%$ ("fluid B" in Fig. 3B). The latter can be interpreted as groundwater of meteoric origin equilibrated with the host-rocks.

4.2 Quantitative modeling of fluid evolution

δ¹⁸Ο-δ¹¹Β Quantitative modeling of tourmaline composition has been performed for fluid evolution scenarios considering fluid mixing as well as cooling, Rayleigh fractionation, and fluid-rock interaction (Fig. 3C). In each scenario, the starting magmatichydrothermal fluid was assumed to have a temperature of 500°C, a salinity of 45 wt% NaCl eq, δ^{18} O=11.5‰, and $\delta^{11}B=-9.5\%$. Simple cooling of such a fluid down to 250°C results in a trend of increasing δ^{18} O and decreasing δ^{11} B, which do not reproduce the isotopic compositions of tourmaline. A Rayleigh fractionation process results in a trend of near-constant $\delta^{18}O$ and increase in δ^{11} B, which reproduces closely the isotopic compositions of Tur 1 and Tur 2 hosted in granites with fractionation grades of 10% to 90% of the initial magmatic fluid at constant temperature. Fluid-rock interaction involving oxygen and boron isotope exchange between a magmatic fluid and typical Early Paleozoic Andean shales (δ^{18} O=18‰, Bindeman et al. 2016; $\delta^{11}B=-6\%$, Kasemann et al. 2000) produces a trend of increasing δ^{18} O and δ^{11} B for moderate water/rock ratio of ~0.5, which is consistent with the isotopic compositions of Tur 2 hosted in shales. A model involving fluid mixing between a hot and saline magmatic-hydrothermal fluid (500°C, 45 wt% NaCl eq, δ^{18} O=11.5‰, and δ^{11} B=-9.5‰) and a cooler meteoric fluid (250°C, 0 wt% NaCl eq, δ^{18} O=0‰, and δ^{11} B=0‰) reproduces the full range of isotopic values for Tur 3.



Figure 3. A) Plot of δ^{18} O vs. δ^{11} B composition of tourmaline from the San Rafael tin deposit determined by SIMS. B) Calculated δ^{18} O vs. δ^{11} B composition of water in isotopic equilibrium with tourmaline assuming formation temperatures of 600°C for Tur 1, 500°C for Tur 2, and 350°C for Tur 3 (see text). The field for S-type granites is from Trumbull and Slack (2018) and Harris et al. (1997). Calculated δ^{18} O values for water in equilibrium with ore and gangue minerals from the pre-ore stage (Qtz: n=16, Tur: n=7) and the main ore stage (Qtz: n=13, Cst: n=14, Chl: n=5) are from Wagner et al. (2009), Prado Flores (2015) and this study. C) Modeling of δ^{18} O vs. δ^{11} B composition of tourmaline based on different fluid evolution scenarios (cooling, Rayleigh fractionation, fluid-rock interaction, and fluid mixing).

This suggests that Tur 3 records variable degrees of mixing with 10% to 80% of pre-heated meteoric fluid. If the initial $\delta^{11}B$ composition of the magmatic-hydrothermal fluid was -8.5‰ or -7.5‰, the results are similar.



Figure 4. Plot of δ^{18} O values for coexisting quartz (Qtz) and tourmaline (Tur) from the San Rafael tin deposit. Isotherms are calculated using fractionation factors for quartz-tourmaline from Zheng (1993).

5 Conclusions

In situ oxygen and boron isotope analysis of tourmaline allowed to effectively trace the fluid evolution of the San Rafael magmatic-hydrothermal system. The similar δ^{18} O- δ^{11} B values for Tur 1 and Tur 2 are consistent with crystallization driven by Rayleigh fractionation in a continuously evolving magmatic-hydrothermal closed system, likely under lithostatic pressure conditions. In contrast, the $\delta^{18}O-\delta^{11}B$ linear array observed for Tur 3, interpreted as the result of mixing with external fluids, indicates an opening of the hydrothermal system during the main ore stage, likely related to a transition from lithostatic to hydrostatic pressure conditions. Mixing of a hot, saline, and reducing Sn-rich magmatic fluid with a cooler and more oxidizing meteoric fluid resulted in destabilization of tin-chloride complexes, which is the decisive parameter for cassiterite precipitation (Schmidt 2018). Therefore, the $\delta^{18}O{-}\delta^{11}B$ compositions of Tur 3 unambiguously demonstrate that fluid mixing was the key process triggering cassiterite deposition in the giant San Rafael Sn deposit.

Acknowledgements

This research was supported by the Swiss National Science Foundation (SNSF S19053_169901) and the company MINSUR S.A.

References

Arenas MJ (1980) El distrito minero San Rafael: Estaño en el Perú. B Soc Geol Perú 66:1–11.

- Bindeman IN, Bekker A, Zakharov DO (2016) Oxygen isotope perspective on crustal evolution on early Earth: A record of Precambrian shales with emphasis on Paleoproterozoic glaciations and Great Oxygenation Event. Earth Planet Sc Lett 437:101-113.
- Černý P, Blevin PL, Cuney M, London D (2005) Granite-related ore deposits. Econ Geol 100th Anniversary Volume:337-370.
- Corthay G (2014) The Quenamari prospect, San Rafael tin District, southern Peru: geology, mineral assemblages, fluid inclusion microthermometry, and stable isotopes. M.Sc. thesis, Switzerland, University of Geneva, 113 p.
- Gialli S, Chauvet A, Kouzmanov K, Dini A, Spikings R, Kalinaj M, Fontboté L (2017) Structural control of the world-class Sn district of San Rafael, Peru. In Proceedings of the SEG 2017 Meeting, 17-20 September 2017, Beijing, China.
- Gialli S, Harlaux M, Kouzmanov K, Chauvet A, Laurent O, Dini A, Kalinaj M, Fontboté L (2019) Early hydrothermal alteration stages at the giant San Rafael tin deposit, Peru. In Proceedings of the 15th Biennial SGA Meeting, 27-30 August 2019, Glasgow, Scotland (this volume).
- Harlaux M, Kouzmanov K, Gialli S, Laurent O, Marger K, Baumgartner L, Dini A, Chauvet A, Kalinaj M, Fontboté L (2018) Magmatic-hydrothermal transition traced by in situ tourmaline analysis at the San Rafael tin deposit, Peru. Goldschmidt Abstracts, 12-17 August 2018, Boston, USA, 2018:949.
- Harris C, Faure K, Diamond RE, Scheepers R (1997) Oxygen and hydrogen isotope geochemistry of S- and I-type granitoids: the Cape Granite suite, South Africa. Chem Geol 143:95-114.
- Heinrich CA (1990) The chemistry of hydrothermal tin (-tungsten) ore deposition. Econ Geol 85:457-481.
- Kasemann S, Erzinger J, Franz G (2000) Boron recycling in the continental crust of the central Andes from the Palaeozoic to Mesozoic, NW Argentina. Contrib Mineral Petr 140:328-343.
- Kontak DJ, Clark AH (2002) Genesis of the giant, bonanza San Rafael lode tin deposit, Peru: origin and significance of pervasive alteration. Econ Geol 97:1741-1777.
- Meyer C, Wunder B, Meixner A, Romer RL, Heinrich W (2008) Boron-isotope fractionation between tourmaline and fluid: an experimental re-investigation. Contrib Mineral Petr 156:259-267.
- Mlynarczyk MS, Williams-Jones AE (2006) Zoned tourmaline associated with cassiterite: implications for fluid evolution and tin mineralization in the San Rafael Sn–Cu deposit, southeastern Peru. Can Mineral 44:347-365.
- Mlynarczyk MS, Sherlock RL, Williams-Jones AE (2003) San Rafael, Peru: geology and structure of the worlds richest tin lode. Miner Deposita 38:555-567.
- Palma VV (1981) The San Rafael tin-copper deposit, SE Peru. M.Sc. thesis, Kingston, Ontario, Queen's University, 235 p.
- Prado Flores E (2015) San Rafael Tin Mine, Peru: Geology, Mineralogy, O and H Stable Isotopes, and Fluid Inclusions Microthermometry of the deep level 3600m. M.Sc. thesis, Switzerland, University of Geneva, 89 p.
- Romer RL, Kroner U (2016) Phanerozoic tin and tungsten mineralization-tectonic controls on the distribution of enriched protoliths and heat sources for crustal melting. Gondwana Res 31:60-95.
- Schmidt C (2018) Formation of hydrothermal tin deposits: Raman spectroscopic evidence for an important role of aqueous Sn (IV) species. Geochim Cosmochim Ac 220:499-511.
- Slack JF, Trumbull RB (2011) Tourmaline as a recorder of oreforming processes. Elements 7:321-326.
- Trumbull RB, Slack JF (2018) Boron isotopes in the continental crust: granites, pegmatites, felsic volcanic rocks, and related ore deposits. In Marschall HR, Foster GL, eds., Boron Isotopes - The Fifth Element, Advances in Isotope Geochemistry, Springer-Verlag, 249-272.
- Wagner T, Mlynarczyk MS, Williams-Jones AE, Boyce AJ (2009) Stable isotope constraints on ore formation at the San Rafael tin-copper deposit, Southeast Peru. Econ Geol 104:223-248.
- Zheng YF (1993) Calculation of oxygen isotope fractionation in hydroxyl-bearing silicates. Earth Planet Sc Lett 120:247-263.