

## Isotopic fluid composition of rare-metal pegmatites, Sierra de San Luis, Argentina

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Fluid inclusion studies and stable isotope measurements of fluids from small (ca. 0.5 grams) samples have been carried out on rare-metal (Be, Li, Nb, Ta, Sn) granitic pegmatites from the Sierra de San Luis (Argentina) in order to trace the source and evolution of the mineralizing fluids. The granitic pegmatites are related to syn-tectonic, meta- to peraluminous S-type granites (Sosa et al. 2007). They were emplaced during the Ordovician magmatism during the Famatinian Orogeny. Nb-Ta-pegmatites are concordantly emplaced in fine-grained quartz-mica schist of the Conlara Metamorphic Complex in the east, while Sn-bearing pegmatites are emplaced in the westerly schist of the Pringles Metamorphic Complex (Sosa, 2002; Sims et al, 1998). The sedimentation age was ca. 587 to 498 Ma for the Conlara Complex (Steenken et al. 2006) and significantly younger (ca. 530 to 498 Ma) for the Pringles Complex (Sims et al. 1998). The Nb-Ta-pegmatites were dated (K-Ar) ca. 404-444 Ma, the Sn-pegmatites slightly younger ca. 398-411 Ma (Sosa et al. 2002). The metamorphic grade of the country rocks varies from greenschist to lower-amphibolite facies. The concordant textural relation between the pegmatites and country rocks indicates a plastic behaviour of the schist during the pegmatite intrusion. The larger Nb-Ta pegmatites show a clear internal fractionation, whereas the smaller Sn pegmatites are homogeneous.

Fluid inclusions are present in most pegmatite minerals (apatite, beryl, cassiterite, columbite-tantalite, plagioclase, quartz) and, except in quartz, show primary features like the occurrence in growth zones. In apatite, cassiterite, beryl and plagioclase, the majority of the fluid inclusions are mixtures of H<sub>2</sub>O-NaCl-CO<sub>2</sub>-CH<sub>4</sub>-N<sub>2</sub>, and the rest are H<sub>2</sub>O-NaCl (Van den Kerkhof et al. 2005). In contrast, columbite-tantalite contains

almost only aqueous inclusions. Non-aqueous carbonic inclusions are found in quartz and plagioclase. In all minerals the salinity of the aqueous inclusions is typically 4 to 7 eq mass% NaCl, whereas the aqueous-carbonic inclusions have higher salinity. High CH<sub>4</sub> and N<sub>2</sub> contents were found in cassiterite, plagioclase and quartz with highest contents in cassiterite (up to 58 mol% CH<sub>4</sub>, incidentally pure CH<sub>4</sub>, and up to 32 mol% N<sub>2</sub>; Fig. 1). The carbonic inclusions in the quartz show always much higher CH<sub>4</sub>-concentrations in the Sn-pegmatites compared to Nb-Ta-pegmatites.

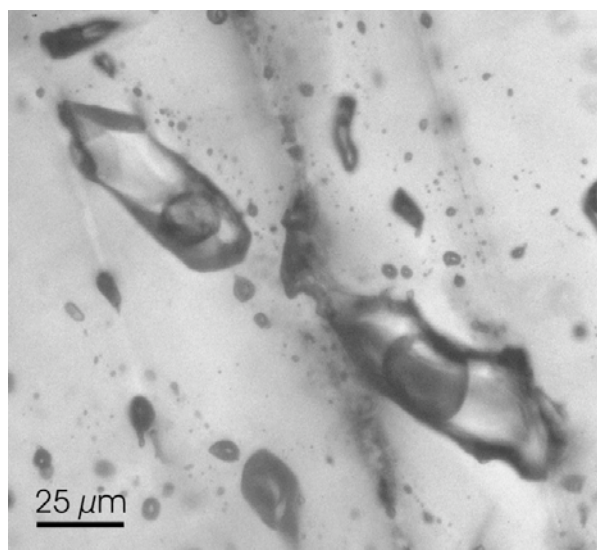


Fig. 1. Primary aqueous-carbonic inclusions in cassiterite (Yolanda pegmatite). The larger inclusion shows  $T_m(\text{CO}_2) = -63.2$ ;  $T_m(\text{ice}) = -5.4$ ;  $T_m(\text{cla}) = +10.7$ ;  $T_h(\text{LV} \rightarrow \text{V}) \text{CO}_2 = +0.4$  °C. The gas phase contains  $\text{CO}_2(61)\text{CH}_4(14)\text{N}_2(25)$ . The isotopic composition of this sample is  $\delta^{13}\text{C}(\text{CO}_2) = -12.4$ ‰;  $\delta^{13}\text{C}(\text{CH}_4) = -47.7$ ‰ VPDB and  $\delta^{15}\text{N}(\text{N}_2) = +0.4$ ‰.

Rare high-salinity inclusions (29-32 eq mass% NaCl) in quartz may originate from the magmatic stage, but most fluid inclusions

represent later hydrothermal fluids. The pegmatite minerals must have crystallized from a H<sub>2</sub>O-NaCl-CO<sub>2</sub> (±CH<sub>4</sub>-N<sub>2</sub>) dominated fluid, preserved as primary inclusions in beryl and plagioclase (trapped at 400-500 °C /2-3 kbar as estimated from isochores). These conditions are in agreement with regional metamorphism and the liquidus conditions of rare-metal pegmatite crystallization. Subsequently, columbite-tantalite or cassiterite crystallized at 300-400 °C, and finally apatite at 200-300 °C. The CO<sub>2</sub>-concentration became progressively lower, resulting in H<sub>2</sub>O±CO<sub>2</sub> preserved in apatite. Fluid inclusions in quartz represent the full temperature range with the latest fluids (re)trapped in the immiscible aqueous-carbonic field at 100-150°C/0.5 kbar. The different modified fluid inclusions reflect the mineral-specific properties of preserving fluids. Halo textures in quartz indicative of implosion-decrepitation testify isobaric cooling. Methane-bearing inclusions indicate reducing conditions during cassiterite crystallization, or re-equilibration of aqueous-carbonic inclusions (graphite-bearing inclusions in plagioclase and quartz). Late low-salinity water found in all minerals must have been introduced after crystallization and represent meteoric water.

Stable isotope (δ<sup>13</sup>C and δ<sup>15</sup>N) studies were carried out on gas-rich inclusions in quartz from both types of pegmatites and in cassiterite (analysis of tantalite in progress) using crusher which is connected to an elemental analyzer and isotopic mass spectrometer. CO<sub>2</sub> in quartz from Nb-Ta-pegmatite (Conlara Complex) shows δ<sup>13</sup>C values between ca. -10 and +4‰ VPDB, with frequency maximums around -4 and -9‰. The magmatic signatures of ca. -4‰ are found for 3 pegmatites (Los Chilenitos, La Beatriz, La Violeta), all situated in the central easternmost part of the Sierra de San Luis; the lower δ<sup>13</sup>C values are found for pegmatites more to the west. The CO<sub>2</sub> in quartz from the westernmost Sn-pegmatites in the Pringles Complex shows lightest δ<sup>13</sup>C values (ca. -8 to -17‰ VPDB) suggesting that the main oxide-silicate stage fluid was contaminated with carbon derived from the meta-sedimentary country rock. The δ<sup>13</sup>C values of CO<sub>2</sub> in cassiterite coexisting with the quartz is slightly higher compared to the CO<sub>2</sub> in quartz (e.g. -9.3‰ and -14.7‰ for cassiterite and quartz, respectively;

Neutrón pegmatite), but in one example (Irene pegmatite) we found clearly lower δ<sup>13</sup>C (-16.4‰) than for the CO<sub>2</sub> in cassiterite (-8.6‰ PDB), suggesting the local uptake of organic carbon during cassiterite crystallization.

The δ<sup>13</sup>C values of the abundant CH<sub>4</sub> in cassiterite are very low (-47.7‰ VPDB), but also the quartz in Nb-Ta-pegmatites with magmatic CO<sub>2</sub> contains minor CH<sub>4</sub> with low δ<sup>13</sup>C (ca. -42‰ VPDB). These values suggest that a part of the carbonic fluid must be of thermogenic origin (from kerogen at elevated temperatures) in both Conlara and Pringles metamorphic complexes.

The δ<sup>15</sup>N values of N<sub>2</sub> which occurs as a minor constituent in the carbonic inclusions is ca. +3 to +6‰ for quartz and slightly lower, i.e. ca. 0 to +3‰ for cassiterite. These values confirm the contamination of the mineralizing fluid with organogenic material.

Based on regional isotopic variation of carbon in fluid inclusions we can distinguish between fluids with a magmatic signature, which correlate with Nb-Ta-pegmatite mineralization, and fluids which changed their isotopic composition due to interaction with the surrounding metasediments. The abundance and isotope compositions of CH<sub>4</sub> and N<sub>2</sub> suggest that the uptake of organic material in the mineralizing fluids must have been much larger in the western part of the Sierra de San Luis (Pringles Complex) and resulted in Sn-pegmatite mineralization.

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