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Solubility of cassiterite in evolved granitic melts: effect of *T*, *f*O_2, and additional volatiles

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Abstract

The aim of this experimental study was to determine the solubility of cassiterite in natural topaz- and cassiterite-bearing granite melts at temperatures close to the solidus. Profiles of Sn concentrations at glass–crystal (SnO_2) interface were determined following the method of (Harrison, T.M., Watson, E.B., 1983. Kinetics of zircon dissolution and zirconium diffusion in granitic melts of variable water content. Contributions to Mineralogy and Petrology 84, 66–72). The cassiterite concentration calculated at the SnO_2–glass interface is the SnO_2 solubility. Experiments were performed at 700–850 °C and 2 kbar using a natural F-bearing peraluminous granitic melt with 2.8 wt.% normative corundum. Slightly H_2O-undersaturated to H_2O-saturated melt compositions were chosen in order to minimize the loss of Sn to the noble element capsule walls. At the nickel–nickel oxide assemblage (Ni–NiO) oxygen fugacity buffer, the solubility of cassiterite in melts containing 1.12 wt.% F increases from 0.32 to 1.20 wt.% SnO_2 with an increasing temperature from 700 to 850 °C. At the Ni–NiO buffer and a given corundum content, SnO_2 solubility increases by 10% to 20% relative to an increase of F from 0 to 1.12 wt.%. SnO_2 solubility increases by ~20% relative to increasing Cl content from 0 to 0.37 wt.% in synthetic granitic melts at 850 °C. We show that Cl is at least as important as F in controlling SnO_2 solubility in evolved peraluminous melts at oxygen fugacities close to the Ni–NiO buffer. In addition to the strong effects of temperature and fO_2 on SnO_2 solubility, an additional controlling parameter is the amount of excess Al (corundum content). At Ni–NiO and 850 °C, SnO_2 solubility increases from 0.47 to 1.10 wt.% SnO_2 as the normative corundum content increases from 0.1 to 2.8 wt.%. At oxidizing conditions (Ni–NiO +2 to +3), Sn is mainly incorporated as Sn^{4+} and the effect of excess Al seems to be significantly weaker than at reducing conditions.

Keywords: Granite; Cassiterite; Concentration; SnO_2 solubility; Cl; F

1. Introduction

Tin deposits display a wide range of structural and mineralogical types (Taylor, 1979a) and are generally spatially related to evolved granite intrusions. Sn and

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associated rare-element mineralisation (W, Be, Nb, Ta) are frequently associated with chemically specialized granites, with high contents of SiO_2, alkalis, Sn, W, Mo, Be, B, Li, and F, and low contents of CaO, MgO, Ba, and Sr (Tischendorf, 1977). The deposits themselves characteristically contain fluorite, topaz, tourmaline and Li-micas (Pollard et al., 1987). In a number of natural processes, F and B contribute to the magmatic and post-magmatic evolution of the tin systems, including fractionation/crystallization, fluid phase evolution, wall-rock alterations, metal transportation, and deposition (Pollard et al., 1987).

A fundamental concept in understanding the relationship between Sn mineralisation and magmatism is that variations in the basicity of a melt (i.e., the activity of free oxygens) play an important role (Taylor, 1988). Peralkaline magmas display high melt basicities, and, consequently, will generate fluids during resurgent boiling that are markedly less acid than fluids associated with peraluminous melt systems (Taylor, 1988). Hence, peralkaline magmas have the capacity to store a far greater concentration of Sn than peraluminous magmas and Sn would be less prone to remobilization in peralkaline magmas by a fluid phase. Sn will be most effectively partitioned from reduced, high-temperature, potassium-rich, aluminous magmas (Taylor, 1988). These characteristics describe a major portion of the Sn-mineralized granitoids (see also Štemprok, 1971; Štemprok and Skvor, 1974). Bivalent Sn is a relatively large cation and is considered to behave as an incompatible element during the evolution of granitoid suites (Taylor, 1979a,b; Eugster, 1985). Crystal fractionation, crystallochemical dispersion, magma mixing, and assimilation are the main processes that account for the generally systematic trends in Sn distribution in natural granitoid systems (Barsukov and Durasova, 1966; Kovalenko et al., 1968; Tauson, 1968, 1974; Groves, 1972, 1974; Tauson, 1974; Groves and McCarthy, 1978; Taylor, 1979a; Lehmann, 1982; Taylor and Wall, 1992).

Taylor (1988) concluded that, across a broad range of physical and chemical conditions, resurgent boiling is a viable mechanism for mobilising substantial amounts of Sn that can be readily accommodated in many granitoid magmas. Taylor (1988) suggested that large quantities of Sn can be efficiently extracted from the magmas by relatively dilute, supercritical Cl solutions, and transported as a complex series of Cl-bearing stannous species. However, if the chlorinity of the fluid coexisting with melt is low, less Sn will be partitioned into the fluid. This may be an important parameter influencing the formation of magmatic cassiterite (Linnen, 1998). Without a good understanding of the solubility systematics of Sn in natural granitic magmas, and a knowledge of the solubility of Sn in Cl-bearing melts (+Cl-bearing fluid), it is difficult to predict the influence of these or other mechanisms that control the distribution of Sn in granitic rocks. In this respect, the solubility behavior of Sn in natural granitic systems containing halogens (Cl, F) has received little systematic attention.

Studies on ongonites (subvolcanic analogues of Li–F granites) show that Sn accumulates in the residual magma and may reach concentrations high enough to promote SnO_2 precipitation. Other examples of this level of accumulation include the Beauvoir Granite (Cuney et al., 1992), which is an example of a Li–F granite containing disseminated SnO_2, and the Macusani glasses (Pichavant et al., 1987). The presence of B and F in granite magmas results in the reorganisation of melt structure (Manning, 1981) by promoting depolymerisation and the creation of new complex species in the melt. In this process, the number of structurally favorable sites for incorporation of lithophile elements such as Sn increases, which may result in enhanced solubility of these elements (Manning, 1981; Pollard et al., 1987).

Ryabchikov et al. (1978a,b) were the first to study the solubility of SnO_2 in a synthetic granitic system under geologically relevant conditions. They determined that at 750 °C, 1.5 kbar, and fO_2 buffered by the nickel–nickel oxide assemblage (Ni–NiO), a haplogranite melt saturated with SnO_2, fluorite, and topaz, and in equilibrium with a 4.0 M chloride solution contained 1100 (±500) ppm SnO_2. Štemprok and Voldán (1978) determined the concentration of Sn in SnO_2-saturated natural granite and sodium disilicate glass at 1300–1600 °C, at oxygen fugacities controlled by atmospheric pressure. They found that the Sn concentration in equilibrium with cassiterite ranged from 5 to 7 wt.% SnO_2 at 1300 °C, up to 20 wt.% at 1600 °C, and was directly proportional to the Na content of the peralkaline glasses. Equal concentrations of stannic and stannous ions in basaltic liquids (hawaiite) at 1200 °C and at oxygen fugacity