Experimental techniques for determining tin solubility in silicate melts using silica capsules in 1 atm furnaces and rhenium capsules in the piston cylinder

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ABSTRACT

The reactivity, oxygen fugacity, volatility, and wetting properties of tin complicate experimental work in tin-bearing systems. Open-graphite and vitreous-carbon crucibles may be used for preparing tin-rich glass starting materials. Such glasses are prepared by fusing mixtures of stannous oxalate with oxides, crushed rocks, or silicate gels. Decomposition of SnC$_2$O$_4$ into CO+CO$_2$ and SnO provides a reducing atmosphere for the incorporation of Sn$^{4+}$ into the silicate melt, while Sn$^{2+}$ provides an effective flux. Such melts can incorporate Sn far in excess of any reasonable abundance of this element in natural silicate magmas. Experiments where constant bulk composition is required are best conducted in sealed crucibles because SnO is lost as gas. Evacuated silica tubes may be used for such purposes if saturation in SiO$_2$ is desired; however, oxygen fugacity cannot be independently controlled. Rhenium metal is a useful crucible material for relatively reduced Sn-bearing experiments (below oxidation to ReO$_2$), and the coexistence of metallic Sn and stannic oxide controls oxygen fugacity. Adverse mechanical properties inherent to Re, such as work-hardening and embrittlement, are addressed by the use of thick-walled capsules in the piston-cylinder apparatus. Such capsules behave elastically at temperatures of geological interest (~1100 °C), producing higher sample pressures than those provided by the surrounding solid media. These high sample pressures are found to partially relax in week-long experiments. Sealed graphite, sintered SnO$_2$, and Re-foil capsules are plausible crucible materials for Sn-bearing experiments, but may only be used if their porosity and brittleness can be moderated.

Keywords: Tin solubility, cassiterite, rhenium, piston cylinder

INTRODUCTION

Tin is concentrated in granitic and rhyolitic rocks via fractional crystallization of silicic magmas and through dissolution and precipitation of tin from magmatic-hydrothermal and lower-temperature hydrothermal fluids. In some situations, extreme differentiation of felsic magmas generates cassiterite mineralization (Tischendorf 1977). Recent studies have determined that the concentrations of tin in chemically specialized granitic melts range from tens to hundreds of parts per million and, more rarely, to thousands of parts per million (Webster et al. 2004; Thomas et al. 2005, 2006). To better understand how tin is dissolved and concentrated to form hydrothermal cassiterite deposits, however, we need improved constraints on cassiterite solubility in silicate melts, but the determination of cassiterite solubility in silicate melts has been limited by various experimental challenges.

The successful determination of Sn solubility in silicate melts includes the solution to one or more of the following experimental problems.

1) Oxygen fugacity ($f_{O_2}$) has to be controlled because the solubility of the Sn cation in a silicate melt is highly dependent on its valence state. At relatively low temperatures, Sn$^{4+}$ is sparingly soluble, while Sn$^{2+}$ is readily incorporated into the silicate melt structure. This dependency was initially established for Sn-SiO$_2$ glasses by Keysselitz and Kohlmeyer (1933) and recently quantified by Linnen et al. (1995, 1996) for a portion of the H$_2$O-Na$_2$O-K$_2$O-Al$_2$O$_3$-SiO$_2$ system.

2) Mass exchanges between the crucible and the melt (such as loss of Sn to a noble-metal capsule) are to be avoided, since prolonged exposure to Sn may lead to the failure of crucible materials. In addition, steady-state run products may be misinterpreted as equilibrium assemblages.

3) Loss of gaseous SnO to the furnace atmosphere leads to progressive changes in the bulk composition of the melt. Such changes in bulk composition also limit the use of gas mixing control of $f_{O_2}$. The volatility of dissolved SnO is not recognized in the geological literature, although vapor-pressure measurements over mixtures of Sn$^+$ and SnO$_2$ do exist (Colin et al. 1965; Plateeuw and Meyer 1956; Spandau and Ullrich 1953). Furthermore, volatilization of SnO from slags produced during the smelting of Sn ore has been suggested as an extraction method (Barret et al. 1975; Deb-Roy et al. 1978; Decroly et al. 1967).

A synopsis of experimental methods that may be used in the production of Sn-rich silicate glasses, including a new technique involving Re capsules that successfully solves these problems, is presented below.

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