



Tungsten solubility in evolved granitic melts: An evaluation of magmatic wolframite

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Abstract

A variety of parameters that potentially control the solubilities of synthetic hubnerite (MnWO_4) and ferberite (FeWO_4) in haplogranitic melts rich in fluxing compounds have been determined at 200 MPa in order to test the hypothesis that wolframite can occur as a magmatic mineral. The melts, considered representative of highly evolved pegmatites, contain 1.1, 1.7 and 2.02 wt.% of Li_2O , P_2O_5 , and B_2O_3 , respectively. Although the molar $\text{Al}/(\text{Na} + \text{K})$ ratio is one, if Li is considered to be an alkali element the molar $\text{Al}/(\text{Na} + \text{K} + \text{Li})$ (ASi_{Li}) of the melt is 0.88, and the melt is peralkaline. Hubnerite and ferberite solubilities at 800 °C are strongly controlled by melt composition. They are much lower in subaluminous melt, ($\text{ASi}_{\text{Li}} = 1.05$), than in peralkaline melt. By contrast, hubnerite and ferberite solubilities are nearly independent of the fluorine content of the melt, for up to 8 wt.% F. Hubnerite and ferberite solubilities at 800 °C are also nearly independent of oxygen fugacity over a $\log f_{\text{O}_2}$ range of approximately $\text{Ni-NiO} - 3$ to $\text{Ni-NiO} + 2$, which implies that the predominant oxidation state of tungsten in the melts is +6, even at moderately reduced conditions. A series of experiments on haplogranitic melt, rich in fluxing compounds, with 0 and 6 wt.% F at 850–650 °C shows that temperature strongly influences hubnerite solubility, e.g., the solubility product of hubnerite ($K_{\text{sp}}^{\text{hub}}$) in the melts with 6 wt.% F decreases from $71.0 \pm 7.9 \times 10^{-4} \text{ mol}^2/\text{kg}^2$ at 850 °C to $4.4 \pm 2.3 \times 10^{-4} \text{ mol}^2/\text{kg}^2$ at 650 °C.

Our experimental results show that ferberite solubilities are much higher than those of hubnerite with the same composition of melt, but the Mn, Fe and W concentrations in natural melt inclusions indicate that these melts were undersaturated with wolframite at 800 °C. However, flux-rich melts crystallize at lower temperatures in nature and the occurrence of natural, magmatic wolframite was evaluated by comparing experimental solubility product values extrapolated to 500 °C with wolframite activities at these temperatures. Magmatic wolframite is unlikely in flux-rich peralkaline melts but by contrast, flux-rich subaluminous to peraluminous melt inclusions appear to have been saturated with wolframite at approximately 500 °C. Because of the strong temperature dependence of wolframite solubility the dominant effect of fluxing compounds is to lower the solidus temperature of the melt.

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1. INTRODUCTION

Tungsten deposits are generally associated with granitic rocks and are products of hydrothermal processes. They form vein, stockwork and skarn-hosted deposits. However, there are also occurrences of wolframite in granites or pegmatites that appear to be magmatic in origin (Breiter and Škoda, 2004; Alekseev et al., 2011; Che et al., 2011). The purpose of the current study is to evaluate whether wolframite can directly crystallize from magma. Štemprok (1990) reviewed experimental work on the solubility of tungsten in silicate melts and concluded that more than 1000 ppm WO_3 is required for granitic melts to be saturated in WO_3 at 750–800 °C. By comparing the experimental data with the tungsten whole-rock concentrations (lower than 12 ppm), he concluded that W-bearing minerals should be undersaturated even in natural highly evolved granites. Recent studies show that tungsten concentration in granites or pegmatites can be much higher than 12 ppm tungsten (e.g., Breiter et al., 1997; Förster et al., 1999).

It should be noted that whole-rock tungsten concentrations depend on mineral-melt tungsten partition coefficients and the extent of fractional crystallization. Whole-rock tungsten concentrations are most likely controlled by the degree of crystallization and the abundances and mineralogy of micas and oxide minerals (see Linnen and Cuney, 2005 and the references therein). A similar relationship holds true for lithium and fluorine. Their whole-rock abundances are largely controlled by the degree of crystallization and the amount and type of mica in the rock (London, 2008), i.e., in a highly fractionated melt if only quartz and feldspar crystallize the resulting rock will have a low tungsten content, but if micas also crystallize the resulting rock will have a much higher tungsten content. Given these relationships it is not surprising that tungsten-rich rocks are commonly also lithium- and fluorine-rich.

Analyses of melt inclusions should give a more reliable estimate of the tungsten concentrations in melts than whole-rock values, because they are not dependent on the modal proportions of micas and oxide minerals. Rickers et al. (2006) reported up to 292 ppm tungsten for melt inclusions from the Ehrenfriedersdorf pegmatite; Zajacz et al. (2008) measured an average of 112 ± 19 ppm tungsten in melt inclusions from this pegmatite. The concentrations of tungsten in natural melts that appear to have been saturated with wolframite thus are on the order of a few hundred ppm tungsten. If the source melts were on the order of 10 ppm, the presence of magmatic wolframite $[(\text{Mn},\text{Fe})\text{WO}_4]$ likely indicates >95% fractional crystallization.

There have been some recent experimental studies of wolframite solubility in granitic melts (e.g., Linnen, 1998, 2005; Linnen and Cuney, 2005). However, several parameters need to be investigated to constrain tungsten solubility in evolved granitic or pegmatitic melts. Temperature is an important parameter that can affect the solubility of tungsten in the melt (Manning and Henderson, 1984; Štemprok, 1990), but Manning and Henderson (1984) used sodium tungstate gel and Štemprok (1990) used tungstic oxide and sodium tungstate gels as starting materials and did

not determine wolframite solubility. Linnen (1998) reported the solubility of hubnerite as a function of Li content in fluid-saturated haplogranitic melt at 800 and 1035 °C and 200 MPa. His results showed that wolframite solubility is temperature-dependent, but solubilities were determined at only two temperatures, which is not enough data to unambiguously characterize the effects of temperature.

The abundances of fluxing compounds in the melt, e.g., H_2O , Li, F, B, and P are also important, as noted above. Linnen (2005) showed that the solubility of hubnerite is nearly constant in granitic melts with water concentrations higher than ~2 wt.% and Linnen (1998) demonstrated that wolframite solubility is independent of Li content in fluid-saturated haplogranitic melts, where the molar $\text{Al}/(\text{Na} + \text{K} + \text{Li})$ and Na/K ratios are constant.

The fluorine content of the melt is known to affect the solubilities of zircon, rutile and hafnon in granitic melts (Keppler, 1993; Aseri and Linnen, 2011), although recent work by Fiege et al. (2011) indicates that the solubilities of manganotantalite (MnTa_2O_6) and manganocolumbite (MnNb_2O_6) in granitic melts are not affected by fluorine. The influence of fluorine on the solubility of wolframite in melts has not been investigated, yet some of the granites related to tungsten deposits are fluorine-rich. The effects of boron and phosphorous on the solubility of the wolframite in the melt similarly are not known.

The role of oxygen fugacity (f_{O_2}) on wolframite solubility in granitic and pegmatitic melt has also received little attention. Ertel et al. (1996) determined that tungsten is dissolved in haplobasaltic melt in the +4 valence state at temperatures ranging from 1300 to 1600 °C and $\log f_{\text{O}_2}$ values of approximately –9 to –14. However, O’Neill et al. (2008) reported that the predominant valence state of tungsten in silicate melt at 1400 °C is +6 by using $\text{CO}-\text{CO}_2$ and H_2-CO_2 gas mixtures to control the f_{O_2} . The valence states of tungsten in granitic or pegmatitic melts at temperatures lower than 1000 °C are still not known.

Hubnerite solubility is also affected by alumina saturation index (molar $\text{Al}/(\text{Na} + \text{K})$) in granitic melts (Linnen and Cuney, 2005), but the effects of melt composition remain poorly constrained. In particular, the solubility of wolframite has not been investigated in pegmatitic liquids that commonly contain high amounts of F, Li, B, and P. Consequently, four series of experiments were designed to examine the effects of fluorine, temperature, f_{O_2} and ASI on the wolframite solubility in fluid-saturated, flux-rich haplogranitic melts.

2. EXPERIMENTAL METHOD

2.1. Starting materials

Experiments utilized a hydrous haplogranitic starting glass doped with constant amounts of phosphorus, boron, lithium, and different amounts of fluorine. The starting glass has an aluminum saturation index ($\text{ASI} = \text{molar Al}/(\text{Na} + \text{K})$) of 1.0 (Table 1) with a composition that corresponds to the projection of the granite minimum caused by phosphorous addition to the intersection of the Ab–Or tie line in the Q–Ab–Or system ($\text{Ab}_{72}\text{Or}_{28}$ on weight basis;

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