Stability of Laurite Under Controlled Oxygen and Sulfur Activities at Magmatic Temperature – An Experimental Study

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Abstract

We present experimental results on the stability of RuS_2 and FeS at magmatic temperature and controlled f_{O2} and f_{S2}. Our results show that an Fe-dominated monosulfide liquid solution has a larger stability field in T-f_{S2} space than crystalline RuS_2. The slope of the Ru-RuS_2 equilibrium in log a_{S2}-$1/T$ space is less sensitive to temperature than implied by the thermodynamic data. Consequently, laurite solid solution (Ru, Os, Ir)S_2 cannot crystallize directly out of a basaltic melt that is undersaturated with respect to monosulfide liquid solution, contrary to petrographic evidence. As such, it is unable to fractionate PGEs at magmatic temperature relative to each other.

Introduction

Numerous studies have shown that the IPGE (Ru, Os, Ir) behave differently in magmatic systems relative to the less refractory PPGE (Pt, Rh, Pd). IPGE are commonly enriched in chromian spinel in chromitite ore whereas PPGE are enriched in basaltic melt. PGE patterns normalized to chondrite are nearly complementary to each other. The reasons may be founded in different solubilities of the PGEs in silicate melt (Borisov and Palme 2000 and refs. therein). With the exception of Pt, the PPGE are more soluble in basalt than the IPGE at given f_{O2}, by about an order of magnitude. Consequently, PGE fractionation could be accomplished by fractionation of discrete PGE phases of the least soluble noble metals. A monosulfide liquid solution would be unable to fractionate the PGEs relative to each other because the sulfide-silicate partition coefficients are too large.

It is not surprising that discrete PGEs are quite common in chromitite ore and that they are dominated by the least soluble noble metals Os, Ir, and Ru (cf. Legendre and Auge 1986, Talkington and Lipin 1986). A particularly interesting case in point is laurite RuS_2 as laurite would theoretically be able to fractionate the IPGE from the PPGE (cf. Brenan and Andrews 2001). Laurite frequently occurs as euhedral inclusions within chromian spinel of chromitite ore from both layered intrusions and ophiolites (Stockman and Hlava

1984). Based on petrographic evidence it appears that laurite may be a liquidus phase that co-precipitated with chromite. The preference toward chromite may be reflecting an epitactic relationship with the chromite lattice, perhaps necessary to facilitate laurite crystallization by heterogeneous nucleation (Hiemstra 1979).

The fundamental question is – can crystalline sulfide minerals such as laurite nucleate directly from a silicate melt (Peck et al. 1992)? Available thermodynamic data (Barin 1995) suggest otherwise: The log a_{S2} - $1/T$ stability field of crystalline RuS_2 at magmatic temperature is considerably smaller than that of crystalline $Fe_{1-x}S$ or Fe-dominated monosulfide liquid solution. Therefore, a basaltic melt would first exsolve a monosulfide liquid solution before laurite would be a stable phase. A sulfide melt should prevent laurite from crystallizing at magmatic temperature as the common textural association with chromite implies. Ru concentrations in average basaltic melt ($\sim$ 4 ppb) are so low that all Ru would immediately be taken up by the sulfide melt.

Experimental techniques

To evaluate existing thermodynamic data for Ru and RuS_2, we calibrated the Ru-RuS_2 equilibrium in T-f_{S2} space at 1 atm under controlled temperature and sulfur activity. Sulfur activity in equilibrium with crystalline Ru and RuS_2 is given by

$$\log a_{S2} = \Delta G^\circ_{f,T}/(2.303RT).$$

In the presence of crystalline Ru and RuS_2, it is only a function of the free energy of formation of RuS_2 from the elements ($\Delta G^\circ_{f,T}$) at the temperature of interest.

All experiments were performed with CO-CO_2-SO_2 gas mixture and temperatures from 900-1200°C using a vertical tube furnace. f_{O2} and f_{S2} imposed by the CO-CO_2-SO_2 mixtures were calculated using thermodynamic data of Gurvich et al. (1989). Care was taken that the oxygen activity imposed by the gas mixture was within the stability field of Ru metal. Oxygen fugacities imposed by the gas mixture usually were close to the iron-wuestite equilibrium. Temperatures were monitored

using a type B thermocouple (Pt_6Rh - $Pt_{30}Rh$) calibrated against the melting point of gold. Gas mixtures were controlled using Millipore flow meters calibrated against Ar, to a precicion of 0.03 percent. All experiments were done in corundum crucibles with run times ranging from 1 to 20 h depending on temperature. The results reported here used 10 mg starting mix of either Ru or RuS_2 powders and are reversal experiments. Reaction rates were quantified by measuring weight changes using a micro-scale, to a precision of 100 µg. Run products either are metallic Ru or RuS_2 and were analyzed with X-ray powder difraction.

Results and discussion

Experimental results are summarized in Fig. 1 as a function of $1/T$ and $\log a_{S2}$. Also shown is the slope of the Ru-RuS_2 equilibrium calculated with thermodynamic data of Barin (1995). Our experimentally determined slope in $\log a_{S2}$-$1/T$ space is less sensitive to temperature than the one calculated with the thermodynamic data, implying that standard enthalpies of RuS_2 tabulated by Barin

(1995) may be slightly in error. The melting point of RuS_2 is above 1200°C. For savety reasons, we have limited our experimental temperatures to 1200°C, so we are as yet unable to determine coexistence of crystalline Ru and RuS_2 with a ruthenium sulfide liquid, i.e. an invariant point in $\log a_{S2}$-$1/T$ space.

Discussion

The stability field of RuS_2, at a temperature where chromite is a liquidus phase (~ 1200°C), is smaller than implied by the thermodynamic data and shifted to higher sulfur activities. To test if RuS_2 could theoretically crystallize directly out of a sulfur-bearing silicate melt, we have also carried out one reconnaissance experiment using powdered Fe and FeS as starting mixes. These were reacted with gas mixtures in equilibrium metallic Ru. At 1200°C and sulfur activity one log unit below the Ru-RuS_2 equilibrium, both metallic Fe powder and crystal-line $Fe_{1-x}S$ react within 3 hours to sulfide liquid.
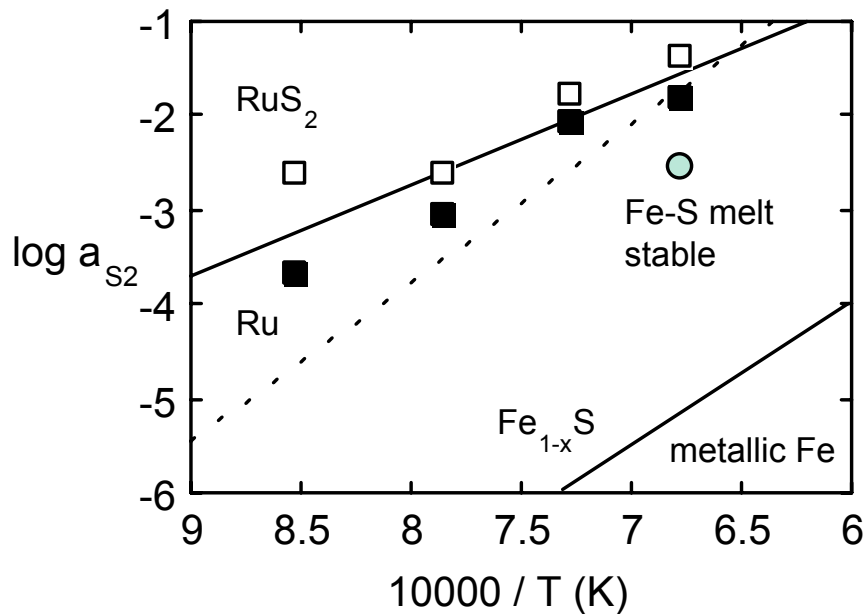

Figure 1. *Stability of Ru and RuS$_2$ as a function of inverse temperature (K) and sulfur activity. All experiments shown are reversal experiments. The solid line is a linear fit to the experimental data. Filled symbols (inside Ru stability) used RuS$_2$ as starting mix, open squares (RuS$_2$ stability field) used metallic Ru. The equilibrium calculated with Barin's (1995) data is shown by the dashed line. The stability limit (solid line separating FeS and monosulfide liquid solution from metallic Fe) is from Toulmin and Barton (1964). The shaded circle represents one experiment with Fe and FeS as starting mix, equilibrated with a gas atmosphere stable with metallic Ru (see text). The liquidus temperature of an average, chromite-saturated basaltic melt (about 1200°C) corresponds to about 6.8 on the x-axis.*

According to these results, a basaltic melt is unable to crystallize laurite as a liquidus phase directly out of silicate melt. The FeS stability field (where FeS refers to both crystalline sulfide and monosulfide liquid solution) is considerably larger than that of RuS_2. Sulfur activities defined by the Ru-RuS_2 equilibrium lie well within the stability field of a monosulfide liquid solution. According to this data, euhedral laurite crystals included in chromite are unlikely to be magmatic liquidus phases from sulfur-undersaturated basaltic melt. They do not crystallize directly out of a basaltic melt, contrary to petrographic observations. Alternative models of origin must therefore be sought.

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