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

C. Bockrath, A. Holzheid and C. Ballhaus
Institut für Mineralogie, Universität Münster, Corrensstrasse 24, 48149 Münster (Germany)
Email: bockrat@nwz.uni-muenster.de

Abstract
We present experimental results on the stability of RuS₂ and FeS at magmatic temperature and controlled fO₂ and fS². Our results show that an Fe-dominated monosulfide liquid solution has a larger stability field in T-fS² space than crystalline RuS₂. The slope of the Ru-RuS₂ equilibrium in log aS²-1/T space is less sensitive to temperature than implied by the thermodynamic data. Consequently, laurite solid solution (Ru, Os, Ir)S₂ 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 fO₂, 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 RuS₂ 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 aS² - 1/T stability field of crystalline RuS₂ at magmatic temperature is considerably smaller than that of crystalline Fe₁₋ₓS 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 (~ 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 RuS₂, we calibrated the Ru-RuS₂ equilibrium in T-fS₂ space at 1 atm under controlled temperature and sulfur activity. Sulfur activity in equilibrium with crystalline Ru and RuS₂ is given by

\[
\log a_{S^2} = \frac{\Delta G_f^o}{(2.303RT)}. 
\]

In the presence of crystalline Ru and RuS₂, it is only a function of the free energy of formation of RuS₂ from the elements (\(\Delta G_f^o\)) at the temperature of interest.

All experiments were performed with CO-CO₂ gas mixture and temperatures from 900-1200°C using a vertical tube furnace. fS₂ and fO₂ imposed by the CO-CO₂-SO₂ 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-wustite equilibrium. Temperatures were monitored
using a type B thermocouple (Pt<sub>Rh</sub> - Pt<sub>Rh</sub>) calibrated against the melting point of gold. Gas mixtures were controlled using Millipore flow meters calibrated against Ar, to a precision 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<sub>2</sub> 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<sub>2</sub> and were analyzed with X-ray powder diffraction.

**Results and discussion**

Experimental results are summarized in Fig. 1 as a function of 1/T and log a<sub>S2</sub>. Also shown is the slope of the Ru-RuS<sub>2</sub> equilibrium calculated with thermodynamic data of Barin (1995). Our experimentally determined slope in log a<sub>S2</sub>-1/T space is less sensitive to temperature than the one calculated with the thermodynamic data, implying that standard enthalpies of RuS<sub>2</sub> tabulated by Barin (1995) may be slightly in error. The melting point of RuS<sub>2</sub> is above 1200°C. For safety reasons, we have limited our experimental temperatures to 1200°C, so we are as yet unable to determine coexistence of crystalline Ru and RuS<sub>2</sub> with a ruthenium sulfide liquid, i.e. an invariant point in log a<sub>S2</sub>-1/T space.

**Discussion**

The stability field of RuS<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> equilibrium, both metallic Fe powder and crystalline Fe<sub>1-x</sub>S react within 3 hours to sulfide liquid.

![Figure 1. Stability of Ru and RuS<sub>2</sub> 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<sub>2</sub> as starting mix, open squares (RuS<sub>2</sub> 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.](image-url)
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 RuS₂. Sulfur activities defined by the Ru-RuS₂ 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.

References