Ruthenium solubility in hematite

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ABSTRACT

Solid binary oxides of the platinum-group elements (PGE) decompose on heating in air to metal, oxygen, and often, a mixture of volatile PGE oxides. Compared to most other transition metal oxides, these decomposition temperatures are low, generally below 1100 °C. The modest exception is RuO₂, which remains stable in air until 1400 °C. Because of its comparatively high oxide stability, Ru, among all the PGE, is the one with the greatest potential for a significant oxidic, i.e., lithophile, geochemistry. A series of 1 atm phase equilibrium experiments were made to establish the limits of solid solution of Ru in hematite (Fe₂O₃) and help evaluate the significance of the oxidic geochemistry of Ru.

The solid-solution limit for Ru in hematite may be represented by the following oxidation-reduction reaction:

$$2RuO_2 + Fe_2O_3 = 2FeRuO_3 + 1/2O_2$$
.

Experiments equilibrated between 1012 and 1490 °C were buffered with respect to oxygen fugacity by the coexistence of Ru metal and solid RuO₂, both as essentially pure phases. Solution of Ru in hematite is enhanced at lower oxygen fugacity, but reaches a maximum fixed by the presence of Ru metal. An endothermic enthalpy for the reaction (188.1 \pm 0.7 kJ/mol) was retrieved from the redox-controlled solubilities was as a regular solution interaction parameter (18.5 \pm 0.5 kJ/mol) that indicated small positive deviations from ideality in the solid-solution region investigated. Estimates based on the new data for solubilities of Ru in a rhombohedral oxide at geologic conditions suggest that natural concentrations might be accommodated at high temperatures without saturation in Ru metal, but that exsolution of Ru metal from oxides would be favored at low temperature.