**EXPERIMENTAL DETERMINATION OF SPINEL/MELT, OLIVINE/MELT, AND PYROXENE/MELT PARTITION COEFFICIENTS FOR Re, Ru, Pd, Au, AND Pt.** K. Righter<sup>1</sup>, A.J. Campbell<sup>2</sup> and M. Humayun<sup>2</sup>; <sup>1</sup>NASA Johnson Space Center, Mail Code ST, Houston, TX 77058, kevin.righter-1@nasa.gov; <sup>2</sup>Department of the Geophysical Sciences, The University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637.

# Introduction

Experimental studies identified have spinels as important hosts phases for many of the highly siderophile elements (HSE) [1-4]. Yet experimental studies involving chromite or Cr-rich spinel have been lacking. Experimental studies of partitioning of HSEs between silicate, oxides and silicate melt are plagued by low solubilities and the presence of small metallic nuggets at oxygen fugacities relevant to magmas, which interfere with analysis of the phases of interest [5]. We have circumvented these problems in two ways: 1) performing experiments at oxidized conditions, which are still relevant to natural systems but in which nuggets are not observed, and 2) analysis of run products with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), allowing a combination of high sensitivity and good spatial resolution.

### **Experimental and analytical**

Partition coefficients for Re, Ru, Pd, Au and Pt have been measured using three different compositions. Ankaramite, doped with Cr<sub>2</sub>O<sub>3</sub>, encapsulated with AuPd tubing, and buffered with Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub> and MnO-Mn<sub>3</sub>O<sub>4</sub>, was used to study spinel/melt and olivine/melt partitioning. Two synthetic basalts, encapsulated by Pt and buffered with Ni-NiO and Ru-RuO<sub>2</sub>, were used to study spinel/melt and clinopyroxene/melt partitioning. The 1 bar experiments were carried out in evacuated silica tubes, and the 20 kbar experiments were carried out in a piston cylinder apparatus. An electron microprobe was used to analyze major elements in all phases, and Ru and Rh in some spinels. Highly siderophile elements were measured by LA-ICP-MS, using 100  $\mu$ m, 50  $\mu$ m and 25  $\mu$ m spot sizes, respectively, in glass, olivine and spinel. HSE abundances were determined relative to MgO contents of the phases, which were analyzed independently by electron microprobe. The absence of nuggets was inferred from the smooth quality of the time dependent LA-ICP-MS signals, the reproducibility of analyses in adjacent regions of the glass, and the agreement with HSE solubility studies [6-11].

# Results

When our new results for Ru (Table 1) are combined with previous results [1]. it is evident that spinel/melt partition coefficients for Ru are highest at the lowest oxygen fugacities (D = 1100-2300), and/or when the spinel is inverse such as magnetite (# 118; D = 870). These results suggest that both inverse and chromian spinels can be important hosts for Ru at mantle oxygen fugacities, in agreement with partition coefficients inferred from komatiite lava lakes (D(Ru) spinel/melt = 151; [12]). On the other hand, Re is incompatible in all spinels produced experi-These trends may reflect mentally so far. higher valences for Re and Ru at oxidized conditions (6+ and 4+), compared to reduced conditions (3+?). Platinum is compatible, whereas Re is incompatible in clinopyroxene (Table 1). Ruthenium, Au and Pd are incompatible in olivine (Table 1), in agreement with previous experimental work [1,3].

### Applications

Correlations of Ru, Ir and Rh with Cr and MgO observed in komatiites and basaltic komatiites from Kostomuksha (Figure 1) [12], Cape Smith [13], and the Vetreny Belt [14] can all be explained by a combination of olivine and chromite fractionation, using the partitioning results from this study. Incompatibility of Re in oceanic basalt suites [15,16] is also supported by our measured D(Re) spinel/melt <<1. In addition, the mildly compatible nature of Pt in clinopyroxene (D(Pt) cpx/melt = 1.5), together with the affinity of Pt for sulfide melt [17,18] can explain the very similar Pt concentrations observed in martian clinopyroxeneites (sulfidebearing; [19]) and shergottite basalts. Application of these new results will also be made to Apollo 12 and 15 basalt suites.

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 Table 1: Summary of experimental conditions and partition coefficients

| run                | 158  | 118                 | 153         |
|--------------------|--|---------------------|-------------|
| phase              | sp, ol   | sp                  | cpx         |
| P, T (°C)          | 1 bar, 1300  | 20 kb, 1275         | 1 bar, 1300 |
| buffer             | Fe <sub>2</sub> O <sub>3</sub> -Fe <sub>3</sub> O <sub>4</sub> | Ru-RuO <sub>2</sub> | Ni-NiO      |
| logfO <sub>2</sub> | -1.5   | -1.3                | -6.7        |
| D(Re)              | -  | -                   | 0.18        |
| D(Ru)              | 76, 0.24   | 870                 | -           |
| D(Pd)              | 0.14, 0.12   | -                   | -           |
| D(Pt)              | -  | -                   | 1.50        |
| D(Au)              | 0.08, 0.13   | -                   | -           |

#### References:

[1] Capobianco, C. J., R. L. Hervig and M.J. Drake (1994) Chemical Geology 113, 23-43; [2] Capobianco, C. J. and M. J. Drake (1990) Geochimica et Cosmochimica Acta 54, 869-874; [3] Capobianco, C. J., M.J. Drake, and Rogers, P.S.Z (1991) Lunar Planet. Sci. XXII, 179-180; [4] Righter, K. and R.T. Downs (2001) Geophysical Research Letters 28, 619-622; [5] Lindstrom, D.J. and Jones, J.H. (1996) Geochimica et Cosmochimica Acta 60, 1195-1203; [6] Borisov A. and Palme H. (1995) Geochim. Cosmochim. Acta 59, 481-485; [7] Borisov, A. and H. Palme (1996) Mineralogy and Petrology 56, 297-312; [8] Borisov, A. and Nachtweyh, K. (1998) Lunar. Planet. Sci. XXIX, abstract #1320; [9] Ertel, W., O'Neill, H.St.C., Sylvester, P.J. and Dingwell, D.B. (1999) Geochimica et Cosmochimica Acta 63, 2439-2449; [10] Ertel, W., O'Neill, H.St.C., Svlvester, P.J., Dingwell, D.B. and B. Spettel (2001) Geochimica et Cosmochimica Acta 65, 2161-2170; [11] Righter K, Drake MJ. (1997) Earth Planet.

Sci. Lett. 146:541-53; [12] Puchtel I. and Humayun, M. (2000) Geochimica et Cosmochimica Acta 64, 4227-4242; [13] Barnes, S.-J. and Picard, C.P., 1993. Geochim. Cosmochim. Acta 57, 79-87; [14] Puchtel I. and Humayun, M. (2001) Geochimica et Cosmochimica Acta 65, 2979-2993; [15] Hertogen J., Janssens M.-J. and Palme H. (1980) Geochim. Cosmochim. Acta 44, 2125-2143; [16] Righter, K., Chesley, J.T., Geist, D. and Ruiz, J. (1998) Journal of Petrology 39, 785-795; [17] Fleet, M. E., W. E. Stone, et al. (1991) Geochimica et Cosmochimica Acta 55, 2545-2554; [18] Fleet, M. E., J. H. Crocket, et al. (1996). Geochimica et Cosmochimica Acta 60, 2397-2412; [19] Bunch, T.E., and A.M. Reid (1975) Meteoritics 10, 303-315; [20] Ghiorso M. S. and Sack R. O. (1994) Contrib. Mineral. Petrol. 119, 197-212.



Figure 1: Cr, Ru and Pd trends with MgO in the Kostomuksha komatiite suite (from [12]). Major element modelling of crystal fractionation of the proposed Kostomuksha parent liquid [12] using the MELTS program [20] is coupled with new partitioning data. Asterisks indicate the calculated trends using the major element results, and D(Ru) and D(Pd) olivine/melt and chromite/melt measured here.