

ACTINIDE ELEMENT FRACTIONATION IN SOLAR SYSTEM PROCESSES: THE ROLE OF OXYGEN FUGACITY; T. Z. La Tourrette, M. L. Johnson, and D. S. Burnett, Division of Geological and Planetary Sciences, 170-25 Caltech, Pasadena, CA, 91125.

Because of their high degree of incompatibility in igneous processes and overall chemical similarities, relatively little fractionation of actinides is expected in planetary materials. While there is a strong coherence for U and Th [1], there are well documented internal fractionations in ordinary chondrites (e.g. [2,3]), in CAIs [4], and in terrestrial basalts [5]. The mechanisms responsible for these fractionations are still unknown, but since U is multivalent and Th is solely tetravalent, oxygen fugacity can play a major role in the relative partitioning of U and Th. Experiments have been carried out to assess the role of oxygen fugacity (fO_2) on the partitioning of U between diopsidic pyroxene and melt.

During planetary differentiation, actinide elements are highly concentrated in the crust, but significant fractionation of U and Th can occur. The magnitude of this fractionation in terrestrial volcanic rocks is best revealed by ^{238}U - ^{230}Th isotopic disequilibrium. Th/U enrichments as high as 60% have been observed in MORBs [6]. Significant Th/U enhancements are also observed in Apollo 17 mare basalts (e.g. [7]). An understanding of these fractionations is important because: 1) U-Th fractionations may provide unique clues to planetary melting processes. Some workers believe that ^{230}Th disequilibrium can only be produced by very small degrees of partial melting [8]. 2) In principle whole-planet U, Th, and K concentrations can be obtained by combining relative abundances from crustal samples with the average global heat flux (e.g. [1]). In the next 10 years orbiting gamma ray spectrometers (Mars Observer, Lunar Geophysical Orbiter) will obtain important new data for U, Th, and K for the Moon and Mars, which can be used to address both problems, but a better understanding of actinide fractionation mechanisms is required.

U-Th fractionation in CAIs has generally been attributed to the higher volatility of U [9,4]. Compounds of U^{+3} are known in the laboratory, and, given the reducing conditions of the solar nebula, it is possible that a significant amount of trivalent as well as tetravalent U was present. We have studied the effect of oxygen fugacity on the crystal-liquid partition coefficient of U (D_U). In clinopyroxene D_U will increase strongly as the U goes from +5 to +3. Since the valence state of Th (hence D_{Th}) will not change, D_{Th}/D_U will change greatly with fO_2 . Oxygen fugacity is the primary factor in determining the valence state of U, and the presence of U^{+3} in our experiments would be good evidence for its importance in the solar nebula.

Experiments were run at one atmosphere and fO_2 was controlled with CO-CO₂ gas mixtures. Clinopyroxene was chosen as the crystal phase, as it is usually regarded as the most important mineral host for lithophile trace elements. The bulk composition was synthetic AbAnDi₂ mixture (by weight) spiked with 50 ppm ^{235}U . The most reducing experiment was run in a graphite crucible in a pure CO atmosphere; all other charges were suspended on Pt loops. Crystals were grown by fractional crystallization, initially melting the charge for 1.5 hours 8 °C above the liquidus (liquidus = 1270 °C), then dropping the temperature to 5 °C below the liquidus, holding it there for 23 hours to nucleate the crystals and allow for fO_2 equilibration, and finally lowering the temperature 1.7 °C/hour to 65 °C below the liquidus. The lowest fO_2 run produced both pyroxene and anorthite. While all runs extended into the plagioclase stability field, plagioclase crystallization is normally not observed for AbAnDi₂. However, all runs show major Na loss, apparently facilitating plagioclase crystallization. U concentrations were determined by fission track radiography.

Data shown in the figure are preliminary at this point, but the measured D_U s are unquestionably small. Each point represents a 3-7 crystal average for a single run, and the error bar is the standard deviation. An approximate fractional crystallization correction (for crystal zoning) has been applied. The data seem to show an increase in D_U

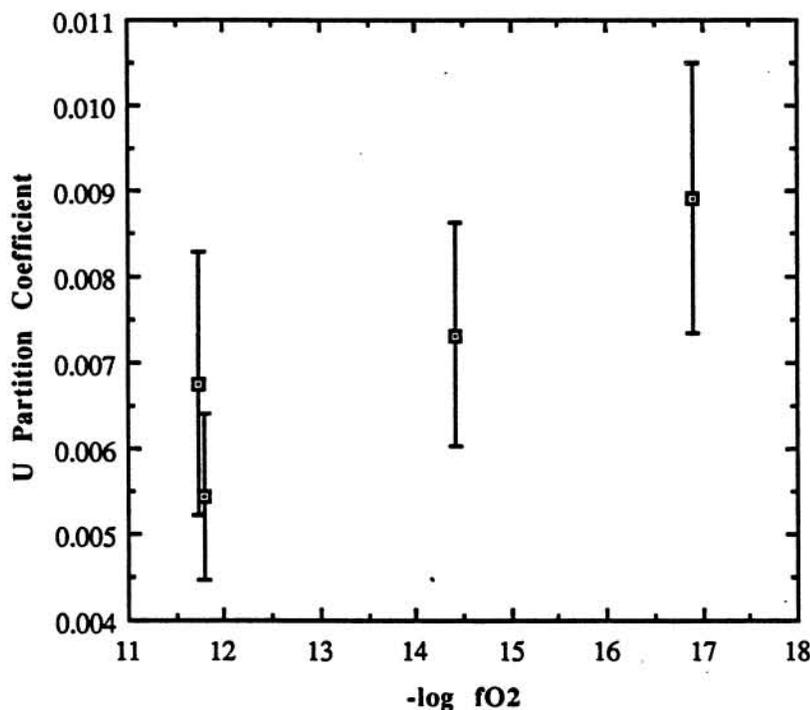
ACTINIDE ELEMENT FRACTIONATION: La Tourrette T. Z. et al.

with decreasing fO_2 , but the relatively large intergrain range for a single run precludes any strong interpretations and the data are consistent with a constant D_U at the limits of error. With further study we should be able to decrease the errors. In the intermediate fO_2 run U is highly concentrated in the Pt wire (apparent Pt-liq partition coefficient of 1.0). A similar result was found by [10] for much more reducing conditions, and the high $D_U(\text{Pt})$ is surprising at an fO_2 within 3 log units of Fe-FeO. The U in the Pt and in the glass is homogeneously distributed. We assume that most of the U had partitioned into the Pt by the onset of crystallization; thus, the Pt has been ignored in calculating $D_U(\text{cpx})$. The crystal-liquid partition coefficients from this run are consistent with the other runs at both lower and higher fO_2 s, which are not affected by U loss to Pt.

The fO_2 s of the experiments span from those of mare basalts and eucrites down to solar nebula conditions. By analogy with La (similar ionic radius), a partition coefficient of 0.05 is expected for purely trivalent U. This is such a large increase that even a small amount of trivalent U should cause a significant change in D_U . The absence of a large increase in the reducing run argues that most of the U was tetravalent, but 10% U^{+3} at the lowest fO_2 cannot be ruled out and this amount would be important. Based on the data of [11], the U in the most oxidizing runs is 50% U^{+5} and 50% U^{+4} . As U is usually regarded as tetravalent in igneous environments, this amount of U^{+5} is surprising, but our results are consistent with [11]. If we assume that $D_U=0$ for U^{+5} , then the slight increase in D_U with decreasing fO_2 is most likely due to an increasing proportion of U^{+4} . Our experiments provide no evidence that U^{+3} is present at lunar or solar nebula fO_2 s, although valence state distributions depend on composition as well as fO_2 [11].

All our clinopyroxene-liquid partition coefficients are 2-3 times lower than a value reported by [12] for the same composition and higher fO_2 . This difference requires further study, but both our lower D_U and the possible importance of U^{+5} makes U-Th fractionation by igneous processes even more difficult to explain. Melt composition is an important variable, and it is possible that the presence of Fe in natural melts helps stabilize U^{+4} .

References: [1] Taylor S. R. (1982) *Lunar Planetary Inst.*, Houston. [2] Crozaz G. et al. (1989) *Earth Planet. Sci. Lett.* 93, 157-169. [3] Murrell M. T. and Burnett D. S. (1983) *Geochim. Cosmochim. Acta* 47, 1999-2014. [4] Murrell M. T. and Burnett D. S. (1987) *Geochim. Cosmochim. Acta* 51, 985-999.



[5] Condomines M. et al. (1988) *Earth Planet. Sci. Lett.* 90, 243-262. [6] Newman S. et al. (1983) *Earth Planet. Sci. Lett.* 65, 17-33. [7] Laul J. C. and Fruchter J. S. (1976) *Proc. Lunar Planet. Sci. Conf. 1*, 1545-1559. [8] McKenzie D. (1985) *Earth Planet. Sci. Lett.* 72, 149-157. [9] Boynton W. V. (1978) *Earth Planet. Sci. Lett.* 40, 175-186. [10] Jones J. H. and Burnett D. S. (1980) *Proc. Lunar Planet. Sci. Conf. 11*, 995-1001. [11] Schreiber H. D. et al. (1981) *Lunar Planet. Sci. XII*, 943-945. [12] Benjamin T. M. et al. (1978) *Proc. Lunar Planet. Sci. Conf. 9*, 1393-1406.