
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 (fO2) 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 238U:230Th 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 230Th 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 fO2. 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 fO2 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 235U. 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 fO2 equilibration, and finally lowering the temperature 1.7 °C/hour to 65 °C below the liquidus. The lowest fO2 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)
with decreasing $f_{O2}$, but the relatively large intergran 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 $f_{O2}$ 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 $D_{U}$(Pt) is surprising at an $f_{O2}$ 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 $D_{U}$(cpx). The crystal-liquid partition coefficients from this run are consistent with the other runs at both lower and higher $f_{O2}$s, which are not affected by U loss to Pt.

The $f_{O2}$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% $U^{4+}$ at the lowest $f_{O2}$ 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 $f_{O2}$ is most likely due to an increasing proportion of $U^{4+}$. Our experiments provide no evidence that $U^{5+}$ is present at lunar or solar nebula $f_{O2}$s, although valence state distributions depend on composition as well as $f_{O2}$ [11].

All our clinopyroxene-liquid partition coefficients are 2-3 times lower than a value reported by [12] for the same composition and higher $f_{O2}$. 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 $U^{4+}$.