

PARTITIONING OF K, U, AND TH BETWEEN SULFIDE AND SILICATE LIQUIDS:
IMPLICATIONS FOR RADIOACTIVE HEATING OF PLANETARY CORES

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Abstract. The possibility of heating of planetary cores by K radioactivity has been extensively discussed, as well as the possibility that K partitioning into the terrestrial core is the reason for the difference between the terrestrial and chondritic K/U. We had previously suggested that U and Th partitioning into FeFeS liquids was more important than K. Laboratory FeFeS liquid, silicate liquid partition coefficient measurements (D) for K, U, and Th were made to test this suggestion. For a basaltic liquid at 1450°C and 1.5 GPa, D_U is 0.013 and D_K is 0.0026; thus U partitioning into FeFeS liquids is 5 times greater than K partitioning under these conditions. There are problems with 1-atm experiments in that they do not appear to equilibrate or reverse. However, measurable U and Th partitioning into sulfide was nearly always observed, but K partitioning was normally not observed ($D_K \lesssim 10^{-4}$). A typical value for D_U from a granitic silicate liquid at one atmosphere, 1150°C, and low f_{O_2} is about 0.02; D_{Th} is similar. At low f_{O_2} and higher temperature, experiments with basaltic liquids produce strong Ca and U partitioning into the sulfide liquid with $D_U > 1$. D_{Th} is less strongly affected. Because of the consistently low D_K/D_U , pressure effects near the core-mantle boundary would need to increase D_K by factors of $\sim 10^3$ with much smaller increases in D_U in order to have the terrestrial K and U abundances at chondritic levels. In addition, if radioactive heating is important for planetary cores, U and Th will be more important than K unless the lower mantle has K/U greater than 10 times chondritic or large changes in partition coefficients with conditions reverse the relative importance of K versus U and Th from our measurements.

Introduction

Many authors have discussed the possibility that radioactive decay is an important heat source within planetary cores; however, radioactive decay is not the only possibility [e.g., Stevenson, 1981; Gubbins and Masters, 1979]. Core heat production rates are very poorly known; a lower limit to sustain convection in the earth's outer core has been estimated to be 5×10^{11} W [Gubbins, 1981]. If this heat is supplied solely by the decay of ^{40}K , the K concentration currently required in the core is about 75 ppm. This is a strong lower limit because radiogenic heating is quite

inefficient. Gubbins's preferred power estimate for the earth's core is closer to 10^{13} W, requiring about 1500 ppm K. The K concentration necessary to maintain a partially molten core for Mercury has been estimated to be greater than 1000 ppm [Toksoz and Johnston, 1978]. In addition to the question of potential heat sources for the core, it has also been proposed that large quantities of K in the terrestrial core could explain the difference between the observed terrestrial K/U (about 1×10^4 by mass) and chondritic values (8×10^4) [Lewis, 1971; Hall and Murthy, 1971]. Finally, the amount of heat entering the earth's mantle from the core is important for understanding mantle dynamics [Jeanloz and Morris, 1986].

Furst et al. [1982] and Murrell and Burnett [1982] found that for the reducing conditions accompanying the formation of enstatite chondrites, U and Th deviated from lithophile character and concentrated in CaS, whereas K remained predominantly lithophile. These authors suggested that U and Th should also be considered in discussions of radioactive heating of planetary cores. (To supply 10^{13} W, the actinide core concentrations currently required, exclusive of any other heat source, are about 50 ppb U or 180 ppb Th.)

This paper reports experimental partitioning studies of K, U, and Th between silicate and FeFeS liquids designed to test the proposal that actinide partitioning into sulfide liquids is more important than K partitioning. The present study also provides a reasonable simulation of the partitioning of the radioactive elements accompanying the separation of metal-sulfide and silicate liquids at low pressures. This is important because equilibration with mantle silicates may have occurred only during the early, low-pressure phase of planetary differentiation [Stevenson, 1981]. Finally, although it is uncertain to what extent the earth's present core and mantle can actually equilibrate [see Stevenson, 1981], our data provide some constraints on the difficult problem of high-pressure partitioning between the core and lower mantle in the sense that they permit the required changes in partition coefficients due to differences between laboratory and core-mantle conditions to be calculated. It should be noted that the interpretations of our data are only valid if S is the most important light element in terrestrial planet cores.

Previous Work

As summarized in Table 1, there have been several previous studies of K partitioning between FeFeS liquids and silicates, both crystalline and liquid [Goettel, 1972, 1975;

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TABLE 1. Previous Determinations of Potassium Partitioning Between Fe-FeS Liquids and Silicates

Capsule Material	Sulfide Liquid Composition ^a	Silicate Composition	P, Pa	T, °C	D _K ^b	Reference
SiO ₂ glass	Fe ₃₄ (FeS) ₆₆	roedderite ^c	1 x 10 ^{5d}	1030	0.030	Goettel [1972]
Fe metal	Fe ₄₇ (FeS) ₅₃	K-feldspar ^e	1 x 10 ⁵	1030	0.0014	Goettel [1975] ^f
Fe metal	Fe ₄₇ (FeS) ₅₃	K-feldspar ^e	1 x 10 ⁵	1070	0.0021	Goettel [1975] ^f
Graphite	Fe ₂₅ (FeS) ₇₅	basalt ^g	1.5 x 10 ⁹	1100	0.0067	Oversby and Ringwood [1973]
Graphite	Fe ₂₅ (FeS) ₇₅	basaltic liquid	0.5 x 10 ⁹	1350	0.015	Oversby and Ringwood [1973]
Graphite	Fe ₄₈ (FeS) ₅₀ C ₂	basaltic liquid	0.5 x 10 ⁹	1350	0.0088	Oversby and Ringwood [1973]
Alundum	Fe ₄₈ (FeS) ₅₀ C ₂	basaltic liquid	0.5 x 10 ⁹	1350	0.011	Oversby and Ringwood [1973]
Fe metal	Fe ₄₇ (FeS) ₅₃	omphacite ^e	3 x 10 ⁹	1100	~0.02	Ganguly and Kennedy [1977] ^f

^aRelative percentages by weight.

^bD_K defined as K(Fe-FeS liquid)/K(silicate) by weight.

^cCrystalline phase: K₂Mg₅Si₁₂O₃₀.

^dOne bar.

^eCrystalline phase.

^fAnalysis by electron microprobe; all other analyses by separation of Fe-FeS phases and bulk K analysis.

^gOnly small degree of partial melting under these (PT) conditions.

Oversby and Ringwood, 1973; Ganguly and Kennedy, 1977]. We have not tabulated experiments in which K₂S or KFeS₂ were used as constituents in the starting materials. These are more difficult to interpret and, overall, are insufficiently documented. We have conceivably misrepresented some of the conditions of the Oversby and Ringwood [1973] measurements, as their experimental conditions are only briefly outlined. Experiments in nominally O-free systems, in the presence of K metal, K₂S, and/or other water soluble phases, were used by Ganguly and Kennedy [1977] to estimate K solubilities of 160-380 ppm in FeFeS liquids (see their Table 1 for exact conditions). The K concentrations in FeFeS liquids reported by Goettel [1972; 1975] are similar to or higher than the solubilities of Ganguly and Kennedy, but the experimental conditions are not the same. The reported K partition coefficients, D_K (K wt % in sulfide/K wt % in silicate), span the range from 2 x 10⁻³ to 3 x 10⁻². Given the variety of systems studied and the ranges of temperature and pressure covered, the observed variation could be real.

There has been little previous work on U or Th partitioning into FeFeS liquids. Feber et al. [1984] have recently discussed experiments involving UO₂ and stainless steel at high temperature which suggest to them that UO₂ might be present in the earth's core. We have previously reported initial results for D_K and D_U into sulfide liquids [Murrell et al., 1983; Murrell and Burnett, 1985]. The present discussion draws on a larger data base, including results for D_{Th}, and a better understanding of the processes involved.

Experiments and Results

The systems studied exhibit complex behavior, requiring rather detailed discussion in this

section. Readers more concerned with the implications may wish to move directly to the discussion section which begins with a summary of results.

Experiments were done with six different silicate compositions (Table 2). Anticipating that measurement of a very low K partition coefficient would be required, a K-rich silicate liquid was desired. A granitic composition, known as the 60 material, was prepared from natural K-feldspar and SiO₂ glass to correspond approximately to the K-feldspar, SiO₂ eutectic composition. The low eutectic temperature of this material is an advantage, since it minimizes the loss of S or K by volatilization. A variation on this composition is the 61 material which consists of 60 material with 4% FeO. The basaltic compositions were a natural (Juan de Fuca) glass (62 composition) with K added to bring the K₂O content to 2.5% and Di₅₀Ab₂₅An₂₅ (32 composition). Silicates were homogenized by repeated grinding and heating to 1400°C in sealed Pt tubes and spiked with ²³⁵U to about 10 ppm. Compositions 60 and 32 were also spiked with ²³⁰Th to about 50 ppm. Composition 63 consists simply of powdered Juan de Fuca glass, and composition 64 is powdered natural K-feldspar; neither of these are U-, Th-, or K-spiked. The sulfide liquid composition is Fe₂₀FeS₈₀ on the Fe-rich side of the Fe-FeS eutectic, and was prepared by heating reagent Fe metal and S in a SiO₂ glass tube. To minimize oxidation of the sulfide, starting materials were stored in a desiccator until used. No rusting was observed, although small amounts of Fe-oxide formation probably cannot be avoided.

Initially, experiments were run in Fe capsules [Murrell et al., 1983], but the sulfide liquid is fluid and very difficult to contain, breaking through welds to run to the outside of the capsule. Consequently, to provide containment and maintain reducing conditions, graphite

TABLE 2. Microprobe Analyses of Quenched Samples of Silicate Starting Compositions

	60	61	62	32*	63	64†
Na ₂ O	1.08	0.89	2.65	2.85	2.70	1.54
MgO	-	-	7.19	8.76	7.28	-
Al ₂ O ₃	11.70	10.25	13.38	13.65	13.94	17.43
SiO ₂	77.73	76.42	49.40	56.63	50.53	64.72
K ₂ O	9.00	8.56	2.57	-	0.15	14.69
CaO	-	-	10.98	18.00	11.18	-
TiO ₂	-	-	1.73	-	1.78	-
FeO	0.35	3.64	11.90	-	12.22	0.18

60 material = K-feldspar - SiO₂ eutectic + 10 ppm ²³⁵U ± 50 ppm ²³⁰Th; 61 material: 60 material + 4% FeO; 62 material: Juan de Fuca glass + 2.5% K₂O + 10 ppm ²³⁵U; 32 material: Di₅₀Ab₂₅An₂₅ + 10 ppm ²³⁵U + 50 ppm ²³⁰Th; 63 material: Juan de Fuca glass; 64 material: crystalline K-feldspar. Values are in weight percent.

* Jones [1981].

† Crystalline.

capsules with press-fit graphite tops were used. To reduce volatile loss, many experiments were run with graphite capsules sealed in evacuated silica tubes or in a piston-cylinder apparatus with a 1.27-cm pressure assembly and a NaCl cell. The piston-cylinder experiments used the piston-in technique. Pressure for this apparatus has been calibrated against the reaction $ab = jd + qz$ at 2.95 GPa and 1100°C [Holland, 1980] and a -7% correction applied. Temperature was measured with a W3%Re - W25%Re thermocouple. The piston-cylinder runs were quenched by turning off the furnace power (cooling rate of 150°-200°C s⁻¹). The silica-sealed, 1-atm runs were quenched by pulling the run out of the furnace into either air or liquid N₂. Neither the piston-cylinder pressure assembly nor the sealed silica tubes at 1 atm were perfect containers in regard to K loss. A comparison of microprobe data for the quenched silicate starting materials with those of the run products indicates an apparent K loss of about 30% for the piston-cylinder runs. For the silica capsules, K loss by volatilization was not observed from the granitic liquids (60, 61) but was rapid from the basaltic liquids (62, 63) at superliquidus (above 1200°C) temperatures. Some of the 1-atm experiments were "open" in a N₂ atmosphere (i.e., graphite crucible not sealed in silica glass). Such experiments are open to the loss of volatiles such as K, CO, CO₂, etc. K was quickly lost from the basaltic liquids in such experiments at T > 1200°C, but at the lower run temperatures, such loss was not observed with the granitic liquids. In an "open" experiment containing KFeS₂ plus sulfide liquid without a silicate liquid present, large K loss was also observed at 1150°C. Values of D_K have not been calculated for runs with severe (50% or larger) K loss.

Experiments consisted of mixing 10-20 µg (by eye) of sulfide and silicate starting materials, placing the mixture in a graphite crucible and heating between 1100° and 1450°C for 8-140 hours at 1 atm either "open" or sealed in silica, or in a piston-cylinder apparatus at 0.7 or 1.5 GPa. The basic run product consists of two principal parts: (1) quenched silicate glass containing

globes of sulfide liquid at all size scales, from submicrometer to many hundreds of micrometers, and (2) a main mass of quenched FeFeS liquid (a eutectic mixture of FeS and dendritic metal) which is usually silicate-free. The granitic glasses (60, 61) are vesicular. The vesicles are present in quench runs of the starting material and are thus not due to any interaction with the sulfide liquid. Infrared absorption spectra show that the bubbles are not H₂O (not expected given the highly reducing conditions) or CO₂. Although N₂, H₂, or CO cannot be ruled out, our best interpretation is that the bubbles were caused by Na (and possibly K) vapor trapped due to the high viscosity of the silicate liquid. Sodium loss is observed in all runs. The basaltic compositions (32, 62, 63) are much less viscous and do not retain bubbles. In addition to the eutectic quench material the sulfide contains metal spheres of all sizes ranging from submicrometer up to hundreds of micrometers. Because the sulfide liquid composition is on the Fe-rich side of the eutectic, some metal should form during the quench as the sample cools from the run temperature through the eutectic temperature, but there is no reason why this metal should be spherical. Also, the large size of some of the spheres is hard to explain as quench features. A better explanation is that the metal spheres represent a separate Fe-Si-C-S liquid. The metal spheres do contain up to 5% levels of Si, and semiquantitative C microprobe analyses of Au-coated samples using CaCO₃ as the standard indicate that metal spheres from one run contain 2-4% C by weight. (The C concentration at the eutectic temperature in the binary Fe-C system is 4%.) Optical examination shows tiny sulfide inclusions in many spheres, suggesting a S component in the original liquid drop. Some spheres appear to have rims of metal and/or sulfide, indicating that the spheres served as nucleation sites during the quench of the FeFeS liquid. Many, but not all, runs also contain small amounts of a gray (in reflected light) phase interstitial to the FeS quench crystals. This interstitial phase shows only Fe and S peaks (no K) in an X ray spectrum, with Fe/S peak intensities higher than FeS and appears to be an

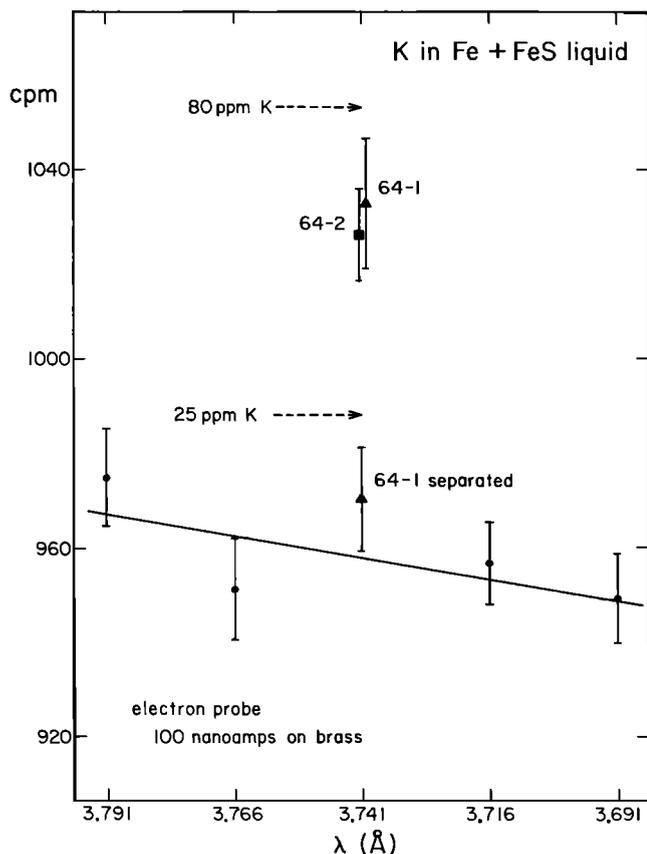


Fig. 1. The data points are the average counting rates in counts per minute at wavelengths in the vicinity of the potassium K line (3.741 Å). Note the expanded counting rate scale. The data for the background represent 19 analyses. A linear background is indicated; consequently, a linear least squares background line was calculated. The data for 64-1 and 64-2 represent six analyses and 10 analyses, respectively, for sulfide mounted in the same mount with silicate. These show higher K counting rates compared to 64-1 separated which represents the average of three analyses of 64-1 sulfide mounted in a separate mount. The higher counting rates in 64-1 and 64-2 are due to K contamination from the silicate smeared over the softer sulfide during polishing. The dashed arrows indicate the levels of 25 ppm and 80 ppm K.

Fe-S-O residual liquid. Other more exotic phases form under certain conditions and will be discussed later on.

K Analyses

K analyses were performed on polished sections of the run products using an electron microprobe. The bremsstrahlung background in the region of the K X ray line is relatively low for metal or sulfide phases giving fairly high sensitivity for K. However, with a signal to noise ratio of 1/10, care must be taken with background subtractions. Typically, a single measurement consisted of three peak counts of 90 s interspersed with 45-s background counts at two wavelength positions on each side of the peak (four background points total). Beam currents of 100 nA on the sulfide with a 1-20 μm spot size

were used. Analyses of the silicate glass by the same technique used a 25- μm spot size. No sample pitting or K vaporization loss was observed. In most cases, 10-12 individual points were analyzed in each sulfide sample. If analyses of individual points are statistically indistinguishable, the results of several analyses can be averaged together to give very high sensitivity, and, as shown in Figure 1, a concentration of roughly 25 ppm can be relatively precisely measured. However, because K from the silicate can be smeared over the softer sulfide during polishing, it is necessary at these levels to make separate silicate and sulfide mounts. Runs were first mounted in epoxy and polished. A portion of the sulfide was then separated from the glass using a low-speed saw and a diamond-impregnated blade, remounted, and polished separately. To reduce external K contamination, it is advantageous in the polishing to substitute the commercial diamond paste for a mixture of 1- μm raw diamonds and petroleum jelly (recipe courtesy of I. Hutcheon). Since K sulfides are very water soluble, 100% ethanol was used in sample preparation, and the polished sections were stored in a desiccator. Samples prepared in this manner can show a fivefold decrease in the apparent K content of the sulfide compared to the unseparated, conventionally polished case. This is illustrated in Figure 1 where sulfide from runs 64-1 and 64-2, analyzed with both K-feldspar and sulfide together in the same mounts, shows higher K contents compared to a reanalysis of 64-1 after the sulfide was mounted and polished separately. Our general lab K background, as estimated from FeS polishing blanks, is normally 10 ppm or less. To adequate accuracy, K partition coefficients are equal to relative sulfide/glass counting rates since matrix correction factors for FeS and glass are similar (within 6% of each other). Si and Al were usually measured simultaneously with K on separate spectrometers to monitor any silicate contamination in the sulfide. However, reliable quantitative Si analyses in the sulfide liquid were not possible [Murrell et al., 1983] because the general Si background in our probe is rather high at 300 ppm which is probably a silicon surface film of unknown origin.

Uranium and Thorium Analyses

The U analyses were performed on polished sections of the run products by fission track radiography [Murrell and Burnett, 1982; Burnett and Woolum, 1983]. The Th analyses were done using alpha track autoradiography [Benjamin et al., 1980; Burnett and Woolum, 1983]. These techniques permit quantitative analyses on 30- μm or larger areas and semiquantitative analyses of U- or Th-rich phases down to the micrometer scale. Fission track densities are proportional to the uranium concentration and fission fragment range in kilograms per square meter. Thus to allow for the greater range of fission fragments or alpha particles in FeS compared to glass, our U and Th partition coefficients have been corrected by 24%. U contamination due to polishing does not appear to be a problem. For example, good agreement is obtained on several samples for replicate measurements of D_U on the same sulfide area before and after sawing of the mount to separate silicate and sulfide for K analysis. Also, the full range of track lengths

TABLE 3. Results For K, U, and Th Partitioning Between Fe-FeS and Silicate Liquids

Run	Temperature, °C	Pressure, Pa	Time, hours	$D_K \times 10^{-3}$ (FeS/glass)	$D_U \times 10^{-3}$ (FeS/glass)	$D_{Th} \times 10^{-3}$ (FeS/glass)	Comments
62-5	1450	1.5×10^9	8	2.7 ± 0.5	14	-	
63-6	1450	1.5×10^9	8	2.4 ± 1.1	-	-	reversal of 62-5: KFeS ₂ in starting materials
61-1	1250	0.7×10^9	24	<0.7	4	-	
60-60	1150	$(1-2) \times 10^5$	136	<0.2	19	-	sealed in silica glass
64-1	1070	$(1-2) \times 10^5$	105	0.1 ± 0.1	-	-	crystalline silicate sealed in silica glass
63-2	1450	1.5×10^9	8	-	12	-	reversal of 62-5: U metal in starting materials
60-45	1150	1×10^5	17	-	120;2	75;-	Run in "open" graphite; bimodal U and Th distribution; see text
62-4	1300	1×10^5	21	-	1600	-	run in "open" graphite, CaS formed
32-58	1300	1×10^5	19	-	1400	45	run in "open" graphite, CaS formed

are observed, whereas a surface film would produce predominantly long tracks.

In some sulfide liquid samples with a fine quench texture, the track distribution is homogeneous, but in many samples the tracks are distributed along grain boundaries. It appears that U is effectively excluded from crystalline FeS and is sufficiently mobile to concentrate on grain boundaries during the quench. This is not a problem for U analysis, since by counting all tracks over "large" areas (100 μ m dimensions or larger) the average U concentration of the FeFeS liquid, and thus the U partition coefficient, can be obtained. (The equivalent problem for K analysis was addressed by making a large number of analyses with a relatively large beam spot. Spots containing a higher proportion of apparently interstitial material usually did not show higher K.)

Results

The number of experiments is large, over 50. For simplicity, a few of the more illustrative runs have been summarized in Table 3. The runs are labeled using two numbers: the first number indicates the silicate composition, and the second identifies the run. Our experimental results are complex, and the details of all observed features are not completely understood. However, we have devoted considerable effort to checking out possible effects which might change our major conclusion that U and Th partitioning into the FeFeS liquid is much more important than K partitioning.

Potassium Partitioning

Piston-Cylinder Experiments

The piston-cylinder runs are the easiest to interpret. Run 62-5 (Table 3) consists of comparable amounts of basaltic silicate and FeFeS run in a graphite capsule in a piston-cylinder apparatus at 1450°C and 1.5 GPa for 8 hours. The

D_K for this run is $2.7 \pm 0.5 \times 10^{-3}$, where the uncertainty is the standard error of the probe data for several points. A reversal of this run was apparently successful: 63-6 consists of Juan de Fuca glass ($K_2O \approx 0.2\%$) and FeFeS, plus ~10% KFeS₂. Run under the same conditions as 62-5, all KFeS₂ disappeared and the K_2O content of the glass rose to 1.3% with D_K , $2.4 \pm 1.1 \times 10^{-3}$, in good agreement with 62-5. (We are somewhat cautious about this value since the K content of the sulfide in 63-6 is only 25 ppm, which is nearing our background levels.) Since the K partition coefficient appears reversible, the measured D_K should be approximately correct. As discussed below, this set of experiments is the only one in which anything approaching equilibrium K partitioning was observed. A piston-cylinder run done with the granitic composition, run 61-1, at somewhat lower temperature and pressure (see Table 3), produced $D_K = 0.7 \pm 0.2 \times 10^{-3}$. However, it was not possible to separate this run into separate sulfide and silicate mounts, and the sulfide analysis could be high because of K contamination during polishing. If the reversibility documented above holds for this experiment, then 0.7×10^{-3} can be regarded as an upper limit on D_K .

One-Atmosphere Experiments

No consistent K partitioning into sulfide liquid was observed in the 1-atm experiments. For example, run 60-60, which consists of granitic material and sulfide run at 1150°C for 136 hours in a graphite capsule sealed in silica glass, shows blank K levels in the sulfide. The D_K values for runs made with the granitic compositions were usually less than about 4×10^{-4} . The story is similar for the basaltic composition at 1 atm, although the limits on D_K are higher since the K_2O content of the glass is lower and K is lost much more easily from this system during the run. Our inability to move K into FeS at 1 atm is in marked contrast to the

data of Goettel [1972; 1975] where D_K ranges from 0.03 to 0.001 (see Table 1). One big difference between his experiments and ours is that we studied partitioning between sulfide and silicate liquids, whereas Goettel used crystalline silicates. In order to determine the importance of this difference, we repeated one of Goettel's experiments. Run 64-1 (see Table 3 and Figure 1) consists of K-feldspar and FeS run at 1070°C for 105 hours in graphite sealed in silica. Except for the substitution of a graphite capsule for an iron capsule, this run duplicates one of the Goettel [1975] experiments. The D_K value he determined using an electron microprobe was 2×10^{-3} with 300 ppm K in the sulfide; our value is $1 \pm 1 \times 10^{-4}$ with less than 25 ppm K in the separated sulfide. Goettel analyzed for Si as well as K in the sulfide in order to check for silicate contamination. The Si values he reports would be consistent with K and Si contamination of the sulfide by silicate, perhaps from polishing, as he did not separate sulfide from silicate. If the K values found by Goettel are not due to contamination, we are unable to explain the difference between his D_K value and ours.

Although K partitioning from silicate into sulfide was not observed in the 1-atm runs, reversals of these experiments were not successful. In runs where $KFeS_2$ was added, large increases in apparent D_K values are observed. Higher apparent D_K values were also measured when additional K was added as $KF \cdot 2H_2O$ or K_2CO_3 . In many of these runs a K-, Fe-rich sulfide liquid is found interstitially to the FeS. Goettel [1975] also found high interstitial K concentrations in sulfide from roedderite-FeS experiments which he interpreted as being due either to a separate K-rich sulfide liquid or to K excluded during quenching as FeS crystallized. Texturally, the latter case is more plausible. We estimate that K concentrations in the sulfide liquid prior to the quench could be 2500-5000 ppm with apparent D_K of 0.03-0.06. Such concentrations are much higher than the solubilities reported by Ganguly and Kennedy [1977]. Our results are not quantitatively reproducible, but increased D_K is always observed when K is added external to the silicate liquid for both the granitic and basaltic liquids. The K_2O content of the glass also goes up but never above 10-11%, and K-rich silicate crystals are never observed. Such a situation is not obviously equilibrium partitioning. It may be that K added to the system as KF , K_2CO_3 , or $KFeS_2$ dissolves slowly in the silicate liquid (both from the sulfide and the vapor) but rapidly in the sulfide liquid. Literature K diffusion coefficients [Margaritz and Hoffman, 1978] and the observation that the K gained by the silicate, while not totally homogeneous, is reasonably well mixed show that slow K diffusion in the silicate liquid is not the cause of the lack of equilibration. There might be a barrier which prevents K from going into the silicate liquid, such as sluggishness in recombining with oxygen or in the passage of K across the sulfide/silicate and vapor/silicate interface. Because the 1-atm experiments failed to reverse, there is no rigorous interpretation of the D_K results, even as limits. However, this

is not true of the piston-cylinder experiments which appeared reversible, probably due to the higher temperatures (1450°C) compared to the 1-atm experiments.

Potassium Measurements in Chondritic Sulfides

Although not directly comparable to the above data, it was of interest to check on K partitioning in meteoritic samples, given our relatively good sensitivity for K analyses. In a study of the E3 enstatite chondrite, Qinzhen, Woolum et al. [1984] reported a large (100 μm size) binary troilite/djerfisherite association. A binary grain provides the best opportunity for equilibrium, although the equilibration temperature is unknown. The K content of the troilite was 32 ± 13 ppm K or, expressed as a troilite/djerfisherite solid-solid partition coefficient, 4×10^{-4} . Troilite from the St. Severin ordinary equilibrated chondrite (LL6) was also checked and found to contain less than 50 ppm K. Relative to coexisting oligoclase, a troilite/oligoclase solid-solid partition coefficient of less than 0.09 is obtained. This applies to the metamorphic equilibration temperature of LL6 chondrites, probably about 800°-900°C [Dodd, 1981]. These are upper limits due to the possibility of polishing contamination and indicate that the solubility of K in crystalline FeS is quite low, probably at all temperatures where this phase is stable. For comparison to K, in enstatite and ordinary chondrites U and Th are concentrated relative to FeS in CaS and Ca-phosphates, respectively, by factors of at least 10 [Murrell and Burnett, 1982; Jones and Burnett, 1979]. In equilibrated enstatite chondrites, U and Th are totally concentrated in sulfides.

Uranium Partitioning

Piston-Cylinder Experiments

Excellent fission track images of the polished sections of the run products were obtained, and simple visual inspection shows that significant U partitioning into the sulfide liquid nearly always occurs. As was true for K, U results are most interpretable for the piston-cylinder runs. The basaltic run 62-5 (Table 2) has a uniform U track pattern over both glass and sulfide with $D_U = 0.014$. A reversal of this run (63-2) consisted of unspiked Juan de Fuca glass mixed with $FeFeS$ and U metal run under the 62-5 conditions. The D_U for this run is 0.012; however, this is not a complete reversal, since the fO_2 in the piston-cylinder experiments is high enough ($\sim 10^{-4}$ Pa or 10^{-9} bar) to convert U metal to UO_2 , and a small piece of UO_2 remained at the end of the run. The dissolution of the UO_2 in the glass appears to be the rate limiting step, but the silicate and sulfide liquids seemed to equilibrate in 63-2, giving the same D_U as 62-5. As will be seen below, this is not the case for the 1-atm U reversals. Run 61-1 (granitic liquid + FeO) was run at somewhat lower temperature and pressure and gave $D_U = 0.004$. This lower value could be due to the lower temperature and/or differences in the silicate compositions (discussed below).

One-Atmosphere Experiments

The value for granitic run 60-60, $D_U = 0.019$, is typical. The mean D_U value for the granitic composition at 1 atm and 1150°C is about 0.02. In contrast, the metal spheres have negligible U concentrations (D_U , metal/silicate, $<10^{-4}$). The range of D_U values for sulfide is quite large, 0.002-0.2, and in some cases the total range is observed between the U content of different globs of sulfide liquid within a run. This variability is far outside analytical error. It is not due to gradients within sulfide or glass. The key to understanding the variability in D_U comes from experiment 60-45 which consists of granitic material and FeS run for 17 hours at 1150°C. The graphite capsule was not sealed in silica glass, so the conditions are quite reducing for this run. By chance, there was a high ratio of silicate to sulfide, which prevented the separation of a main sulfide mass, leaving the sulfide dispersed as a relatively large number of 100- μm -sized globs. These globs showed a large overall range in D_U , from 0.002 to 0.12, but with an essentially bimodal distribution into high-U and low-U globs. Detailed study revealed that the U-rich ones contained metal grains which were much higher in Si than the U-poor globs. These metals also contained detectable amounts of Pt which presumably is contamination from the capsule used to synthesize the silicate starting material. The higher concentrations of Si in metals from the U-rich globs indicate locally more reducing conditions than for the U-poor globs. The U-rich globs are observed to be either on the sample surface or exposed to large vesicles which could have been open to the surface. Some of the U-poor globs are enclosed by silicate, although others are adjacent to smaller vesicles. The surface location of the U-rich globs could produce the reduction of UO_2 (and SiO_2) upon direct contact with the walls of the graphite crucible. Alternatively, f_{O_2} may be lower at the surface, e.g., due to direct oxygen loss or because oxygen can react to form CO or CO_2 , and (because the system is open) may be carried away from the surface.

In general, there appears to be a tendency for higher D_U with lower f_{O_2} . The "open" graphite runs experience very low f_{O_2} and are essentially unbuffered since CO and CO_2 are not retained. These runs typically show higher D_U than the silica-sealed graphite runs which should experience higher f_{O_2} because CO and CO_2 are retained. Also, the relatively low D_U (0.004) for the granitic piston-cylinder run 61-1 may be due to the higher f_{O_2} for that run, compared to the 1-atm runs, despite the higher temperature.

The U-rich sulfide globs in granitic sample 60-45 also contain small ($<20 \mu\text{m}$) crystals of Al-rich, K-, U-poor phases, some of which are euhedral in shape. These phases are also found near the surfaces within sulfides in other granitic samples run open. Some of these grains show only Al peaks in their X-ray spectra; others appear to be mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). These Al-rich phases are probably formed in response to surface losses either of K and Si by volatilization or by loss of Si to the graphite capsule. In either case, crystallization of Al-rich phases occurs faster than mixing in the silicate liquid. Occasionally, these phases are

also found near the surface of the silicate liquid. In such cases, the U content in the silicate surface region is quite high. This is probably due to the enrichment of the refractory UO_2 or reduced U phase during evaporation at the rim. For an open run at 1300°C, analyses with a light element spectrometer gave high N counting rates in an Al-rich rim totally enclosing the silicate liquid, indicating formation of an aluminum nitride (U-rich). The presence of U-rich regions on the rim of silicates from some runs appears to have no effect on the D_U values for the rest of the sample. In fact, the chemistry of the rest of the silicate looks perfectly normal. We do not understand why the Al-rich phases are predominately found in the sulfide. As volatilization and/or reduction occurs on the surface of the silicate liquid, submicrometer grains of Al-rich phases may form, and the FeFeS liquid may simply serve as a "flux" for crystal growth. The method by which the submicrometer grains would be transported along the silicate surface into the sulfide is unclear. However, the observed mobility of the sulfide liquid opens the possibility of a sulfide liquid surface film moving over the whole sample, although such films are not usually observed in the quenched run product. Regardless of how they got there, the Al-rich grains in the sulfide are protected from dissolution back into the silicate melt. The U-rich phases on the silicate surface are also probably metastable, formed in response to surface volatilization, before diffusion could erase the chemical inhomogeneities produced by the volatilization.

In five experiments at 1 atm where $\text{KF} \cdot 2\text{H}_2\text{O}$ was added in order to provide a source of volatile K, the U partitioning behavior has been quite anomalous. Two sulfide masses show quite low $D_U \sim 10^{-4}$; however, other sulfide masses, in one case even in the same run, show more typical $D_U \sim 0.01$. The overall tendency, although not reproducible, is for lower D_U for these samples. We have not pursued the origin of these effects, but they must be related in some way to the presence of excess F and/or H due either to the formation of fluoride or hydride complexes (perhaps volatile) or to surface chemistry effects on the partitioning of U across the liquid interface.

The influence of silicate composition on D_U is quite apparent in comparisons of the granitic runs with the basaltic runs. Overall, both show a wide range in D_U . Runs made with the basaltic material at 1 atm produce D_U values from 0.01 up to 2, over the temperature range 1150°-1350°C. D_U values for similar runs made with granitic material are between 0.002 and 0.2. The high values in the basaltic runs are correlated with the presence of Ca in the sulfide liquid. In some of the basaltic runs, CaS is present as a quench feature in the FeFeS liquid. For example, 62-4 (Table 3) displays a complex sulfide assemblage consisting of metal, FeFeS quench, and CaS. The CaS occurs as rounded ($\sim 100 \mu\text{m}$) globs (crystals?), as veins, and dendritically in the FeFeS quenched liquid. X ray spectra of the quenched FeFeS liquid show detectable Ti but little Ca. The silicate contains large quantities of skeletal MgAl_2O_4 spinel crystals and Al-rich phases in addition to glass. Many of

these phases were also observed by Jones and Boynton [1983] in a study of REE partitioning under reducing conditions. Most of the glass has suffered extensive Ca depletion presumably to the sulfide, although some local areas encased in spinel crystals have retained Ca. K is absent from all glass, presumably lost by volatilization. All X ray spectra of the glass show a distinct S peak which suggests that S is dissolved in the silicate liquid, since most of the glass is optically free of sulfide inclusions.

The U distribution is correspondingly complex. In the silicate the U correlates with Ca, being high in the Ca-rich, spinel-enclosed pockets and lower in the bulk Ca-depleted glass. The spinel and Al-rich phases are U-free. Relative to the Ca-depleted liquid, the large CaS globs have $D_U = 0.50$. Perhaps the most exciting result is that the FeFeS liquid has a very high $D_U = 1.6$; that is, it concentrates U relative to the silicate glass. Within the sulfide are highly enriched ($D_U > 4$) grains of what appears to be a Ca-, Ti-rich pyroxene. The entire sample, both sulfide and silicate, has a 1-2 μm U-rich rim composed of fine-grained refractory (Ca, Ti, Mg) oxide and/or silicate. The following is a plausible set of reactions to explain the observations:

1. Loss of Fe, Ca, Ti and U to the FeFeS liquid. At least two (Fe-C-S-Si metal, sulfide) liquids were present and possibly three (metal, Fe-rich sulfide, Ca-rich sulfide). The CaS contains detectable amounts of Fe, and the Fe-rich sulfide liquid contained (prior to quench) Ca, as dendritic CaS is observed. In any case, the incorporation of Ca into the sulfide has been accompanied by a large amount of U.

2. Loss of Ca and Fe, triggering spinel crystallization in the silicate liquid. Steps 1 and 2 probably occur simultaneously.

3. Volatilization and/or reduction, producing the refractory rims and the Al-rich phases.

CaS was not present in all the basaltic runs. It was not observed in short 1-2 hour runs, in runs below 1200°C, or in the piston-cylinder experiments. When CaS was not present, the D_U values were 10-100 times lower than runs where CaS was observed. It is clear that in Ca-bearing systems under reducing conditions, U and Ca partitioning into sulfide liquids is of great importance.

A check on the effects of changes in the FeFeS liquid composition on U partitioning was made by preparing a sulfide liquid on the S-rich side of the eutectic composition. An experiment done with this sulfide and the 60 composition produced a $D_U = 0.02$. This is the typical value and indicates that D_U is not highly sensitive to the composition of the FeFeS liquid.

Goettel and Lewis [1973] proposed that D_K increased rapidly with temperature. Qualitatively, our data for D_U (and D_K) do show an increase but not necessarily large. Runs made with the granitic material at 1 atm over different temperatures give higher D_U at higher temperature but not by orders of magnitude. Our best estimate is that in going from 1150°C to 1400°C, D_U increases by a factor of 2-4.

Goettel [1972] reported a correlation between D_K and quench time, and suggested that K was

extremely mobile in the FeFeS liquid and returned to the silicate during quench. We have employed a variety of quench techniques: air, water, liquid nitrogen, and slow cooling. There is no correlation between the apparent D_U or D_K and quench technique. The time required for visible thermal radiation to cease ranged from roughly 3 to 30 s; however, the significance of these observations is questionable, since the actual quench time is probably controlled by the quality of the thermal contact between the sample and the graphite crucible, which may vary between runs. Cooling will be slowed by the fact that neither liquid wets the graphite container. The quench texture and the U fission track distribution within the FeFeS liquid are probably good measures of quenching. A slower quench would produce relatively coarser sulfide texture, and more U should be found on grain boundaries. We observe a correlation between fine textures and relatively homogeneous track distributions, which suggests that fairly effective quenches have been obtained in many runs. More specifically, if U was unable to move 10 μm during the quench, is it reasonable that K can move millimeters? The required diffusion coefficient for K would be $10^{-2} \text{ cm}^2 \text{ s}^{-1}$, which is quite high even for metallic liquids. We conclude that our measured D_K are not anomalously low due to difficulties in holding K in the FeFeS liquid during the quench nor have D_U values been perturbed during quenching.

Several U reversals have been attempted at 1 atm. They have not been successful. When either U metal or UO_2 is added to the starting materials and the graphite capsule is run "open" (not sealed in silica), US_2 is present in the run products. The US_2 appears as large (greater than 100 μm) crystals in the FeFeS liquid. (As discussed above for the case of the Al-rich crystals produced by volatile loss, the sulfide liquid seems to be an effective flux for crystal growth.) The UO_2 content of the silicate glass does not go up, and UO_2 gradients are not seen in the glass along FeS- US_2 -glass contacts. However, the U content of the sulfide liquid does show large increases, but U varies between different globs of sulfide in a run. When U metal or UO_2 is added to the starting materials and the graphite capsule is run sealed in silica (higher $f\text{O}_2$), UO_2 is observed as distinct grains within the FeFeS liquid. The U metal not converted to UO_2 appears to be preferentially dissolved into the sulfide leading to high apparent D_U (~ 3). The granitic glass in the 1-atm runs appears to dissolve US_2 and UO_2 very slowly, even for runs lasting 6 days, but U metal dissolves readily in the sulfide liquid. The situation seems similar to that encountered for the K reversals at 1 atm, that is, sluggishness in the oxidation step and/or the transport of K and U across the sulfide/silicate interface.

Thorium Partitioning

D_{Th} has been determined for three granitic experiments and two basaltic experiments, all of which were run "open" in graphite. The D_{Th} for the granitic runs range from 0.03 to 0.08 which is similar to the range in D_U for these runs. The Th distribution is also quite similar to that

observed for U. For example, in a granitic run like 60-45 which has both high- and low-U sulfide globs, the Th concentrations track the U in these globs; or if there is a U-rich rim on the silicate, the rim is also rich in Th.

In the basaltic experiment 32-58 (Table 3), 32 material was mixed with FeFeS and run open in graphite for 19 hours at 1300°C. This run produced a sphere which is half silicate and half sulfide. The quenched sulfide liquid contains large (millimeter-sized) metal spheres, typical FeS with dendritic Fe, and CaS distributed in veins and spherical globs. The D_U (FeFeS/silicate) for this experiment is 1.4. However, D_{Th} (FeFeS/silicate) is 0.045, which would be a typical value for a granitic experiment. A second experiment gave $D_U = 2.2$ and $D_{Th} = 0.12$. Apparently, U partitioning is preferentially enhanced over Th partitioning for Ca-bearing systems. This suggests a unique mechanism for fractionating U from Th.

Discussion

The piston-cylinder experiments are the easiest to interpret since they appear reversible; therefore the following discussion will emphasize these data. At 1450°C and 1.5 GPa, D_U is 0.013 and D_K is 0.0026; thus U partitioning into FeFeS liquids relative to the silicate liquid is about 5 times greater than K partitioning under these conditions.

There are problems with the 1-atm experiments; specifically, they do not appear to equilibrate or reverse. Although the 1-atm D_U and D_{Th} may be close to the equilibrium values, the variation in the D_U and D_{Th} within runs can be large, probably reflecting more reducing conditions on the surface as compared to interior locations for isolated sulfide globs. It is clear that D_U increases with decreasing oxygen fugacity, but the dependence is not quantitatively established. Silicate liquid composition also affects D_U : Using the basaltic compositions above 1200°C, there is strong partitioning of both Ca and U (D_U roughly 2) into the FeFeS liquid, accompanied by the formation of CaS. However, until strong Ca miscibility with the FeFeS liquid occurs, U partitioning, although much more important than K partitioning, is still not strong. The presence of Ca in the sulfide liquid seems to have little effect on D_{Th} ; otherwise, D_U and D_{Th} are similar. The 1-atm experiments are obviously complicated and difficult to interpret; however, the important fact remains that measurable U and Th partitioning into sulfide was nearly always observed but K partitioning was never observed (excluding those experiments where "external" K was introduced).

These experiments are challenging in that it is desirable to perform sealed experiments to prevent K and CO/CO₂ loss, but at very low f_{O_2} there are no inert containers; thus there are problems with long runs. The failure of reversals at 1 atm indicates that there are problems with K and U equilibration in at least our granitic experiments. The basaltic material has a problem with volatile loss of K, but this can be somewhat controlled by running near 1200°C in sealed silica tubes. Below this temperature

there is extensive crystallization of the silicate liquid. It is difficult to ascribe our low D_K values to these problems. Since many elements, such as U, Ca, Si, Ti, and Fe, are observed in our experiments to partition from the silicate liquid into metal or sulfide, it is unreasonable that K should be partitioned much less rapidly than U, unless there is an inverse correlation between the silicate to sulfide transport rate and the degree of lithophile character or unless the observed amount of U partitioning represents a metastable situation; that is, U transport from silicate to sulfide liquid has overshot, producing a D_U that is too high. K might be preferentially lost from the sulfide liquid by volatilization; however, this should not be a major problem in runs sealed in silica, since KFeS₂ is lost only slowly from the sulfide liquid during sealed "reversals." It seems most reasonable that D_K is actually quite low at 1 atm and 1150°C (~10⁻⁴ or less) and that the value of 0.0026 obtained at 1450°C, 1.5 GPa represents an increase in K partitioning with temperature.

Our D_K upper limits at 1 atm and the 15 kbar value of 0.0026 are lower than most literature values (Table 1). This may reflect differences in experimental conditions, or it may be that K contamination has affected the results of the other studies. Except for Goettel [1972], none of the other studies considered this potential problem. Experiments which started with K metal or sulfide may suffer from the equilibration problems documented above. In some respects the study of Goettel [1972] is the most carefully done, yet it is striking that he reports the highest D_K values. The obvious difficulty, leaching of K from roedderite during the HCl differential dissolution of the sulfide, was checked with roedderite solubility measurements and controlled by Mg analyses of the sulfide solutions. Higher Mg concentrations in the sulfide solution than could be accounted for by the roedderite solubility were explained by partial dissolution of a Mg-rich glass formed as a product of K extraction into the FeFeS liquid. Glass was observed optically, but no compositional data are given. Conceivably, this glass contained some K also leading to apparently high D_K values. In Goettel's [1975] study using K-feldspar instead of roedderite, the K measurements were made with an electron probe. As previously discussed, when we duplicate these experimental conditions, no K partitioning is observed which suggests that K contamination, perhaps from polishing, affected his results.

The possibility that the whole earth has a chondritic K abundance and K/U ratio but that K is hidden in the core [Lewis, 1971; Hall and Murthy, 1971; Goettel, 1976] has been challenged on the basis of the previous D_K measurements [Oversby and Ringwood, 1973; Ganguly and Kennedy, 1977]. Our data make it still more difficult: $D_K/D_U > 1$ is required to have the terrestrial K and U abundances at chondritic levels, but we consistently observe $D_K/D_U < 1$. If only a negligible fraction of terrestrial U is in the core, then 7/8 of the terrestrial K must be there to have an overall chondritic K/U for the earth. Making the favorable assumption of total equilibration of these elements between crust,

mantle, and core, an effective $D_K = \text{core}/(\text{crust} + \text{mantle}) = 14$ is implied. This is ~ 5000 times larger than our measured D_K . Assuming only core/lower mantle equilibration makes the required D_K even larger. It is conceivable that effects of this magnitude could accompany the metallization of K at high pressures, as proposed by Bukowinski [1976]. If the high-pressure, siderophilic character of K can be demonstrated (this has not been possible to date [Sommerville and Ahrens, 1980]) and if similar siderophile character is not acquired by U or Th, then our relative D values could be reversed at the terrestrial core-mantle boundary conditions. More precise resolution of this question will require partitioning experiments at high (10 GPa) pressures.

The occurrence of a K-sulfide mineral (djerfisherite) in enstatite chondrites has been used as an argument that K is likely to partition into the core. The existence of djerfisherite per se can also be interpreted as indicative of the unusual (essentially no O_2 , lots of S) formation conditions of enstatite chondrites. At issue is the relevance of such conditions to the earth today or during its formation stages. Furst et al. [1982] noted that djerfisherite occurred only in the unequilibrated enstatite chondrites, while K was found in feldspar in the more equilibrated (metamorphosed?) enstatite chondrites. These authors interpreted this as indicating that djerfisherite was a disequilibrium phase, perhaps produced as a consequence of K mobilized by impacts. This impact model has problems explaining the large djerfisherite grains in Qinzhen reported by Woolum et al. [1984]. Nevertheless, the systematics of djerfisherite occurrence noted above still suggests that this phase is not stable under presumably uniform (PT) conditions associated with equilibrated E-chondrite formation, with K concentrating into silicate phases.

Summarizing, given the chemical complexities, one cannot dogmatically say that there are no conditions whereby K could be preferentially partitioned into the core relative to U to a sufficient degree to permit a chondritic K/U ratio and K abundance for the earth. However, all experimental data indicate this is not the case, supporting the generally accepted view that the inner solar system is depleted in volatile constituents, including K.

The question of core heating by K or U is more difficult because lower concentrations of K or U are involved. It should be strongly emphasized that the partition coefficients depend on temperature, pressure, silicate composition, and oxygen fugacity, so any application is dependent on the model adopted for composition and thermal history. Further, our experiments cover only a small range of (P, T, composition) space. As discussed below, they permit significant radioactive heating in planetary cores but do not prove that such heating is important. More elaborate calculations than those given below do not seem warranted.

If we assume that the concentrations of K, U, and Th in the earth's core are determined primarily by partitioning between an equilibrated lower mantle and the core and make the favorable assumption of a relatively undifferentiated terrestrial lower mantle with 500 ppm K, D_K must

increase by at least a factor of 50 from what we observed in the piston cylinder experiments for minimum core heat production, 5×10^{11} W, or a factor of 1000 for the preferred 10^{13} W [Gubbins, 1981]. Such increases would have to be ascribed to changes in (P, T, composition) or to preferential K metallization. For the same heat production estimates, the required core actinide concentrations are 2-50 ppb U or 9-180 ppb Th. For a 30 ppb U and 120 ppb Th lower mantle, effective D values of 0.03-1 are required which do not look unreasonable, especially in light of our experiments with Ca-bearing systems. Of course, our partition coefficients are measured relative to a silicate liquid, whereas some crystalline solid is probably the U reservoir in the lower mantle; nevertheless, it is possible that the same order of magnitude partition coefficient might be involved. Further, earlier in geologic time, ^{235}U would also make important contributions to heat production.

As a general, relatively model-independent statement, we can conclude that if radioactive heating is important for planetary cores, U and Th will be more important than K unless (1) the lower mantle has $K/U > 10$ times chondritic or (2) large changes in partition coefficients with conditions (e.g., by preferential K metallization) reverse the relative importance of K versus U and Th from our measurements. There is certainly no basis for focusing only on K as a source of radioactive heating. Because of the extremely high pressures of the terrestrial core-mantle boundary and the uncertainty of the actual materials present, application of all laboratory geochemical data, including ours, is clearly tentative. Because of the higher probability of reducing conditions, our results may be more applicable to the core-mantle boundaries of Mercury and the moon (if it has one), but any application is still model-dependent. Nevertheless, it seems permissible to speculate that conditions could exist such that the time scale for the existence of a lunar dynamo would be set by the ^{235}U lifetime.

Our data are most applicable to the general problem of low pressure differentiation of planetary objects. We have found conditions in Ca-bearing systems where significant U partitioning into an FeFeS liquid has occurred (high temperature, very reducing conditions) accompanied by Th-U fractionation. It may be that these rarely occur in the early stages of planetary differentiation; if so, partitioning of U into FeFeS liquids may never be significant. However, during surface melting on enstatite chondrite parent planets, or perhaps during impact heating of E-chondrite planetesimals on the earth, it seems quite plausible that Ca-, U-rich FeFeS liquids could form and sink into the interior. Stevenson [1981] has argued that kilometer-sized FeFeS blobs sinking into the core on a time scale of 10^6 years would not completely equilibrate with mantle material; however, complete equilibration is not required to "back-extract" U from a U-rich FeFeS glob passing through a more oxidized mantle. Within the plausible range of parameters involved, back-extraction may or may not take place; so sinking of FeFeS blobs from locally reducing surface environments is a possible mechanism for carrying actinide elements to the core. Whether or not the actinides remain depends on the degree

of core-lower mantle equilibration. This is a critical issue for core heating, but even if the core actinides are partitioned back into the lower mantle thermal boundary layer and not mixed upward, they might still represent an important heat source for mantle dynamics. Because of overall more reducing conditions and smaller length scales, actinide transport to the cores of the moon and Mercury might be more important. More quantitative statements are possible in the context of specific models, but development of preferred models seems premature.

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