Observation of Non-lithophile Behavior for U

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Abstract. In the Hvittis enstatite chondrite fission track radiography shows that U is highly concentrated in CaS (oldhamite), with a concentration of 400±50 ppb. The oldhamite U concentrations are equilibrated, although intergrain concentration variations of less than 15% would not be detected. Various approaches to a U material balance do not agree, but at least 50% and, more likely, nearly 100% of the U is concentrated in CaS. It is likely that CaS is the major reservoir for other actinide and lanthanide elements as well. Consequently, enstatite chondrites may provide reliable Pu/U abundance ratios. The highly reducing formation conditions for enstatite chondrites have caused U to deviate from lithophile behavior, but K is observed to remain lithophile. Although this observation may not be generalizable, we propose that discussions of radioactive heating of planetary cores should include U and Th and not focus exclusively on K.

Introduction

In essentially all natural occurrences U exhibits strongly lithophile character, concentrating in silicate, oxide or phosphate minerals. Deviations from lithophile character are important because incorporation of U into sulfide or metallic phases would potentially serve as a heat source for planetary cores. Heating of metal or metal-sulfide cores is necessary for a variety of reasons, e.g. to generate fluid motions to produce planetary magnetic fields (Jacobs, 1975; Gubbins and Masters, 1979; Stevenson, 1981). Although radioactive heating may not be necessary, K is usually taken as the important radioactive element in discussions of core heating by radioactive decay (relevant literature reviewed in Jacobs, 1975; Brett, 1976). An exception is Ruff and Anderson (1980) who also considered heating by U and Th. Laboratory experiments have shown that Pu, U and to a lesser degree Th can be reduced from a silicate melt to dissolve in Pt-metal alloys but very low limits were set on the partitioning of U into FeS and FeC alloys (Jones and Burnett, 1980). This paper demonstrates that in the Hvittis B6 enstatite chondrite, extremely reducing formation conditions have caused U no longer to be lithophile, but rather to assume chalcophile character and concentrate in CaS. However, K has remained lithophile.

Experimental

Quantitative U fission track radiography, as described in Stapanian (1980) or Jones and Burnett (1979), was performed on three polished sections of Hvittis. Muscovite mica track detectors were clamped on the sections during irradiation by ~2x10^{18}/cm^{2}/thermal neutrons. The distribution of 235U fission tracks on the mica provides an image of the distribution of U in the meteorite. By comparison of the densities (tracks/cm^{2}) of tracks with the densities of a standard, U concentrations can be determined for regions (phases) which are large compared to the fission fragment ranges (10-20 microns).

Results

The fission track images of the Hvittis sections showed an unusually high degree of track localization. Mapping of the locations of the track clusters back onto the sections showed that U was highly concentrated in CaS (oldhamite). The sources of 42 track localisations were investigated with an SEM plus semiconductor X-ray detector, yielding 39 CaS grains, two holes (either plucked CaS or contamination U) and one K-Al-Si-rich region. Despite a deliberate search, no U-poor CaS grains were located. U concentrations, based on the track density in the center of the grain, were measured for the larger CaS grains (usually >50 microns since the calculated fission fragment range in CaS is 20 microns). U concentrations were uniform within counting statistics (50-200 tracks/grain) within a given section. For the three sections the U concentrations are 387, 351 and 323 ppb U with a precision (standard deviation of mean) of ±4% for each measurement. The differences are significant and cannot be explained by reactor flux gradients. The U concentrations include a 30% correction for the fission fragment range difference between CaS and our glass U standard. Microprobe analyses of CaS grains after irradiation indicate S loss, probably due to oxidation (CaS is a metastable phase under terrestrial conditions). Assuming no U volatilization, this could lead to underestimation of U concentrations by up to 30%, because of overcorrection for range differences, if complete oxidation has occurred. Variations in the degree of oxidation among sections could explain the variations in average U content in CaS for different sections. Other sources of systematic error (poor sample-detector contact, track counting at high track densities, etc.) will also lead to low concentrations, although these should not be significant. Consequently the best estimate of the U concentration of Hvittis CaS is 400±50 ppb. Random scans over 0.6 mm^{2} of one mica...
detector gave a total rock concentration of 4.4±0.2 ppb in reasonable agreement with the neutron activation U content (6.2ppb) by Morgan and Lovering (1968), but, more importantly, documented that at least 80% of the tracks are not randomly distributed but are localized in regions of dimensions of 10 microns or larger. Because the large (50-100 micron) track localizations were seen to correspond to CaS, the observed localization down to ~10 microns suggests that essentially all of the U in Hvittis is found in CaS. Coupled with the uniform U concentrations among CaS grains, this is suggestive of an equilibrium distribution of U. In this sense E5 chondrites may be more equilibrated than type 6 ordinary chondrites, for which U may not have an equilibrium distribution among the various phases (Jones and Burnett, 1979).

However, modal estimates of CaS do not account for all of the 6 ppb total rock U: Keil (1968) gives 0.2% by weight CaS based on petrographic point counting of 6 cm$^2$ of section; however, this seems low for our sections since the area of large CaS grains investigated for tracks alone corresponds roughly to this value. Using total rock Ca, Al, Mg concentrations (Von Michaelis et al., 1969), and microprobe mineral concentrations (Keil, 1968), a CaS modal abundance of 0.7% is obtained from mass balance. This would still only account for ~50% of the U in CaS. Plagioclase and enstatite are ruled out because they would be required to have 20 and 5 ppb respectively to account for the missing U. Enrichments of this magnitude would have been readily recognized in the track distributions. Large metal or FeS grains have at least an order of magnitude less U than CaS. In other E5 chondrites MnS has ~1/20 the U of CaS (Murrell et al., 1977) has found K-sulfide in a kimberlite nodule, but formation as a vapor-phase product of a K, S, Cu-rich vapor (impact produced?) reacting with Fe-Ni metal or Fe-Ni sulfide. Vapor phase alteration, probably impact-derived, is a very plausible mechanism to explain high U in Fe-Ni metal (consistent with Jones and Burnett, 1980) or FeS, although reasonably high U concentrations (4-17ppb) have been reported in FeS from iron meteorites (as tabulated by Morgan, 1971). For comparison with U, one of our sections was more strongly into such phases and perhaps be incorporated under less extreme (e.g. F$_2$O$_3$) conditions. Thus it is not clear to us that the

Discussion

Our data indicate that CaS in E-chondrites is the analog of the Ca-phosphates in ordinary chondrites in being an important U-bearing reservoir. Subsequent work has shown Th concentration in CaS (Murrell and Burnett, 1981). Oldhamite is also likely to be an important reservoir of Pu and the rare earths, although laboratory observations of U and Pu reduction and alloying from silicate melts were not accompanied by similar behaviour for Sm (Jones and Burnett, 1980). If the highly reducing conditions during the formation of E-chondrites have produced trivalent U as well as Pu (Benjamin et al., 1978), then minimal chemical fractionation of these elements may result. Even if CaS does not contain all of the actinide and lanthanide elements in equilibrated E chondrites, the same valence state (+3) for Pu and U would make these meteorites the best available source for solar system Pu/U ratios.

As with all other geochemical data, our results do not yield unambiguous, model-independent conclusions about the possibility of radioactive heating of planetary cores. Our direct observation is that under low pressure, highly reducing, metamorphic (800-1000°C) conditions, U loses lithophile character but K does not. Even avoiding the semantic discussion of whether "chalco-philic" should be restricted to FeS, our results show no tendency for U to be incorporated into metal (consistent with Jones and Burnett, 1980) or FeS, although reasonably high U concentrations (4-17ppb) have been reported in FeS from iron meteorites (as tabulated by Morgan, 1971). Whether or not significant quantities of highly reduced, E-chondrite-like, materials were accreted into the Earth is unknown. Also, the degree of solubility of CaS or miscibility of liquid CaS with molten Fe-FeS at higher temperatures is unknown. However, if solubility or miscibility is negligible, then, barring transitions to denser phases, the low density of CaS would tend to keep it near the surface if it were a significant constituent in the accreting earth materials. The observation of djerfisherite in some unequilibrated E chondrites andaubrites is a complication to the generality of our observation; however the disappearance of djerfisherite in equilibrated E-chondrites suggests that it is a disequilibrium phase. It has been argued that K-sulfides are stable phases only at high temperatures (Goettel, 1975; Goettel and Lewis, 1973); thus the djerfisherite alternatively could be interpreted as part of a high temperature component in unequilibrated E chondrites which disappears at metamorphic temperatures. However, we speculate that djerfisherite is an alteration product of a K, S, Cu-rich vapor (impact produced?) reacting with Fe-Ni metal or Fe-Ni sulfide. Vapor phase alteration, probably impact-derived, is a very plausible mechanism to explain high U in Fe-Ni metal and coexisting magnetite in some unequilibrated ordinary chondrites (Woolum et al., 1981). Clarke et al. (1977) have found K-sulfide in a kimberlite nodule, but formation as a vapor-phase alteration product was the favored origin by these authors (Clarke, 1977).

Consequently, we consider it entirely possible that under all conditions where K would tend to be partitioned significantly into non-oxygen-bearing phases, U (and Th) would be partitioned more strongly into such phases and perhaps be incorporated under less extreme (e.g. F$_2$O$_3$) conditions.
effect of partitioning of radioactive elements into the core would favor K and thus would lower the K/U of the earth relative to chondrites as has been generally assumed. Measurable K partitioning into Fe-FeS has been reported in several synthesis experiments (Goettel, 1972, 1975; Oversby and Ringwood, 1973; Ganguly and Kennedy, 1977) but, except for Goettel (1972), these are basically qualitative observations. The measured amounts of K in all these experiments would be significant for core heating. The behaviour of U and Th in similar experiments has not been studied. We conclude that, at present, discussions of radioactive heating of planetary cores should not focus exclusively on K, although the necessity for radioactive heating, in general, has not been established.

Bukowski (1979) has calculated that at high pressures the outer electrons in atomic K will be in predominantly d states and thus K will become a transition metal and alloy more readily with Fe. This could invalidate our hypothesis, but similar calculations do not exist for U. Thus, it is possible that U would also show metallic character at high pressures as well. Also, it is not clear that the calculations are valid for K-Fe-S alloys (as opposed to K metal). Finally, Somerville and Ahrens (1980) failed to observe transitions of KFeS 2 to a metallic state for pressures up to 110 GPa.

For some specific models, stronger conclusions are possible. For example, if S is not an important constituent of the Earth's core and if the metal separated near the surface at low pressure, then the present Hvittis results suggest (but certainly do not prove) that U would be more easily reduced and alloyed than K. However the laboratory studies of Jones and Burnett (1980) indicate that the partition coefficients of U between FeC and FeSi alloys and a silicate melt are very small, $10^{-4}$, suggesting that neither U nor K would be incorporated into the core in this model and that radioactive heating would be insignificant. An alternative model is that the Earth's core formed at high pressure with insignificant S. Although strong arguments exist against this model (Stevenson, 1981), it cannot be ruled out. In this case our results along with Jones and Burnett (1980) indicate that hypothetical pressure effects would have to reverse the relative partitioning of behavior of K and U or increase metal-silicate partition coefficients by 2-3 orders of magnitude for radioactive heating to be important.

In summary, we emphasize the important point that data in the literature suggest that a S-rich core will dissolve enough K to produce significant radioactive heating, although additional experiments are desirable. What we have suggested is that U and Th might also be important.

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References


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