POTASSIUM-BEARING IRON-NICKEL SULFIDES IN NATURE AND HIGH-PRESSURE EXPERIMENTS: GEOCHEMICAL CONSEQUENCES OF POTASSIUM IN THE EARTH'S CORE.

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Introduction: Potassium (K) as a large ion lithophile element has dominantly been concentrated in the Earth's crust and the mantle through differentiation, and in the form of ^{40}K contributes to the planet's heat budget. However, whether or not K also enters core-forming phases, has been debated for over three decades. Arguments favoring entry of K in the core are based on: (1) K-sulfide (with Fe, Ni, Cu, Na, and Cl; djerfisherite) found in highly reduced enstatite chondrites (or aubrites, enstatite achondrites); (2) demonstration that K, owing to an *s-d* electronic switch at high-pressure, exhibits transition-element like character, (3) solubility of measurable K in Fe-Ni-S liquids at high pressure, temperature conditions, and (4) models of cooling of the core that seem to require, besides convection, some form of radioactivity, and thus lending support to the experimental work. In this contribution, we assess the effect of sequestering K in the core, as it is perhaps an element that is a key to reconciling geochemistry, paleomagnetism, accretion, and thermal evolution models for the planet.

Occurrences: Djerfisherite, in highly reduced, unequilibrated enstatite chondrites (EH-type), is normally found also with CaS, (Mg, Fe)S, and caswellsilverite (Na, Cr)S. In terrestrial environments, K-bearing sulfides are found in mantle xenoliths in kimberlites [1, 2], as groundmass crystals in low-to-moderately high-pressure alkalic rocks [3, 4], as a replacement mineral in contact-metamorphic rocks [5], and also as inclusions in diamonds [6]. These occurrences demonstrate that unusually reducing conditions are not limited only to enstatite chondrites. In laboratory, studies investigating the partitioning of K between metal-sulfide and silicate, K-bearing sulfides (along with Fe-Ni-S) have also been synthesized at various P-T-X-fO_2-fS_2 conditions [**e.g., 7, 8, 9**]. Significantly, higher-temperature (> 2300 °C) sulfides, CaS (oldhamite) and niningerite (Mg, Fe)S from enstatite chondrites are common, whereas K-sulfide is a trace phase, and the former phases are also the first phases to crystallize from a model chondritic planet experiencing sulfide saturation under very low fO_2 conditions.

Geochemistry: We evaluate the potential effects on the chemistry of the Earth's silicate shell when considering the consequences of sequestering K in the core. To do so, the well-constrained relative abundances of moderately volatile lithophile elements (Na/K), and refractory elements (Ca/Al, Ti/Al, Ti/Sc, and Yb/Sc) in the silicate Earth are used [**10, 11**]. Until recently, only CaS was reported to be a major carrier of REE with levels of 100-400 times higher than CI [**12, 13**]. However, djerfisherite is also now recognized be a significant sink for REE (La, Ce, Pr, Sm, Nd, Gd, Tb, Lu, and Hf) at 1-10 times CI levels [**13**]. There are no data on the trace element chemistry of terrestrial djerfisherite. However, judging from mantle xenoliths, that have undergone metasomatism resulting in an overall enrichment of trace elements, coupled with the metasomatic introduction of djerfisherite owing to CO_2-rich melts, we can assume that this mineral is also an important host for REE in the Earth's upper mantle. This, in turn has tremendous implications for what we know about Na/K in the silicate mantle. It was argued that since K-sulfides are found as inclusions in diamonds, higher-pressure regime would favor alkali partitioning into sulfides [**14**]. However, as we noted above, K-sulfides are also found in low-pressure alkali igneous and metamorphic rocks, thus relaxing the need to have djerfisherite form only at high-pressures. Chondrites have Na/K of 1.1 ± 10%, and the silicate Earth has Na/K that is ~ 10% greater than the range seen in chondrites [**10**]. With the existing data, it was proposed that ~ 30 and 74% of Na and K, respectively were initially removed into the core [**14**]. Assuming a Na/K as seen in djerfisherite, this would produce a change in the Na/K of the residue (silicate), causing a non-chondritic ratio in the Earth's mantle, for which there is very little evidence [**10**]. Moreover, the depletion of K in the bulk-silicate earth (BSE) conforms to the pattern of depletion seen in other moderately volatile lithophile elements (e.g., Na, Rb, Mn, Li), comparable to that seen in carbonaceous chondrites. Volatility alone appears to have established these chemical depletion patterns in chondrites [**10**]. Thus on the bases of these observations, it is unlikely that the partitioning of elements is in the right sense and order of magnitude to match the chondritic pattern. Hence, the Na/K of the silicate Earth imposes a strict limit on the amount of K that can enter the core. Moreover, oldhamite and niningerite in ensta-

tite chondrites provide a more useful guide to the behavior of alkalis and alkaline metals in sulfur rich systems. Under the unusually reducing conditions of high fS_2 and low fO_2 associated with their formation, Ca, Mn, Mg, Cr, Ti, K becomes partially chalcophile, as do other lithophile elements. Experimental work on K partitioning between metal-sulfide and silicate found measurable quantities of Ca and Mg in the sulfides [**15**]. Thus, if conditions in the planet were such that K was lost to the core, it is an inescapable conclusion that Ca, REEs, and Ti would be included in the core. This, in turn produces subchondritic Ca/Al, Ti/Al, Ti/Sc, Yb/Sc, and Zr/Hf in the silicate Earth, for which abundant evidence exists to argue against such a scenario. However, a systematic study at high P-T conditions, of the solubility of Ca and Mg in sulfides and their possible uptake of REEs and Ti needs to be conducted.

Core cooling: Has the core-to-mantle heat flux remained constant? The heat flow into the mantle is the net loss of heat by the core, and has been estimated to be 2.8-3 TW [**16**]. However, recent thermal models imply a range of 2-10 TW for this heat flux [**17**]. Additionally, on the basis of presence or absence of radioactive elements in the core, these models have also been used to constrain the age of the inner core that varies between 1-3 Ga. The models above are at odds with the oldest recorded age of terrestrial paleomagnetism, which is 3.8 Ga [**18**], and are also in sharp contrast with the age constraints provided on core separation and inner core crystallization provide by Hf-W and Pt-Re-Os isotopic systems [**19**]. Both Hf and W are refractory, being lithophile and siderophile, respectively. On this basis, their relative abundance in the silicate Earth is at chondritic levels. The Hf-W work on chondrites and Earth materials now demonstrates that the separation of the Earth's core occurred at <30 m.y after To.

Conclusions: Experimental studies find K-sulfides stable under a range of upper mantle conditions. However, sequestering K into the Earth's core leads to untenable consequences for a wide spectrum of lithophile element ratios in the silicate Earth (e.g., Na/K, Ca/Al, Lu/Hf, Sm/Nd, Zr/Hf), for which there is little evidence. The arguments presented here can perhaps be challenged on the grounds of how well constrained is the chondritic planetary model for the Earth. Evaluating the uncertainties in the construction of silicate Earth composition and that for the bulk planetary is important. Coupled with understanding the liquidus phase relations in sulfur-bearing chondritic systems, a crucial test of the arguments presented above, will also be gained by more focused analytical work on the REE chemistry of natural alkali-bearing sulfides, and K-bearing sulfides in high-pressure experiments.

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