

High-pressure alloying of potassium and iron: Radioactivity in the Earth's core?

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[1] High-resolution x-ray diffraction provides evidence that potassium (K) alloys with iron (Fe) when the two pure elements are heated together at pressures above ~ 26 gigapascals (GPa). Increases of 2–3% in volume of the ϵ (hexagonal close packed: hcp) high-pressure phase of Fe can be attributed to the incorporation of ~ 1 atomic% (~ 7000 ppm by weight) K into Fe. Our results provide experimental support for predictions, derived from quantum mechanical calculations, that pressure can induce the alloying of K with Fe due to a change in the chemical-bonding character of K from alkaline- to transition-metal. Radioactive decay through the incorporation of ^{40}K into the core could therefore be an important source of energy deep inside the Earth, helping to power the geodynamo and mantle dynamics. **INDEX TERMS:** 3924 Mineral Physics: High-pressure behavior; 8124 Tectonophysics: Earth's interior—composition and state (1212); 8130 Tectonophysics: Heat generation and transport. **Citation:** Lee, K. K. M., and R. Jeanloz, High-pressure alloying of potassium and iron: Radioactivity in the Earth's core?, *Geophys. Res. Lett.*, 30(23), 2212, doi:10.1029/2003GL018515, 2003.

1. Introduction

[2] Two sources of heat drive the thermal, tectonic and geochemical evolution of the Earth: the release of gravitational potential energy and the decay of naturally occurring radioactive nuclides. The first includes the energy associated with accretion and differentiation of the planet. Its magnitude is hard to quantify, because doing so requires a detailed understanding of the Earth's formation and earliest evolution. The role of radioactive heating is potentially easier to estimate, based on chemical analyses of crust and mantle rocks and of meteorites.

[3] A detailed study of terrestrial and chondritic samples [Wasserburg *et al.*, 1964] found that the K/U (potassium/uranium) ratios of $\sim 1 \times 10^4$ on Earth are distinct from the 8×10^4 ratio found in chondrites. If one is to assume a chondritic model for the Earth, where did the rest of the potassium go? Some have argued that because potassium is a moderately volatile element, it is depleted due to the high temperatures present during accretion [McDonough and Sun, 1995]. On the other hand, Humayun and Clayton [1995] found that although there is a wide range of K/U ratios between chondritic, lunar and Earth samples, potassium isotopic ratios barely vary. This finding suggests that evaporation cannot be

responsible for the depletion of K in the terrestrial planets, as a mass-dependent depletion of the isotopes would then be expected.

[4] Alternatively it has been suggested that the K “missing” from mantle rocks may have been segregated into the Earth's core [Hall and Murthy, 1971; Lewis, 1971]. Indeed, quantum mechanical calculations [Bukowinski, 1976] as well as experiments show that the chemical bonding in potassium changes under pressure [Ito *et al.*, 1993; Parker *et al.*, 1996; Takemura and Syassen, 1983]. The change in electronic structure with pressure (from 4s-like to 3d-like bonding orbitals) makes potassium more like a transition metal, hence increasing its tendency to alloy with other transition metals such as iron [Parker *et al.*, 1997]. This electronic transition is bracketed by two structural phase changes, from KII to KIII structures at 11.6 and 23 GPa, respectively [Winzenick *et al.*, 1994]. Once above this transition, potassium can bond with iron according to previous quantum mechanical calculations [Bukowinski, 1976]. However, there have been more recent theoretical calculations [Sherman, 1990] which do not find an increased affinity of K for Fe at high pressure for the composition KFe_{14} . Although we do not fully understand this apparent discrepancy, it may be due to the calculation being for a large amount of K alloyed with Fe (large relative both to what experiment reveals, and to the maximum amount indicated for the core based on cosmochemical grounds).

[5] The change in bonding character of elemental potassium is an important result for chemistry, but it is more geophysically interesting to determine whether K could partition into and alloy with the iron-rich core of the Earth. The radioactive isotope ^{40}K (which decays by β -decay, electron capture and positron emission) is relatively abundant in nature and has a long half-life (~ 1.25 billion years), so it serves as an important heat source over all of Earth's history. If present in the Earth's core, potassium could be a major source of energy for the geodynamo that creates our planet's magnetic field, and even for mantle plumes and convection.

2. Experiment

2.1. Experimental Methods

[6] Potassium (ingot packaged under argon, $>99.95\%$ pure, Aldrich) and iron powder ($>99.9\%$ pure, Alfa Products) were mixed and loaded under an argon atmosphere into a pre-compressed rhenium (Re) gasket in a diamond-anvil cell. Ruby grains ($<10 \mu\text{m}$ in diameter, and smaller than the pre-compressed gasket thickness of 30–45 μm in order to avoid diamond bridging) were placed into the

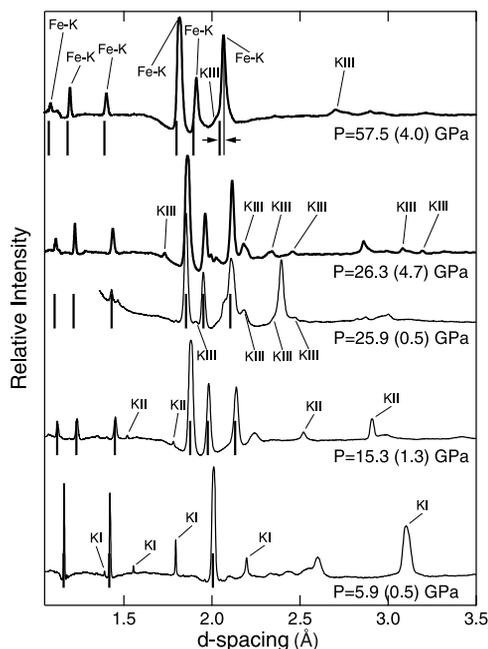


Figure 1. X-ray diffraction patterns at 5.9, 15.3 and 25.9 GPa prior to heating (thin curves), and at 26.3 and 57.5 GPa after laser-heating (thick curves). The expected diffraction-peak locations are labeled for the three phases of potassium: KI, KII, KIII, and for both phases of Fe (thick vertical lines). At the highest pressure, an example of the offset of the Fe peak position with that of the Fe-K alloy (thin vertical line) is displayed. The large peak at ~ 2.4 Å at 25.9 GPa is due to diffraction from the argon pressure medium.

sample chamber for pressure calibration [Mao *et al.*, 1978]. Liquid argon (Ar) was loaded cryogenically as a pressure medium and thermal insulator. At each pressure above ~ 26 GPa, the samples were laser-heated to temperatures >2500 K (above the melting point of iron and potassium) with a Nd-YAG laser ($\lambda = 1064$ nm) to synthesize the alloy and alleviate any deviatoric stresses. In one run, we also laser heated at lower pressures (13.2, 19.8, 25.1 GPa). High-pressure x-ray diffraction patterns were collected at room temperature on image plates at beamline 10-2 of the Stanford Synchrotron Radiation Laboratory, and at beamline 7.3.3 of the Advanced Light Source. Great care was taken to measure the sample-to-image plate distance, determined by Au diffraction, for each diffraction pattern taken (an Au calibration foil was placed on the backside of the diamond closest to the image plate, and the thickness of the diamond was taken into account). We performed six different experimental runs to verify the reproducibility of our results. Separate experiments on only K were also performed using the above methodology, and confirm that K is not amorphous after laser-heating above 26 GPa.

2.2. X-Ray Diffraction Measurements

[7] At low pressures, the phases of K [Liu, 1986; Takemura and Syassen, 1983; Winzenick *et al.*, 1994] and Fe [Jephcoat *et al.*, 1986; Mao *et al.*, 1990; Takahashi *et al.*, 1968; Wilburn and Bassett, 1978] are identifiable by their most intense x-ray diffraction peaks (Figure 1). Diffuse and

broad diffraction lines at the lowest pressure, with d-spacings between ~ 2.2 and 2.6 Å, may be due to minor oxidation or hydration of the initial K, which is highly reactive. Below ~ 26 GPa, the measured unit-cell volumes are consistent with the equations of state for pure Fe and pure K (Figures 1 and 2).

[8] After laser-heating above 26 GPa, however, the x-ray diffraction lines for K become much less intense, and the ϵ -Fe unit-cell volume is enlarged by 2–3% relative to that for pure Fe (Figures 1 and 2). We can determine the K:Fe (by atomic percent) ratio at the lowest pressure by comparing the intensities of the diffraction peaks as estimated by Rietveld refinement: $\sim 60:100$ [e.g., Toby, 2001]. The same sample, shown at 57.5 GPa in Figure 1, yields a much

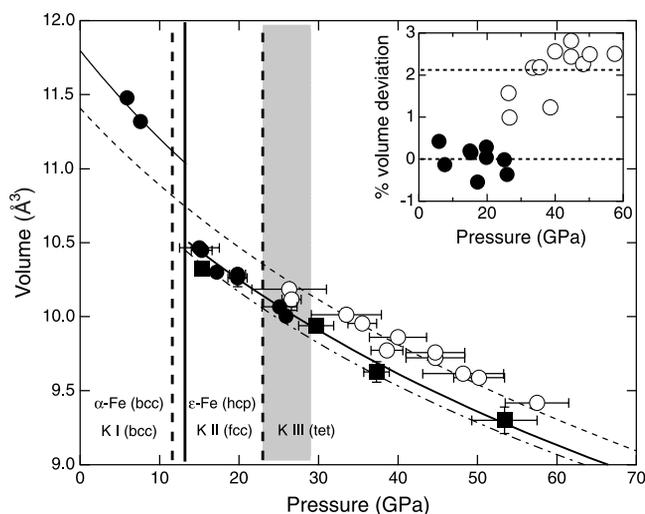


Figure 2. Iron unit-cell volumes observed for K + Fe samples, prior to heating above the sample solidi (solid circles) and after heating above the sample solidi (open circles), are compared with those for pure Fe (solid squares). Solid circles at pressures of 13.2, 19.8 and 25.1 GPa were also laser heated (but to lower than the melting temperature of iron) and do not show evidence of volume expansion. Below ~ 26 GPa and before heating, and at all pressures (measured after heating) for pure Fe, our measurements are in good agreement with prior results for the α (bcc: thin curve, [Takahashi *et al.*, 1968]) and ϵ (hcp: thick curve, [Jephcoat *et al.*, 1986]; dash-dot curve, [Mao *et al.*, 1990]) phases of pure Fe. Dashed curve is the Birch-Murnaghan equation of state for the expanded hcp unit-cell observed after heating Fe with K at pressures above 26 GPa. Phase-transition pressures are indicated by vertical lines for Fe (solid) and K (dashed) (see also Figure 1), with phase stability ranges labeled in between. Shaded vertical bar at 26 (± 3) GPa is our K-Fe alloy transition pressure. **Inset.** Percent volume deviation from the expected volume for Fe [Jephcoat *et al.*, 1986; Takahashi *et al.*, 1968]. Horizontal dashed lines at 0 and 2.1 (± 0.6)% volume deviation correspond to no deviation, as observed for the volumes of unalloyed Fe (closed circles), and the average percent volume deviation of the Fe-K alloy volumes (open circles). Detailed analysis of the diffraction patterns of K + Fe heated at pressures above ~ 26 GPa show that the expansion of the hcp unit cell of Fe cannot be ascribed to overlap of diffraction lines from K III, Ar or the gasket.

decreased K:Fe ratio of $\sim 5:100$, indicative of most of the K being incorporated into Fe.

[9] To verify expansion of the Fe unit cell we also measured the compression of pure Fe, loaded in the same way as the K + Fe sample (including the use of an Ar pressure medium, and laser heating). We obtained results in good agreement with prior measurements [Jephcoat *et al.*, 1986] on the volume of ϵ -Fe as a function of pressure (Figure 2).

[10] Using the Birch-Murnaghan equation of state [Birch, 1978], holding $K_{0T}' = 4.0$ and assuming an initial volume (V_0) expanded by $2.1 (\pm 0.6)\%$ (in line with the average expansion we observe at high pressures), we find a zero-pressure room-temperature isothermal bulk modulus $K_{0T} = 196 (\pm 11)$ GPa for the enlarged ϵ -Fe phase (black dashed curve in Figure 2). This is comparable to the values $K_{0T} = 165\text{--}193$ GPa obtained in previous studies [Jephcoat *et al.*, 1986; Mao *et al.*, 1990] for pure ϵ -Fe, assuming $V_0 = 11.173 \text{ \AA}^3$.

[11] Upon opening the cell at zero pressure, all that is recovered within the Re gasket exhibits only diffraction from Fe and numerous weak diffraction peaks from potassium oxides (K_2O , KO_2 , $KFeO_2$, K_2FeO_4), likely due to the immediate oxidation of any un-alloyed K upon quench. The ϵ -Fe we recover has a slightly expanded unit cell, perhaps due to K remaining incorporated in the Fe upon quenching: the ambient-pressure volume we measure is $0.3 (\pm 0.1)\%$ larger than that expected for pure ϵ -Fe. For comparison, the Re unit-cell volume is as expected [Donohue, 1974], suggesting that the potassium did not alloy with the Re gasket (in contrast with other, much smaller elements like hydrogen [e.g., Benedetti and Jeanloz, 2000]). Rietveld analysis confirms that the amount of K left over (now in the form of oxides) corresponds to a K:Fe ratio of $\sim 5:100$, in good agreement with the K:Fe ratio observed at 57.5 GPa from which it was quenched.

[12] Three separate samples exhibited a decrease in K diffraction intensities, and increase in Fe lattice parameters, upon heating at pressures above ~ 26 GPa. The atomic ratios of K:Fe determined from Rietveld fitting decreased from $56 (\pm 14)$, $17 (\pm 5)$ and $23 (\pm 1)\%$ to $10 (\pm 5)$, $8 (\pm 2)$ and $5 (\pm 3)\%$ respectively. Finally, in a separate experiment, we confirmed that a sample of K + Fe taken directly to 35.6 GPa only exhibits a decrease in K diffraction intensities and expansion in Fe unit-cell volume after heating.

3. Analysis

[13] For hexagonal close-packed (hcp) materials, interstitial occupation can occur with either tetrahedral or octahedral coordination [Smallman *et al.*, 1988]. However, interstitial atoms (in our case, K) must be smaller than the hcp atoms (Fe): K tetrahedral radius $\leq 0.225 \times$ (Fe hcp radius), K octahedral radius $\leq 0.414 \times$ (Fe hcp radius). Even at our experimental pressures, the atomic radius of K is too large for interstitial occupation (at 50 GPa, $r_K = 1.75 \text{ \AA}$ compared to $r_{Fe} = 1.18 \text{ \AA}$) [Winzenick *et al.*, 1994]. This is an approximation, however, as the K radius may change upon combining with Fe. Even so, the pure K radius for our experimental pressure range is more than three (six) times larger than allowed for octahedral (tetrahedral) coordination. Thus we can rule out interstitial occupation because

the atomic volume of K is much larger than that of Fe, even at our experimental pressures.

[14] For substitution, we must also be aware of the atomic sizes. The first of the empirical Hume-Rothery rules states that the atomic radii of the alloying elements must be within $\sim 15\%$ of each other, otherwise the solid solution formed will be restricted to a few atomic percent [Smallman *et al.*, 1988]. Although the size-factor is unfavorable for K, limited solid-solution is still possible with Fe. For substitution, we compare the hcp volume of ϵ -Fe with the volume of a hypothetical hcp phase of K. Assuming Vegard's Law [Vegard, 1921], a linear relationship between volume and composition (in atomic percent), we find that in order to increase the ϵ -Fe unit cell volume by 2–3% we must substitute $\sim 1\%$ of the Fe atoms with K. This $\sim 1\%$ substitution is compatible with the first of the Hume-Rothery rules, though it may be a lower bound because most solid solutions have a concave response to concentration increase (greater than a linear growth) rather than a linear response [Smallman *et al.*, 1988].

[15] This amount of K that apparently can be dissolved into Fe, ~ 7000 ppm ($0.7 (\pm 0.2)$ wt%), is far larger than the amount of K sequestered into the core according to cosmochemical estimates (~ 1200 ppm; see discussion in [Gessmann and Wood, 2002]). It is also larger than the amount that has been experimentally determined to partition into iron-sulfide in previous experiments, conducted at lower pressures than ours ($\sim 10^2$ ppm; [Gessmann and Wood, 2002; Murthy *et al.*, 2003]). The pressures of the earlier experimental studies were too low (< 26 GPa) for the $s \rightarrow d$ electronic transfer to be complete. Ito *et al.* [1993] measured the dissolution of K into molten iron sulfide at 26 GPa and 2900 K, and found partitioning of K into Fe ($D_K = 3.8 \times 10^{-2}$) corresponding to 5 ppm in the Earth's core. However, as Murthy *et al.* [2003] have shown, the distribution coefficient is highly dependent on time and on polishing methods, thus the equilibrium abundance of K in liquid Fe could actually be much higher than measured by Ito *et al.* [1993] (e.g., by more than one order of magnitude). One might therefore expect that if future partitioning experiments are done at pressures above 26–30 GPa, the partitioning of K into iron sulfide would be greater. A shock-wave study of $KFeS_2$ has shown a similar transition from a “low-pressure regime” to a “high-pressure regime” between $\sim 20\text{--}30$ GPa, possibly due to the transition-metal tendencies of K at those conditions [Somerville and Ahrens, 1980].

4. Discussion and Conclusions

[16] There are several scenarios for core formation (e.g., blobs, percolation, diapirs, magma-fracturing; for more details see Stevenson [1990]) which suggest that iron droplets formed and settled through the mantle, possibly at the base of a magma ocean. The base of this magma ocean is inferred to have been at a depth of ~ 400 to 1000 km ($\sim 15\text{--}35$ GPa) and at temperatures of 2200–3000 K [Ohtani, 1985]. Our experiments show that K can alloy with Fe above pressures of ~ 26 GPa and temperatures above 2500 K, compatible with the base of a magma ocean environment. Although we have shown that potassium and iron alloy at deep magma-ocean conditions, without the

presence of sulfur or high oxygen fugacities [Gessmann and Wood, 2002; Murthy et al., 2003], partitioning between silicate and metal also needs to be taken into account. However, uncertainties in the relevant phases and compositions (e.g., light elements in the forming core, nature of silicate and oxide phases that were present) mean that significant assumptions are required if one is to more quantitatively evaluate the partitioning of K between the early core and mantle.

[17] Recent core-energetics calculations [Buffett, 2002; Nimmo et al., 2003] suggest that some amount of radioactivity may be compatible with—or even necessary for—producing the Earth's early magnetic field. Likely candidates for radioactivity in the core are potassium, uranium and thorium (Th). Potassium's relative abundance and now-demonstrated affinity for iron make it a palusible source of radioactive heat in the core. Following Verhoogen [1980], the 7000 ppm maximum amount of K indicated to alloy with Fe from our experiments would currently yield approximately 45 terawatts (TW) of power if present throughout the core: more than the ~40 TW currently being lost at the Earth's surface.

[18] Our experiments only provide an upper limit to the amount of K that might be present in the core, because we have not taken into account the partitioning between silicate and metal phases. Moreover, this amount of potassium is at least one order of magnitude greater than is necessary to satisfy calculated energy requirements to sustain the geodynamo [Buffett, 2002], as well as being greater than cosmochemical estimates. As core differentiation probably began before accretion was complete, the pressure and temperature conditions may not have been favorable early on to alloy potassium and iron, until accretion was nearly finished. Therefore, although we find a high amount of K (relative to that required) alloying with Fe at pressures greater than 26 GPa and temperatures above 2500 K, much of the core could have already formed before the conditions were such that potassium could begin to alloy. Geochemically-based estimates of the abundance of K in the core, 1200 ppm, yield 8 TW of power being currently released, and 100 TW being released from the core 4.5 billion years ago [Gessmann and Wood, 2002]. Considering that U and Th could additionally be present in the core, a much larger amount of radioactive heating than previously recognized could thus be powering the geodynamo, as well as the dynamics of the overlying mantle, throughout geological history.

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