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Geochemical Perspectives Letters

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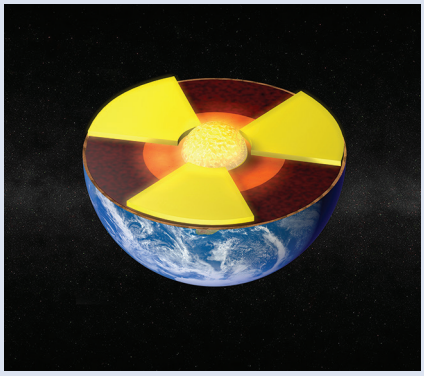
OPEN ACCESS

doi: 10.7185/geochemlet.1737

Abstract



The long term thermal and dynamic evolution of Earth's core depends on its energy budget, and models have shown that radioactive decay due to K and U disintegration can contribute significantly to core dynamics and thermal evolution if substantial amounts of heat-producing elements are dissolved in the core during differentiation. Here we performed laser-heated diamond anvil cell experiments and measured K and U solubility in molten iron alloy at core formation conditions. Pyrolitic and basaltic silicate melts were equilibrated with metallic S–Si–O-bearing iron alloys at pressures of 49 to 81 GPa and temperatures of 3500 to 4100 K. We found that the metal-silicate partitioning of K is independent of silicate or metal composition and increases with pressure. Conversely, U partitioning is independent of pressure and silicate composition but it strongly increases with temperature and oxygen concentration in the metal. We subsequently modelled U and K concentration in the core during core formation, and found a maximum of 26 ppm K and 3.5 ppb U dissolved in the core, producing up to 7.5 TW of heat 4.5 Gyr ago. While higher than previous estimates, this is insufficient to power an early geodynamo, appreciably reduce initial core temperature, or significantly alter its thermal evolution and the (apparently young) age of the inner core.

Received 1 August 2017 | Accepted 7 September 2017 | Published 4 October 2017

Introduction

The long term thermal evolution of the core plays a fundamental role in the potential of a terrestrial planet to sustain life. Indeed, the existence of a magnetic field is one of the tenets of planetary habitability, which is generated by a geodynamo operating in the planet's convective liquid core. The present day geodynamo is mainly driven by compositional buoyancy, due to light element release by the crystallisation of the inner core. A core with large thermal conductivity (*e.g.*, Pozzo *et al.*, 2012; Ohta *et al.*, 2016) yields a young age (less than 1 Gyr) for the inner core (Labrosse, 2015; Nimmo, 2015a), which is in apparent contradiction with palaeomagnetic evidence for an old geodynamo dating back to at least 3.5 Ga (Tarduno *et al.*, 2010). Even with a low core thermal conductivity (Konôpková *et al.*, 2016), the problem is partially mitigated, in that a dynamo can be sustained for 3.5 Gyr (*e.g.*, Labrosse, 2003; Nimmo, 2015a), but initial core temperatures are very high, above 7000 K, which implies a fully molten Earth for extended periods of time.

Recently, MgO exsolution (Badro *et al.*, 2016) and SiO_2 crystallisation (Hirose *et al.*, 2017) have been proposed as an alternative source of chemical buoyancy to drive a dynamo prior to inner core growth. These are potent sources of energy and dissipation, and while they both eradicate the need for a hot initial core, their effect is not predicted to kick in until 1 to 2 Gyr after Earth's formation for MgO, and even later for SiO_2, leaving the Earth devoid of a geodynamo, assuming a young inner core age.

One possible mechanism to drive a very early dynamo, in the first billion years of Earth's history, is the dissolution of radioactive heat-producing elements in the core during formation (Gubbins *et al.*, 2003). Because radionuclide abundance decreases with time, the process is dominant very early in Earth's history and vanishes with time. Potassium and uranium are the main sources of heat in the Earth, and their incorporation in the core has been thoroughly examined through the years (*e.g.*, Buffett, 2002; Gubbins *et al.*, 2003; Labrosse, 2003, 2015; Nimmo *et al.*, 2004), and it was shown that the incorporation of ~100s of ppm K in the core would mitigate the young inner core/early geodynamo/hot initial core conundrum.

Both K and U are nominally lithophile elements, with no predisposition to fractionate in the metallic phase during metal-silicate equilibration. Bukowinski (1976) proposed that potassium might become a transition metal at high pressure, with the ability to dissolve easily in core-forming metal, later confirmed experimentally by Parker *et al.* (1996), which motivated a suite of metal-silicate experiments (performed below

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25 GPa in large-volume presses - LVP) to address and quantify the partitioning of potassium between metal and silicate during Earth's differentiation (Gessmann and Wood, 2002; Murthy *et al.*, 2003; Bouhifd *et al.*, 2007; Corgne *et al.*, 2007).

Similarly, uranium partitioning studies (LVP) have shown a limited solubility in the metal, recently confirmed by a study of U partitioning in the laser-heated diamond anvil cell (LH-DAC). U was shown to become more siderophile with: *(i)* increasing sulphur content in the metal (Wheeler *et al.*, 2006; Malavergne *et al.*, 2007; Bouhifd *et al.*, 2013; Chidester *et al.*, 2017), *(ii)* high temperatures (Chidester *et al.*, 2017), and *(iii)* low SiO_2 concentration in the silicate (Chidester *et al.*, 2017). However, even in the most favourable conditions, including an unrealistically high sulphur content of the core (8 wt. %), no more than 3.5 ppb U could be dissolved in the core (Chidester *et al.*, 2017), providing no more than 2.4 TW as early as 4.5 Gyr ago, which is insufficient to have any effect on an early geodynamo.

The solubility of thorium, the other major radioactive element in the Earth, in metal was not addressed in the present work as LH-DAC experiments from Chidester *et al.* (2017) showed no measurable Th in the metallic phases.

Experiments and Results

Here we investigated the metal-silicate partitioning of both U and K at the relevant P-T conditions of core formation, through LH-DAC experiments. Two silicate compositions were used (pyrolitic and basaltic) to examine the effect of silicate composition on partitioning; similarly, several metal compositions (with various amount of S, Si and O dissolved) were used to examine the effect of metal composition on that same partitioning (see Supplementary Information and Table S-1). The samples were compressed to 41 to 81 GPa and laser-heated to 3600 to 4100 K (Table S-2), achieving conditions above the liquidus of both metal and silicate and efficiently melting the sample. Thin sections were recovered from the centre of the laser-heated area using a focused ion beam (Fig. S-1) and analysed using an electron probe (Tables S-3 and S-5).

K and U partitioning between metal and silicate are driven by an exchange reaction involving Fe in the metal and FeO in the silicate, and are written as:

$$\tfrac{1}{2}\,Fe + \tfrac{1}{2}\,K_2O \leftrightarrow K + \tfrac{1}{2}\,FeO \qquad \text{(Eq. 1)}$$

$$Fe + UO \leftrightarrow U + FeO \qquad \text{(Eq. 2)}$$

The equilibrium constants *K* of reactions (1) and (2) are a function of P, T, and can be expressed as a function of the reaction's exchange coefficient (*D*) and activity coefficients (γ):

$$\log K_K = \log \frac{D_K}{D_{Fe}^{0.5}} + \log \frac{\gamma_K^{metal}}{\gamma_{Fe}^{metal^{0.5}}} = a + \frac{b}{T} + c\frac{P}{T} \qquad \text{(Eq. 3)}$$

$$\log K_U = \log \frac{D_U}{D_{Fe}} + \log \frac{\gamma_U^{metal}}{\gamma_{Fe}^{metal}} = a + \frac{b}{T} + c\frac{P}{T} \qquad \text{(Eq. 4)}$$

where *a*, *b* and *c* are related to change in entropy, enthalpy and volume, respectively; γ the activity coefficients of K, U, and Fe in the metal, which are a function of the interaction parameters ε_i^o, ε_i^s and ε_i^{Si} for K and U. We used a valence of +1 for potassium, and +2 for uranium (as proposed by Chidester *et al.*, 2017) and combined our data with values from the literature (see Table S-6) to perform a least squares linear fit (details of the fitting procedure are in the Supplementary Information) for all the parameters of the equilibrium constant (Eq. 3 and Eq. 4).

The data and the fitted regressions are plotted in Figure 1, and the parameters resulting from the fit are listed in Table 1. We find that potassium has no measurable interaction with O, Si, or S in the metal. Its partitioning in the metal shows a strong pressure dependence (c = 65 ± 2.5 K/GPa) but no intrinsic temperature dependence (b = 0 K), as can be seen from the excellent linear fit to the data (R^2 = 0.94). Uranium, on the other hand, has a very strong interaction parameter with oxygen in the metal, as illustrated from our fitted value of ε_U^O =-31, which signals that oxygen dissolved in the metal enhances the siderophile behaviour of uranium. No measurable effect of Si and S on U partitioning was found. Lastly, a strong temperature dependence (b = -10133 ± 642 K) and no pressure dependence (c = 0 K/GPa) were found, as can be seen once again by the excellent linear fit (R^2 = 0.91). A detailed discussion and comparison of these results with previous estimates is provided in Supplementary Information.

Discussion

Our results were incorporated in a continuous core formation model (Badro *et al.*, 2015), using two different magma ocean geotherms: cool (Andrault *et al.*, 2011) and warm (Fiquet *et al.*, 2010) liquidus, and calculated the concentration of U and K in the core (see Supplementary Information for details). Along a cool geotherm, up to 26 ppm K (corresponding to 40 ppb ^{40}K) can be dissolved in the core (Fig. 2), with less than 0.3 ppm U 4.5 Gyr ago. This produces at most 7.5 TW of radiogenic power after core formation, and decreases to 4 TW after 1 Gyr. Along a warm geotherm (Fig. 2), more uranium (2.5 ppb) can be dissolved in the core, owing its steep partitioning temperature dependence, along with less potassium (13 ppm K — corresponding to 20 ppb ^{40}K) owing to its partitioning increasing with P/T, therefore decreasing in a hotter magma ocean. Since K is a significantly more efficient heat production element than U, the total power produced is surprisingly smaller in a warm than in a cool geotherm: the maximum power generated is 6 TW after core formation and decreases to 3 TW after 1 Gyr.

In either case, the heat production is lower than the minimum heat flow of 15 TW proposed by Nimmo (2015b) to drive a geodynamo. Similarly, Labrosse (2015) showed that the contribution of K in the total dissipation (required to drive a dynamo) is low, even with a core containing 200 ppm K (an order of magnitude higher than our estimates). Our results therefore confirm that heat-producing elements dissolved in the core cannot sustain an early geodynamo.

With a core containing 26 ppm potassium, the initial temperature of the core is virtually unchanged compared to a core containing no K (Labrosse, 2015; Nimmo, 2015b). Therefore, core-mantle boundary temperatures lie above the silicate solidus for an extended period of time (Labrosse, 2015), supporting the existence of a basal magma ocean (Labrosse *et al.*, 2007). The influence of a limited concentration of heat-producing elements in the core on the age of the inner core is negligible. Finally, the heat flow coming from the core nowadays is estimated to be of 12 ± 5 TW (Nimmo, 2015b). We show here that potassium and uranium together contribute at most 1 TW of the overall heat production of the core today.

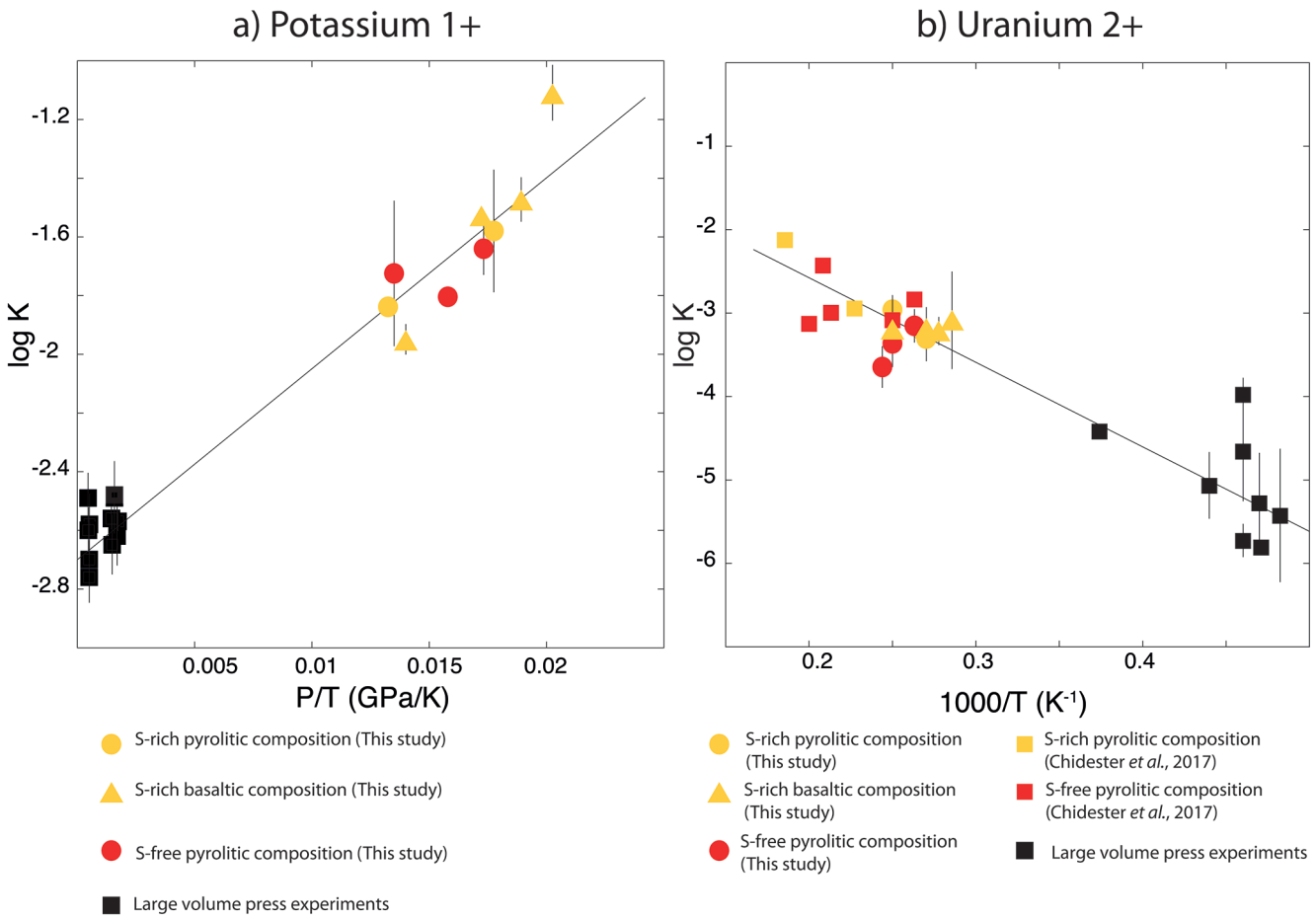

Figure 1 Thermodynamic models of K and U partitioning between metal and silicate. **(a)** Equilibrium constant for potassium metal-silicate partitioning (Eq. 1) as a function of P/T. The line corresponds to the least squares fit (R^2 = 0.94) of the thermodynamic model (Eq. 3) with a = -2.7 ± 0.03 and c = 65 ± 2.5. **(b)** Equilibrium constant of uranium metal-silicate partitioning (Eq. 2) as a function of the reciprocal temperature. The line corresponds to the least squares fit (R^2 = 0.91) of the thermodynamic model (Eq. 4) with a = -0.55 ± 0.21, b = -10133 ± 642 and ε_U^O = -31.

Table 1 Coefficients from Eqs. 3, 4 (and S-3, S-4) obtained by least squares linear regression of the experimental data, along with their associated (1 sigma) uncertainties. Details of the calculation are given in the Supplementary Information.

Element *i*	a	b (K)	c (K/GPa)	ε_i^o (1873 K)	ε_i^S (1873 K)	ε_i^{Si} (1873 K)
Potassium	–2.7 (0.03)	0	65 (2.5)	0	0	0
Uranium	–0.55 (0.21)	–10133 (642)	0	–31	0	0

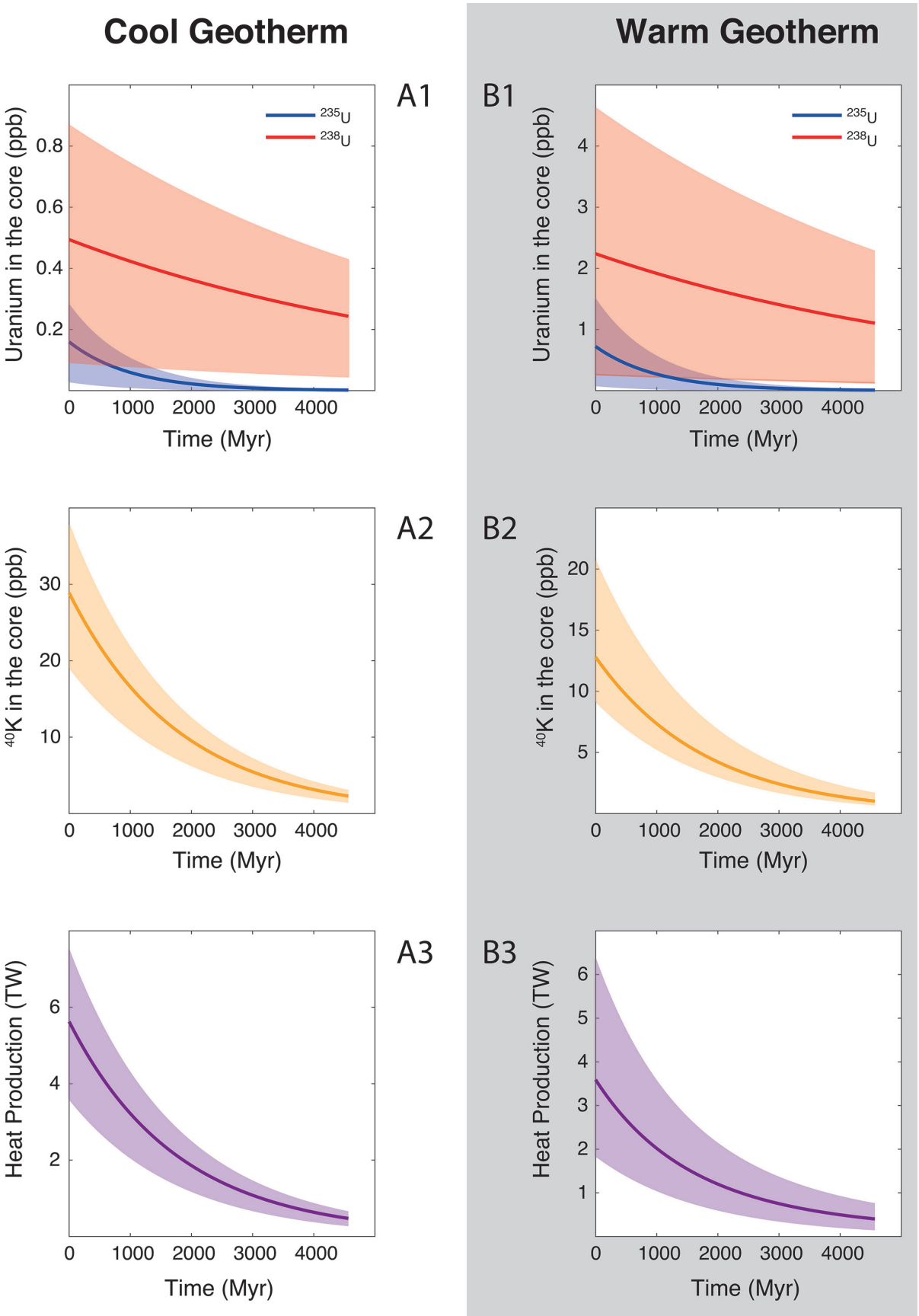

Figure 2 Concentration of K and U in the core from continuous core-formation models, assuming two magma ocean geotherms: cool (A1,2,3) and warm (B1,2,3). The top panel is the abundance of ^{238}U and ^{235}U as a function of time, the middle panel corresponds to that of ^{40}K as a function of time, and the bottom panel is the total power produced in the core by the radioactive decay of these three radionuclides over time.

Conclusions

We measured the simultaneous metal-silicate partitioning of potassium and uranium at the putative high pressure and high temperature conditions of core formation, using laser-heated diamond anvil cell experiments. Potassium solubility in the core increases with pressure and decreases with temperature, whereas uranium solubility in the core increases with temperature and with the oxygen concentration in the core. Despite a higher solubility of those elements in liquid metal compared to low pressure-temperature experiments, the amount dissolved in the core during core formation is too low to have an effect on an early dynamo, the initial temperature of the core or the age or the inner core.

Acknowledgements

This manuscript benefitted from the reviews of two anonymous reviewers that are thanked for their constructive comments. We would like to thank Michel Fialin for his help with EPMA measurements, and Brandon Mahan for his aid in preparing the starting materials. We acknowledge the financial support of the UnivEarthS Labex program at Sorbonne Paris Cité (ANR-10-LABX-0023 and ANR-11-IDEX-0005-02). This work was supported by IPGP multidisciplinary program PARI, and by Paris-IdF SESAME Grant no. 12015908. This work has been written while IB was in BGI, supported by DFG Projekt RU 1323/10-1. JB acknowledges funding from the PNP research program at INSU/CNRS, and the European Research Council under the European Community's Seventh Framework Programme (FP7/2007-2013) / ERC grant agreement n° 207467 (DECore). JS acknowledges funding from the PNP research program at INSU/CNRS and the French National Research Agency (ANR project VolTerre, grant no. ANR-14-CE33-0017-01).

Editor: Wendy Mao

Additional Information

Supplementary Information accompanies this letter at www.geochemicalperspectivesletters.org/article1737

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Cite this letter as: Blanchard, I., Siebert, J., Borensztajn, S., Badro, J. (2017) The solubility of heat-producing elements in Earth's core. *Geochem. Persp. Let.* 5, 1–5.

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