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On the Distribution and Variation of Radioactive Heat Producing Elements Within Meteorites, the Earth, and Planets

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Abstract The heat production budget of a planet exerts a first order control on its thermal evolution, tectonics, and likelihood for habitability. However, our knowledge of heat producing element concentrations for silicate-metal bodies in the solar system—including Earth—is limited. Here we review the chronicle of heat producing elements (HPEs) in the solar system, from the interstellar medium, to their incorporation in the protoplanetary disk and accreting planetesimals, to later collisional or atmospheric-erosion modifications. We summarise the state of knowledge of the HPEs in terrestrial planets and meteorites, and current Earth models from emerging constraints, and assess the effect variations may have on the thermal and tectonic history of terrestrial planets.

Keywords Heat production · Heat producing elements

1 Introduction

Earth is losing heat, and the mechanisms by which it does so largely power the surface geological cycle. High internal temperatures enable convection within the solid Earth, and thus plate tectonics. However, it has not historically been clear how much of this heat is produced contemporaneously by heat producing elements (HPEs), or whether there exists a large thermal repository of fossil-heat (Lenardic et al. 2011; Dye 2012; Korenaga 2003). This knowledge gap is critical, as the heating mode, and thus HPEs, exert a fundamental control over the tectonic regime of a terrestrial planet (e.g. O'Neill et al. 2007; Stein et al. 2004). The tectonic regime determines the rate and style of cooling, the extent and character of resurfacing, and the mode of volatile cycling that ultimately governs atmospheric production and loss, climate, and thus characteristics such as the occurrence

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and longevity of habitable (i.e. surficial liquid water) conditions (e.g. Jellinek and Jackson 2015).

The sources of primordial heat within the Earth include heat from accretion (e.g. Birch 1965; Canup 2008) and core formation (Stevenson 1981; Shaw 1979), and heating due to ancient radioactive isotopes in the past. Early workers (e.g. Tozer 1965) suggested that the temperature dependence of mantle viscosity would result in faster convection for hot planets, leading to rapid heat loss, and equilibration of planetary cooling with the decay of radioactive isotopes.

The balance between contemporaneous heat production, and total heat loss, has previously been expressed in terms of the Urey ratio, which is defined as the ratio of internal heat generation, to total system heat loss (Christensen 1985; Lenardic et al. 2011). The most recent estimate for Earth's heat loss is 47 ± 1 TW (Davies and Davies 2010), and for its radiogenic heat production, about 21.5 TW, assuming a geochemical model for the Bulk Silicate Earth (BSE) based on chondrite meteorites (O'Neill 2016). This value gives a planetary Urey ratio of 0.45, implying that less than half of Earth's heat comes from contemporaneous heat production. Non-chondritic BSE models for the concentrations of the HPEs predict even lower values for the Urey ratio (O'Neill and Palme 2008; Jackson and Jellinek 2013).

A major challenge in interpreting these estimates comes from thermal history modelling, which can project the temperature of the mantle back through geological time using a coupled set of evolution equations for energy conservation and mantle convection scalings. For low Urey ratios, most of the heat flow through time comes from fossil and core heat, with lower contributions from radioactive heat production. This implies temperatures in the past were greater—often much greater than the upper mantle solidus for most of the Archaean. This result has been called the "Archaean thermal catastrophe", and it has historically presented a paradox as there is little evidence for an entirely molten Earth at this time (Christensen 1985; Lenardic 2006; Korenaga 2006). Resolutions to it include alternative tectonic regimes (Christensen 1985; Labrosse and Jaupart 2007; Höink et al. 2013; Moore and Webb 2013; O'Neill and Debaille 2014; Jellinek and Jackson 2015), modifications to subduction efficiency (Conrad and Hager 2001; Korenaga 2003), or deep layering (e.g. Kellogg et al. 1999; Butler and Peltier 2002). The latter class of solutions often involve partitioning of heat-producing elements into deep mantle reservoirs (Labrosse et al. 2007).

There are three critical issues surrounding planetary heat production: i) How many HPEs a planet starts with, and in what proportion—this involves some requisite knowledge of the birth environment of the solar system, and the local composition of the interstellar medium from which the solar system was sourced, as well as the sampling, and mixing efficiency during planetary formation; ii) The extent to which a planet retains its initial inventory of HPEs following accretion. This initial concentration may be modified by collisional erosion (O'Neill and Palme 2008) or atmospheric loss on growing planetesimals (Johnstone et al. 2019; Hin et al. 2017) or redistributed as a result of mantle differentiation and continental crust production; and iii) The interplay and character of thermal exchange among key heat-producing/thermal reservoirs within the Earth. A planet's heating mode through time modulates its tectonic state and, thus, initial thermal configurations (temperature and HPE concentrations and distribution) may determine the evolutionary path of a planet (O'Neill et al. 2016): The key for projecting a planet's future is knowing its formation history.

The purpose of this contribution is to bring new constraints on the heat-production budget of the Earth, from meteoritic, geochemical, and geophysical perspectives, to assess the distribution of heat production within the Earth, and understand its impact on planetary evolution.

2 History and Systematics

The heat producing elements within the Earth currently governing heating via radioactive decay are Uranium, which has two primary contributing isotopes, ^{235}U and ^{238}U, as well as ^{232}Th and ^{40}K. In addition to these four isotopes, ^{26}Al and ^{60}Fe may have contributed to internal heating early in the solar system. The Earth inherited these isotopes from the interstellar medium during the formation of the protoplanetary disk, with some components (notably ^{26}Al) being mixed in heterogeneously during its subsequent evolution (Bizzarro et al. 2007; Makide et al. 2011; Schiller et al. 2015).

These radioisotopes have distinct half-lives and decay energies, and contribute different amounts of power to a planet's heat budget through time. The short half-life ^{26}Al (it decays to ^{26}Mg either via a β^+ decay or electron capture, and had a half-life of $\sim$0.717 Myr, Ruedas 2017) was, for example, probably critical in promoting melting and differentiation within developing planetesimals (e.g. Schiller et al. 2015). In contrast, the concentration of ^{60}Fe in the early disk has been questioned (e.g. Trappitsch et al. 2018), and may not have been present at high enough concentrations to be geodynamically relevant. ^{60}Fe's half-life was $\sim$2.62 Myr (Ruedas 2017), and it decayed via beta (β^-) decays to ^{60}Co and then ^{60}Ni (the half-life applies to the whole chain).

The three elements contributing to present-day heat production (U, Th and K) share the geochemical characteristic of being incompatible during igneous differentiation of the Earth, and as a result have become concentrated in the Earth's continental crust over geological time, particular into the uppermost continental crust, and perhaps also in deep reservoirs (Labrosse et al. 2007).

^{238}U is the most abundant extant isotope of uranium, and has a half life of 4468 Myr (Ruedas 2017, and references therein). It decays via a very complicated decay chain (e.g. Ruedas 2017) to eventually ^{206}Pb (and eight ^{4}He atoms). ^{235}U is much less abundant than ^{238}U (currently 0.72% vs. 99.27% of natural Uranium), and has a much shorter half-life of 704 Myr. It also has a complicated decay chain to eventually form ^{207}Pb, and seven ^{4}He atoms. Lastly, ^{232}Th, essentially the only natural form of Thorium, has a long 14.05 Gyr (O'Neill 2016, and references therein), decaying eventually to ^{208}Pb (and six ^{4}He).

Both U and Th are "Refractory Lithophile Elements" (RLEs), which comprise a group of 28 elements that are calculated to condense from the canonical solar nebula at higher temperatures than the main constituents of the rocky planets (i.e. Mg, Si (and associated O) and Fe, the latter initially condensing as metal). The RLEs occur in approximately the same ratios to each other in most undifferentiated meteorites ("chondrites") and, within uncertainty, the solar composition. This observation is assumed to also apply to the Bulk Silicate Earth (known as the "chondritic model" of the Earth's composition), enabling its concentrations of U and Th to be estimated. The proportion of Th to U is much more tightly constrained than their individual concentrations. That both Th and U decay to isotopes of the same element, Pb, has long fascinated geochemists for its potential in deciphering the evolution of solar-system materials (especially the Earth), hence the ratio Th/U has been intensively studied. The isotopic ratio ^{232}Th/^{238}U is known in geochemistry as κ (Greek kappa). The current estimate of solar-system Th/U from κ via Th-U-Pb systematics is 3.88 ± 0.02 (Blichert-Toft et al. 2010). From the point of view of heat production, it seems reasonable on current knowledge to assume that all the terrestrial planets and meteorite parent bodies of the solar system have similar Th/U (see Sect. 3).

By contrast K is not a RLE, but behaves cosmochemically as a moderately volatile element. Therefore, its abundance in the Bulk Silicate Earth is not constrained by the chondritic model, but must be estimated empirically. This exercise has been traditionally carried out

Table 1 Summary of key physical data for important heat producing elements (HPEs) throughout Earth's history

Isotope	$\tau_{1/2}$: Half-life (Myr)[a,b]	A: Natural abundance[b] (%)	H: Heating rate[a] (W/kg)	C_0: Present mean BSE concentration[c] (kg/kg)	Final decay products[b]
^{60}Fe	2.62	~0	3.6579×10^{-2}	~0	^{60}Ni
^{26}Al	0.717	~0	0.3583	~0	^{26}Mg
^{40}K	1250	0.0117	28.761×10^{-6}	30.4×10^{-9}	^{40}Ar and ^{40}Ca
^{238}U	4468	99.27	94.946×10^{-6}	22.7×10^{-9}	^{206}Pb (+8 ^{4}He)
^{235}U	703.8	0.72	568.402×10^{-6}	0.16×10^{-9}	^{207}Pb (+7 ^{4}He)
^{232}Th	14050	100	26.368×10^{-6}	85×10^{-9}	^{208}Pb (+6 ^{4}He)

[a]Ruedas (2017), [b]O'Neill (2016), [c]Palme and O'Neill (2014)

by using the observation that the ratio K/U is reasonably constant in the major geochemical reservoirs of the Earth, insofar as these are accessible (Sun and McDonough 1989; see Table 2). More detailed investigation takes into account that K is somewhat less compatible than U in some of the most significant processes of planetary differentiation, such that K abundances are obtained from combining information from K/U and K/La ratios (e.g., Jackson and Jellinek 2013; Palme and O'Neill 2014). It is also the most abundant of the extant radioactive heat-producing nuclides. ^{40}K is present in natural potassium at a concentration of 1.668×10^{-4}, and decays into two daughter products: ^{40}Ca (via a β^- decay), which constitutes 89.28% of the decay product, and ^{40}Ar via electron capture, which constitutes the other 10.72%.

Due to their differing half-lives and decay energies, these isotopes have contributed variably to Earth's internal heat production over time. This total heat production can be quantified using the relationship (Turcotte and Schubert 2002):

$$H = \sum_i C_{0i} H_i \exp\left(\frac{t \ln 2}{\tau_{\frac{1}{2}i}}\right) \tag{1}$$

Here the summation is over each extant radioactive nuclide ($i = {}^{40}$K, ^{238}U, ^{235}U, and ^{232}Th), t is the time (in the same units as half-life), and the other values for each species are listed in Table 1 (note the natural abundance A has been factored into C_0 in Table 1). An example of the relative contribution of heat production through time can be seen in Fig. 1. The model here assumes a homogenous primordial mantle, that has not segregated into separate reservoirs—a discussion of Earth's internal reservoirs follows in Sect. 4.

^{26}Al and ^{60}Fe are long extinct, and are excluded from the calculation. ^{235}U and ^{40}K dominated Earth's early planetary heat budget, but due to their shorter half-lives, have waned in influence in the latter half of Earth's history. ^{238}U and ^{232}Th currently dominate Earth's internal heat production, due to their relative abundances, heating rates, and long half-lives, and ^{232}Th is expected to be the predominant heat source for ancient rocky exoplanets.

The heat production of the Earth was essentially set by the initial concentrations of HPEs inherited from the interstellar medium, which collapsed to form the protoplanetary disk. The production and seeding of the interstellar medium with elements other than H and He are

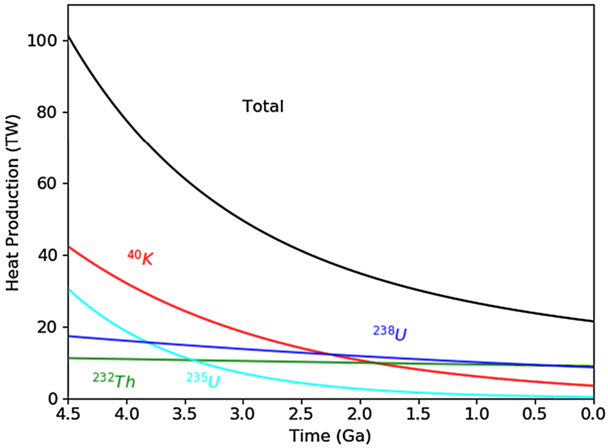

Fig. 1 Relative contribution of radioactive nuclides to Earth's internal heating rate, based on Table 1 and Equation (1)

largely governed by the life cycle of stars including main sequence evolution and supernovae (e.g. Lugaro et al. 2014), white dwarfs (via Type Ia supernovas, e.g. Tinsley 1979), and neutron-star mergers (Kasen et al. 2017; Bartos and Marka 2019). The radionuclides of uranium and thorium are the result of rapid neutron capture, or r-process, thought to occur either during specific supernova conditions, or alternatively via neutron-star mergers (Kasen et al. 2017; Bartos and Marka 2019). ^{40}K is more complicated, with contributions to its production rate from oxygen-burning stellar nucleosynthesis and s (slow neutron capture) processes (e.g. Frank et al. 2014), the latter event occurring largely in asymptotic giant branch (AGB) stars. On the basis of meteoritic concentrations of r-process (^{129}I) and s-process (^{182}Hf) radionuclides, Lugaro et al. (2014) suggested that the last r-process contributing to solar system r-process elements was 100 Myr prior to the formation of the first solar system solids. Brennecka et al. (2010) obtained similar intervals (110-140 Myr) from uranium isotopes. The last s-process addition (constrained by ^{182}Hf), via AGB star winds, was $\sim$30 Myr prior (Lugaro et al. 2014). Extremely short-lived isotopes (^{26}Al and ^{60}Fe, for example) are ascribed to 'self-pollution' of the nebula itself, which is supported by variably mixed ^{26}Al in the earliest solar system material (e.g. Holst et al. 2013).

On a galactic scale, the broad evolution of radionuclides can be considered from the perspective of galactic chemical evolution models. Frank et al. (2014) presented the results from an empirical galactic chemical evolution model that considered the production, mixing, and decay of ^{40}K, ^{232}Th, ^{235}U and ^{238}U throughout the evolution of the galaxy over 12.5 Gyr (Fig. 2). The critical dynamics of this model are that whilst these radionuclides are continually produced over time, they decay, whereas stable species do not. The net result is that the heat-producing radionuclides become diluted over time. Planets that formed early in galactic history would, other factors being constant, have higher heat production than rocky planets forming today. This observation has important implications for planetary evolution, tectonics, and predictions for the likelihood of habitability (Noack et al. 2014).

3 The Solar System Variations in HPEs

Abundances of heat producing elements in terrestrial planets inherit their concentrations from the protosolar nebula and, hence, the Sun's composition is the baseline for primitive disk material, meteorites and planets (e.g., Asplund et al. 2009). A difficulty in using the

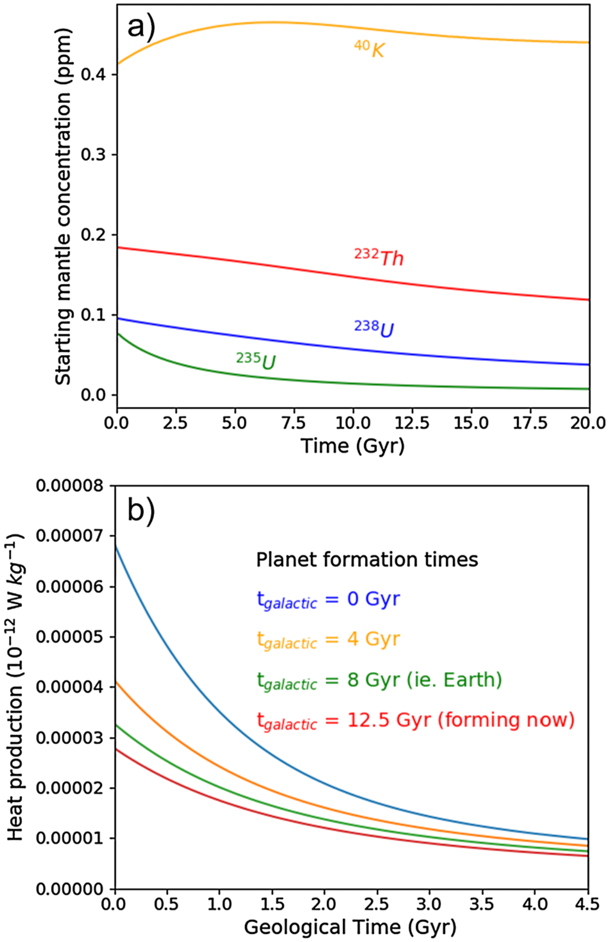

Fig. 2 (**a**) Starting mantle concentration at the time of planetary formation of the heat-producing radionuclides ^{40}K, ^{232}Th, ^{235}U and ^{238}U. (**b**) Evolution in mantle heat production for planets forming 0, 4, 8 and 12.5 Gyr after Galactic formation. Heat production curves are for the geological history of planet, starting from its formation age (set at 0 Gyr). Earth's heat production is equivalent to the example forming 8 Gyr after galaxy formation. Data from Frank et al. (2014)

composition of the Sun, though, is the lack of high-quality spectral lines for U and Th (Grevesse 1984; Grevesse et al. 2015)—a common problem in average or high metallicity stars (e.g. Cayrel et al. 2001). For our solar system, a small group of chondrites, the CI chondrites, are assumed to be reasonable proxies for stellar composition for all elements apart from the most volatile. This general constraint is on the basis of the good match between the concentrations of elements in CIs, irrespective of their distinct chemical properties, with relative solar abundances of those elements best determined in the solar composition, except for H, C, O and N (ice-forming elements), and the noble gases because of their volatility, and also Li, which is consumed by nucleosynthesis in the Sun. Note that there are only three CI meteorites that have been chemically analysed with modern methods, namely Ivuna (which is the meteorite giving the group its designation CI), Alais and Orgueil, and it is the latter meteorite and not the holotype, Ivuna, that overwhelmingly dominates the CI analytical database. However, inferences on solar abundances using the CI-proxy assumption are often supplemented with information from the more abundant CM group and its relations.

A number of syn- and post-accretion factors impact the final composition of planets formed from disk material, but first it is necessary to establish those factors that operated in the disk. It seems plausible that the chemical consequences of the earlier stages of the planet-building process are recorded in the compositional variability of the chondritic meteorites, which sample small parent bodies that have not differentiated by partial melting. Although most of these chondrite meteorites have been metamorphosed in their parent bodies (shock metamorphism associated with the break-up of the parent body is a different phenomenon), there are examples that are pristine, which record directly the agglomeration of the most primitive solar system material. These unmetamorphosed chondrites even host pre-solar grains. Confusingly for non-meteoricists, these most primitive meterorites are designated as having a metamorphic grade of 3. Grades 2 and 1 refer to aqueous alteration, 4 to 6 to thermal metamorphism, grade 7 is sometimes invoked to refer to incipient melting. CIs are all grade 1, so while they are the closest chondrites in composition to the solar composition, they are not texturally primitive. CMs are nearly all grade 2.

Chondrite meteorites in general record several major fractionations:

1. Fractionation of RLEs from the major rocky-planet-forming elements Mg and Si. Compared to the solar composition, both higher and lower RLE/Mg chondrites are known. Carbonaceous chondrites have similar or slightly higher RLE/Mg than the solar composition, but the ordinary chondrites and even more so the enstatite chondrites have lower. This factor affects Th and U contents directly because Th and U are RLEs.
2. Fractionation of Mg from Si, again with both higher and lower Mg/Si than solar. As these are major elements, varying Mg/Si necessarily affects the abundances of other elements.
3. Fractionation of metal (that is, Fe and other siderophile elements that condense into Fe) from silicates, also leads to higher and lower Fe/Mg. This fractionation should not be confused with the metal-silicate segregation that forms planetary cores. It is a nebular process that predates core formation, and is responsible for the division of the ordinary chondrites into their H, L and LL groups (high Fe, low Fe and very low Fe). That the extent of this fractionation among chondrites considered as a whole is usually not significant, is a remarkable feature that is consilient with the similar calculated condensation temperatures of Mg, Si and Fe (1348 K, 1314 K and 1333 K respectively according to Wood et al. 2019) under the canonical conditions used for the calculation, but a difference between the condensation temperatures of the Mg-silicates and Fe metal would open out at different H-C-O ratios or nebular pressures. Much greater metal-silicate fractionation might be expected in other solar systems.
4. Depletion in moderately volatile elements (MVEs), more-or-less according to their calculated condensation temperatures. The MVEs are those elements calculated to condense after Mg, Si and Fe, but before planetary ices (composed of H, C, N, O and noble gases). Chondrites enriched in the MVEs are unknown, except for some enstatite chondrites that show a slight enrichment in the least volatile of the MVEs.
5. Oxidation state – how much Fe is metallic (Fe^0), Fe^{2+} and Fe^{3+}. This is a matter of oxygen content, reflecting oxygen fugacity (fO_2) hence H-C-O ratios.
6. Depletions of the other ice-forming elements (H, C, N), and associated O (as in H_2O) and noble gases. The H content of texturally primitive (hence unmetamorphosed) chondrites varies from virtually nothing, to that in the relatively H_2O-rich CIs (which are not particularly primitive in texture, showing much hydrothermal alteration).

The processes behind these chemical fractionations remain incompletely understood, but likely reflect variations in local pressures and temperatures within the disk, H-C-O ratios, which control fO_2, and other factors that affect the condensation of different phases, generating gradients in major and minor elements (Lodders and Fegley 1999).

Geochemical assessments of the Earth's composition (e.g., Palme and O'Neill 2014 and references therein) show that it is not like any known chondrite group. Early attempts to reconcile this issue postulated complete mixing of different varieties of known chondrites, corresponding to accretion of the Earth from material sourced from different regions of the disk. Paradoxically, although the Earth appears isotopically most similar to the enstatite chondrites (e.g., Javoy 1995; Dauphas 2017), these meteorites have the least similarity to the Earth in terms of the abundances of major elements, which is closer to CV carbonaceous chondrites (Palme and O'Neill 2014). Recent work on the isotopic composition of Earth materials compared to known chondrites has indicated that the Earth may contain material not represented in our chondrite collections. The traditional view of chondrites as the "building blocks of the planets" may be misleadingly naïve (e.g., Burkhardt et al. 2019; Schiller et al. 2018).

Subsequent to the effective isolation of the chondrite parent bodies, further processes have modulated the compositions of the terrestrial planets or proto-planets. These include: i) thorough mixing driven by disk transport processes (e.g. Schiller et al. 2015); ii) impact erosion (O'Neill and Palme 2008) which may preferentially strip off incompatible elements enriched in planetary crusts; iii) the loss of moderately volatile elements after giant impacts, as occurred on the Moon (O'Neill 1991a, 1991b); and iv) hydrodynamic escape of atmospheres (e.g., Johnstone et al. 2019; Hin et al. 2017) which may preferentially blow off moderately volatile elements whilst stellar outflow is active (up to $\sim < 7$ Myr). We will consider the effects of these processes, in turn below.

Condensation Temperatures and Variations Within the Disk Following Urey (1952), many authors, notably Lord (1965), Larimer (1967) and Grossman (1972), see also Grossman and Larimer (1974), have calculated the equilibrium condensation phase relations of a gas of solar composition. Lodders (2003) updated the calculation, which extended it to all of the naturally occurring elements. Results have traditionally been summarized by reporting the temperature at which 50% of an element has condensed. Recently Wood et al. (2019) presented a significant revision of the calculation. To facilitate comparison with Lodders (2003) they used her solar abundances rather than those of Asplund et al. (2009), except for chlorine, which was recently been revised downward by a factor of 6 (Clay et al. 2017), although not uncontroversially (Ebihara and Sekimoto 2019). Among the new findings, one of relevance to the HPEs is that K is now calculated to condense at slightly lower temperatures than its cosmochemically more abundant fellow alkali metal, Na, in agreement with experimental observations (e.g., Kreutzberger et al. 1986).

The nebular condensation calculation should be viewed as a guide to an element's relative volatility under typical—but arguably not all—conditions relevant to the initial processing of material in the earliest history of the solar system. Specifically, the calculation only applies to the period before H_2, which makes up most of the solar composition (together with He), was dispersed. This process occurs over a relatively short timescale of one to a few million years or so (see below), much shorter that the estimated time needed for accretion of Earth-sized bodies. Furthermore, nebular condensation calculations have typically assumed a constant gas pressure (e.g., 10^{-4} bars), which is approximately the sum of the partial pressures of H_2 and He, since these are by far the most abundant gas species in the nebula. The calculations are, however, very sensitive to the selected H-C-O mixing ratios, which determine the important variable of oxygen fugacity. The exact values of H-C-O in the solar composition continue to be a matter of discussion, and have been periodically reassessed over the years (Asplund et al. 2009). Wood et al. (2019) have emphasised the importance of the chlorine abundance to the calculation, which was recently revised by Clay et al. (2017).

This condensation calculation should not be mistaken as modelling a physically plausible process, even if the nebular pressure distribution and the solar composition were well known.

The assumption of chemical equilibrium has long seemed unlikely, especially towards lower temperatures, by analogy with rates of reaction in various geological processes, but has never been investigated. To illustrate the problem, K itself provides a useful example. The canonical condensation calculation has K hosted as the component $KAlSi_3O_8$ in plagioclase feldspar, a solid solution between the components $CaAl_2Si_2O_8$ – $NaAlSi_3O_8$ (e.g., Wood et al. 2019). But the equilibrium calculation does not address the pathway by which this state is reached. Given the constraints of mass balance, condensed phase stoichiometry, and that the vapour pressures of gas-phase components with Si, and especially Al, a refractory element, are extremely low at the calculated condensation of K (that is, 993 K according to Wood et al. 2019), a hypothetical pathway to the state assumed by equilibrium condensation may reflect a multi-phase reaction like:

$$\begin{array}{ccccccc} \mathrm{K} + \mathrm{H_2O} + & 1/2\mathrm{Al_2O_3} + & 3\mathrm{Mg_2Si_2O_6} = & \mathrm{H_2} + & 3\mathrm{Mg_2SiO_4} + & \mathrm{KAlSi_3}O_8 \\ \text{Gas Gas} & \text{Corundum} & \text{Pyroxene} & \text{Gas} & \text{Olivine} & \text{Feldspar} \end{array}$$

This reaction involves four condensed phases, uncompacted by pressure, and having to communicate in a tenuous gas; an additional kinetic constraint is the need for solid-state diffusion in those condensed phases in which the above components have solid solution. Note also that this reaction is not the only possibility: for example, we could equally well write a similar one involving $CaAl_2Si_2O_8$ in feldspar and $CaMgSi_2O_6$ in pyroxene in place of Al_2O_3 in corundum. This is a simple consequence of equilibrium thermodynamics not addressing reaction pathways. The point is, whether any such reaction pathway would proceed on the timescale of the cooling of the solar nebula ($\sim 10^5$ - 10^6 years). Geological experience prejudices us to suppose not – in the absence of hydrothermal fluids (whose existence requires high pressures), metamorphic rocks often preserve equilibrium mineral assemblages and compositions on geologically paced cooling (10^6 – 10^7 years) from not dissimilar temperatures. The actual condensation of K most likely takes place at lower temperatures via a metastable but kinetically feasible reaction pathway. In this regard, K exemplifies a typical consequence of non-equilibrium condensation: the actual condensation of those trace elements that are calculated to condense in pre-existing phases will be at lower temperatures than calculated assuming thermodynamic equilibrium.

Another, separate, problem is that the necessary thermodynamic data are not always available, let alone accurate. Especially difficult is selecting the appropriate thermodynamic components in the condensing phases for many of the less abundant elements, and then finding relevant thermodynamic data for these components, plus their activity-composition relations for their solid solution into the phases determined by major-element condensation. For example, the revision of Wood et al. (2019) places the calculated condensation temperature of Pb some 230 K lower than Lodders (2003) by assuming that it condenses as PbS and not into Fe metal. For these reasons the canonical nebular condensation calculation should still be seen as work in progress. We also emphasise that the sensitivity of an element's volatile tendencies to oxygen fugacities means that the volatility sequence enshrined in the nebular calculation may differ considerably for post-nebular processes (Norris and Wood 2017; Sossi et al. 2019). This is demonstrated by comparing the nearly solar ratio of Mn/Na seen in chondrite meteorites, with the much greater Mn/Na ratios characteristic of all known differentiated solar system bodies, except the Earth (O'Neill and Palme 2008; Siebert et al. 2018).

For our purposes it is interesting to note in which condensing phases U, Th and K first appear in. Figure 3 illustrates an abbreviated version of Lodder's oxidised condensation sequence. U and Th both strongly partition into one of the earliest high-temperature oxide

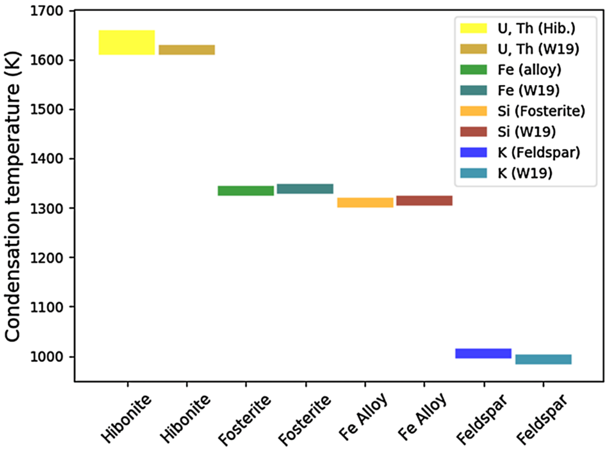

Fig. 3 Plot of the 50% condensation temperatures for the main hosts of the HPEs U, Th and K, based on the results of Lodders (2003) and Wood et al. (2019) for a solar system abundance gas. U and Th are largely taken up by hibonite (a calcium-aluminium oxide), K is not condensed out significantly until feldspars start to form at around ∼1000 K. Bar size denotes nominal uncertainty, and major rock-forming elements Si and Fe are also shown for comparison

phases, hibonite (a calcium aluminium oxide, $CaAl_{12}O_{19}$). This is one of the highest temperature condensates (after corundum), and is expected to be well represented in the hot inner disk. The 50% condensation temperature for U (into hibonite) is 1610 K, and for Th 1659 K. As a result, U and Th should be well-represented in most rocky meteoritic material. K, in contrast, is mostly taken up by feldspars during the condensation sequence, and is 50% condensed at temperatures of ∼1006 K—significantly less than U and Th. There exists the possibility that strong gradients in these heat producing elements may have been generated in the early solar system as a result of local disk temperature evolution, and variations in fO_2, if they existed, may also have had an effect (Lodders 2003).

Variations in Meteoritic Abundances Chondritic meteorites contain significant variations in their HPE concentrations, which can be conceptualized as arising from two factors: 1) variation in the concentrations of Refractory Lithophile Elements (thus Th and U) due to different amounts of the three other main compositional components in the meteorites, namely Mg-silicates, Fe-rich metal and/or sulfide, and H-C-O-N volatile-containing material; and 2) the further depletion of K relative to the RLEs, as expected from its status as a moderately volatile (but still lithophile) element. This factor is conveniently quantified as the K/U ratio. The resulting concentrations of U, Th and K, and the K/U ratio are listed in Table 2, and shown in Fig. 4. Note that even the CIs are greatly depleted in H, C and N (and noble gases) relative to their solar abundances, hence the amounts in meteorites should be regarded as a small difference between large numbers – that is, the solar H,C and N are lost. From this perspective, it is difficult to accord the precise amounts of H, C and N remaining in the volatile-rich chondrites (the CI and CM groups) any particular significance.

With this caveat in mind, primitive chondritic meteorites do demonstrate some significant variations in the HPE budget (Table 2 and Fig. 4). Much of this is related to bulk composition and formation environment. For instance, carbonaceous chondrites (in particular CI chondrites) contain more organic material and ice relative to silicate. Since HPEs are preferentially incorporated into silicates, these chondrite types as a whole tend to show lower HPE abundance (particularly U and Th) than ordinary or enstatite chondrites.

The exception to this is K, which, as a moderately volatile element, seems to show an increased concentration in the least-processed samples (CI, and to a lesser extent CM chondrites), compared to, for instance, CV chondrites, which may reflect a volatility trend in their disk formation environment (Morbidelli et al. 2016). U and Th also increase within the carbonaceous group from low abundances in the most solar-like, the CIs, to the RLE-enriched

Table 2 Concentration of K, Th and U in a variety of chondrites (in ppm). WK88 refers to Wasson and Kallemeyn (1988), CI chondrites and CV (Allende) are from Barrat et al. (2012); CM from Hewins et al. (2014); LL(6), EH(3), and EL(3) are from Barrat et al. (2012) for U and Th, Rubin et al. (2009) for EL K, Lehner et al. (2014) for EH K, and Wasson and Kallemeyn (1988) for K in LL ordinary chondrites

	CI	CM	CO	CV	LL	L	H	EL	EH
K (ppm)	550	363.5	–	277	790	–	–	713.42	735
SD*	77	88.03	–	2.77	158.0	–	–	64.50	30
K (WK88)	560	400	345	310	790	825	780	735	800
Th (ppm)	0.0283	0.0387	–	0.0594	0.04265			0.00233345	0.0296
SD	0.000566	0.0387	–	0.00119	0.00233345			0.00702258	0.00600571
Th(WK88)	0.029	0.040	0.045	0.060	0.043	0.043	0.042	0.035	0.030
U (ppm)	0.0077	0.009866		0.0152	0.0121			0.0083	0.008
SD	0.000385	0.000385		0.000304	0.00212132			0.0009737	0.00184481
U (WK88)	0.0089	0.011	0.013	0.017	0.013	0.013	0.012	0.010	0.009
K/U	62921	36363	26538	18235	60769	63462	65000	73500	88889

*SD is standard deviation

types (CV and CK), reflecting a decreasing amount of H-C-O-N volatile abundances, and an increased amount of a refractory component consisting of phases like hibonite (the main initial condensation carrier of U and Th), which formed in high-temperature inner disk environments.

The dichotomy between the trends observed in the carbonaceous, and non-carbonaceous chondrites, are reflected in nucleosynthetic anomalies in these meteorite groups (e.g. Carlson et al. 2018; Nielsen et al. 2019), which suggest meteorites at greater heliocentric distances are progressively depleted in s-process isotopes. This fundamental distinction is mirrored in the HPE trends observed in Fig. 4.

Impact Erosion and Atmospheric Loss The growth of planetary embryos occurred within a H_2-gas rich disk, for at least the first ∼4 Myr of solar system evolution (e.g. Wang and Goodman 2017). After that time, the stellar activity (in particular, strong EUV radiation) rapidly blows the disk material away. However, if a growing planetary embryo reached 0.5 M_{Earth} within the lifetime of the disk, Johnstone et al. (2019) argue that it may have retained a tenuous H_2 gas envelope, which is subsequently rapidly lost due to initial H_2 boil-off, and later EUV insolation from the early Sun.

The process of early atmospheric loss may preferentially lead to loss of volatile and moderately volatile elements present in the atmosphere. K is a moderately volatile element that would be released from a high-temperature (1500–2500 K) magma ocean (Schaefer and Fegley 2010), to the hot early atmosphere. Having a moderate (∼1000 K) condensation temperature it would have been sensitive to atmospheric loss via hydrodynamic escape (Scherff et al. 2019; Lammer et al. 2019), and this may explain the low K/U ratios of Earth and Venus (e.g. Albarede 2009; Kaula 1995), compared to primitive chondrites.

An argument against late K loss was presented by Humayun and Clayton (1995) who found no evidence of K isotopic variation between the Earth and Moon and suggested this constrained potassium loss due to partial volatilisation to $< 2\%$. However, it was rapidly pointed out that lack of isotopic fractionation does not preclude loss by volatilization, only loss by simple Rayleigh fractionation into high vacuum (e.g., Esat 1996; Young 2000). For example, total loss of a volatile element (like K) from that part of an impacted body that was

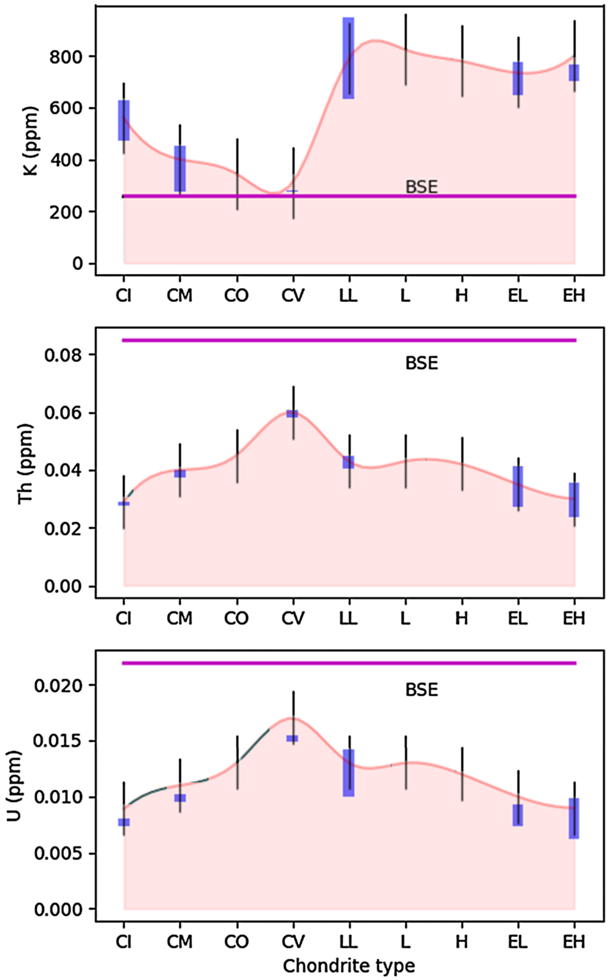

Fig. 4 Distribution of heat producing elements within different chondrite types, in order of approximate decreasing heliocentric distance, from the data listed in Table 2. Black bars represent the data of Wasson and Kallemeyn (1988; note uncertainties were not reported, so the bar height is nominal). Blue bars represented the recompiled data from a number of chondrite groups (see Table 2), and height represents their uncertainties. The red line is a cubic interpolation of the trend. Sequence is ordered in approximate decreasing heliocentric distance from left to right

vaporized, with negligible volatile loss from its other part, would, after rehomogenization of the two parts, result in depletion with no isotopic fractionation whatsoever (e.g. Hin et al. 2017). Subsequently, a small difference in δ^{41}K has been found between the Earth and Moon (Wang and Jacobsen 2016), at a level of 0.4 ‰, smaller than that originally anticipated by Humayun and Clayton (1995), but consistent with the condensation of the Moon from a BSE vapour disk.

The ratio of K/U is far more sensitive to volatile loss than K isotopes, and depletion of K on developing planets is best tracked by considering the K/U ratio. For CI chondrites, this value is 6.3×10^4 (Table 2, Wasson and Kallemeyn (1988), Lodders et al. 2009). For the Earth, K/U ∼13,800 (Lodders et al. 2009) and for Venus it has been constrained to > 7000 (Davis 2005). The K/U ratio has been argued to be sensitive to EUV flux on developing planets, whilst they were immersed in the gas disk, and possessed a more massive H_2-dominated early atmosphere, and blow-off of this gaseous envelope may have driven K/U to lower values. This ratio is perturbed further by the impact history of the planet; depleted (e.g. ureilite) vs. enriched (e.g. CI chondrites) will bring variable amounts of K to the late stages of accretion.

Table 3 Existing data on HPE concentrations within the mantles of terrestrial planets

	U (ppb)	Th (ppb)	K (ppm)	Reference
Mars—Primitive mantle	16	56	315	1
Mars—Primitive mantle	16	56	305	2
Mars—Primitive mantle	16	56	920	3
Earth—BSE—chondritic-RLE	22	85	260	4
Earth—BSE—non-chondritic	11	43	130	4
Venus—Crust (Venera 9)	600	3650	4700	5
Venus—Crust (Venera 10)	460	700	3000	5
Venus—Mean Crust	530	2175	3850	
Venus—Primitive mantle (Kaula 1999)	21	86	153	
Mercury—Northern Hemisphere, MESSENGER	90 ± 20	220 ± 60	1150 ± 220	6
Mercury—primitive mantle (25% melt fraction scaling)	22.5 ± 9.5	55 ± 26	287.5 ± 113	

1. McLennan (2012). 2. Wänke and Dreibus (1988, 1994). 3. Lodders and Fegley (1997). 4. O'Neill (2016). 5. Surkov et al. (1987). 6. Peplowski et al. (2011)

In addition to atmospheric loss, volatiles may also have been removed by impact erosion of planetary crusts. O'Neill and Palme (2008) suggested that Earth may have been shifted from its chondritic original composition, to a non-chondritic bulk-silicate Earth. In this scenario, early crusts on differentiated planetesimals or planetary embryos, or on the proto-Earth itself, enriched in incompatible elements including the HPEs (K, U and Th), would have been preferentially stripped off due to the shallow depth of impact excavation for most early impacts. This process left behind a mantle with a sub-chondritic bulk-silicate composition, and possibly with less than half its original HPE contingent. O'Neill and Palme (2008) noted that the Fe/Mg ratio of the Earth is larger than the solar ratio (2.1 ± 0.1, vs. 1.9 ± 0.1), and they suggested this implies 10% of silicates relative to metal were lost due to collisional erosion.

Variations Among Terrestrial Planets Variations among terrestrial planets have important consequences for the thermal evolution of each body, but are notoriously hard to constrain given the lack of samples from Venus and Mercury. Whilst we have direct samples of the mantle (as xenoliths, etc), these are representative of the depleted upper mantle, and not generally the primitive lower mantle or "bulk silicate Earth" (BSE). Elemental compositions of Earth's mantle can then be estimated from geochemically modelling, or comparisons with chondrites. On Mars, we have both direct measurements of the surface, and Martian meteorites. Together these also allow estimates of Mars' primitive mantle to be made (Wänke and Dreibus 1988, 1994). In addition, modelling Mars as a mixture of meteorite types also allows interior composition to be estimates (Lodders and Fegley 1997), and the results of these approaches are shown in Table 3.

Estimation of the surface composition of Venus and Mercury is more difficult. Venus has been visited by the Venera (8, 9 and 1) and Vega (1 and 2) landers, which analysed the concentrations of heat producing elements using a gamma-ray spectrometer. All the landing sites had compositions consistent with terrestrial basalts, with the exception of Venera 8, which appeared to be a differentiated crustal rock (and thus had elevated U, Th and K). In addition, the Vega missions targeted rocks from Aphrodite Terra (Vega 1 from Mermaid Valley to the north, and Vega 2 from the slopes of Aphrodite Terra). Both returned spectra, despite landing difficulties for Vega 1. However, Aphrodite Terra is a complicated crustal structure, and we have listed the results of Venera 9 and 10, which are probably the closest to mantle-derived volcanism, and presented a mean crustal value. The similarity in the uncompressed density of Venus to Earth, together with the broad similarity in the sampled Venera basalts to terrestrial basalts, is consistent with the composition of Venus's primitive mantle being similar to that of the BSE for the major elements, among which are included the refractory lithophile elements Ca and Al. Therefore, we expect the Th and U abundances of Venus's primitive mantle also to be Earth-like. There may, however, be differences at the level of a few tens of percent related to plausible differences in Venus's RLE/Mg and Mg/Si ratios, which are unconstrained by empirical evidence. The oft-quoted value of 21 ppb U for Venus's mantle given by Kaula (1999) is simply the BSE value from Wänke et al. (1984), under the chondritic assumption.

The K content of Venus's primitive mantle is estimated from this U content and the K/U ratio of 7220 ± 1220 of the Venera basalts, omitting one high K outlier. With only a few samples and such data selection, this estimate should viewed skeptically. The amount of ^{40}Ar, the decay product of ^{40}K, in Venus's atmosphere has been obtained from the ^{40}Ar/^{38}Ar ratio and the estimated abundance of ^{38}Ar (Hoffman et al. 1980), but with considerable uncertainty. This ^{40}Ar corresponds to much less K than estimated from K/U, which has been taken to mean that the mantle of Venus is much less efficiently degassed than the Earth's (Kaula 1999; O'Neill et al. 2014).

For Mercury, our information on its surface comes from gamma ray spectroscopy from the Messenger orbiter. Due to the orbit of Messenger, only results from the northern hemisphere were presented by Peplowski et al. (2011). They identified not only a crust enriched in U and Th, but also significant K, which was unexpected from formation models (e.g. Solomon et al. 2001). We have adopted their approach assuming the crust represents a 25% melt extraction from the mantle to reconstruct Mercury's primitive mantle composition listed in Table 3.

Significant average heat production variation may exist among the different terrestrial planets, and this variation may have been inherited from their disk environment. For instance, McCubbin et al. (2012) plotted the variations in K/U and K/Th for inner solar system bodies. Those results show that both Mars and Mercury are, comparatively, volatile rich bodies, with high K/Th and K/U ratios. Earth and Venus are both lower, and the Moon is extremely low—primarily as a result of it being largely in a rock-vapour state during its formation (e.g. Canup 2008). However, the HED meteorites, representative, of the 4 Vesta parent body, also showed extremely low K/U and K/Th. However, Vesta is not representative of the asteroid belt, and the largest asteroid belt body, constituting most of its mass, is the dwarf planet Ceres, has not been unequivocally sampled in the meteoritic collection. To calculate an additional 'asteroid belt' representative values of K/U and K/Th, we adopt values for CM chondrites in lieu of Ceres, and calculate mass weighted averages of Vesta and Ceres for K/U, K/Th and heliocentric distance. Our results are shown in Fig. 5.

We have left out the Moon in Fig. 5 due to its known formation artefacts. If we consider the "average" composition of the asteroid belt, there is an observed trend of increasing volatility, shown by increasing K/U and K/Th ratios, moving out of the inner solar system. This trend does not really hold for Vesta, and probably reflects the importance of stochastic processes, such as impacting, in the erosion and late delivery of volatiles. Mercury, as well, bucks any simple trend, and its S-composition also suggests additional complexity. Whether this is due to uncertainties in its bulk-silicate estimates, oddities in its accretion of K, or an unusual formation mechanism, remain to be seen. Further generalisations are limited due to our incomplete knowledge of their primitive mantle compositions—a problem even for Earth, as outlined next.

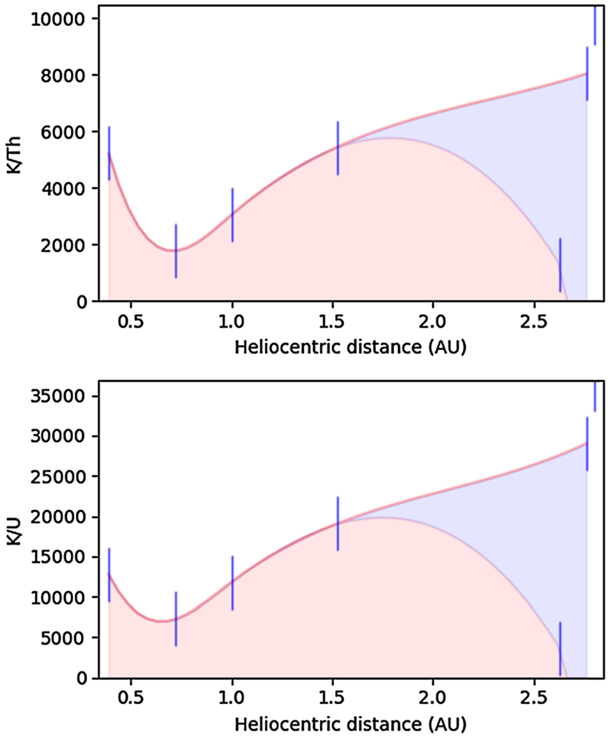

Fig. 5 Variations in K/Th (top) and K/U (bottom) for the terrestrial planets (Table 3), as well as an 'asteroid average' based on a weighted average of Vesta (McCubbin et al. 2012), and a 'CM' Ceres (CM values from Table 2). Individual points (including Vesta and 'CM' Ceres) shown as vertical blue lines at their respective heliocentric distance, and a cubic interpolation through the terrestrial planets and either the asteroid-belt average (red line) or Vesta (purple) is shown

4 Earth's HPE abundance

Earth's internal heat production budget can be estimated in a number of ways. There is a geodynamic approach, using Earth's total heat loss and assuming an energy budget to constrain heat production, and element ratios to constrain HPE concentrations (Turcotte and Schubert 2002). The geochemical approach utilises either direct measurements (including chondrites), and considers partitioning of HPEs into different reservoirs to constrain element concentrations (O'Neill 2016). And more recently, emerging geoneutrino measurements have been able to provide a direct measurement of the concentration (and eventually, the distribution) of HPEs in the Earth's interior.

Each of these approaches has significant limitations, discussed below. Ultimately, we wish to constrain the primary HPE budget of the planet. This is complicated by their enrichment into different reservoirs (e.g. crust, basal magma ocean) and depletion in others (e.g. upper mantle). The most primitive silicate reservoir, the lower mantle, is largely inaccessible (although, see Campbell and O'Neill 2012), and estimates for the bulk silicate Earth (BSE) are largely approached using mixing models.

Uncertainties in these values largely arise from our incomplete knowledge of the composition of the deep interior, and contribution of secular cooling to current heat flow. Geodynamic analysis has suggested that secular cooling contributes 20-25% of Earth's current heat flow (Turcotte and Schubert 2002)—however, this assumes a relationship between Rayleigh number and heat flow which may not be valid for non plate-tectonic regimes (Silver and Behn 2008) or mixed-heating mantle (Moore 2008). In addition, there exists significant timelag between surface heat flux and the thermal state of the interior (Lenardic et al. 2019), and thus these geodynamically-constrained estimates should be treated with caution.

Cosmochemical models suggest that 40-50% of Earth's surface heat flow is from secular cooling (e.g. Schubert et al. 2001; Sun and McDonough 1989), however, observed reservoirs do not reflect cosmochemical (chondritic) abundances. We have, for comparison, split our estimates for the mantle into chondritic and non-chondritic families, following O'Neill (2016). Whilst some reservoirs (crustal, and to some degree mantle lithosphere and upper mantle) can be reasonably well constrained by observations (Table 2), others cannot, and require reference models—typically chondritic compositions, or, more recently, non-chondritic Earths. Consequently, absolute uncertainties for the quantities in Table 2 are generally unknown.

To illustrate this point, Earth has approximately a factor of 2 less K than CI chondrites (Fig. 3), and is enriched in U and Th by a factor of ∼2-3. As a moderately volatile element, K is depleted in the Earth, and Earth has only around 50% of the atmospheric ^{40}Ar expected from ^{40}K decay throughout geological time for BSE models (Kaula 1999). This may be a factor of degassing efficiency under different tectonic regimes (O'Neill et al. 2014), or alternatively suggest lower total K abundances. Likewise, isotope systematics have been used to argue for a deep enriched reservoir within the Earth, segregated during early magma ocean crystallisation (Rizo et al. 2013; Rizo et al. 2016), which may potentially contain a high HPE concentration (Jellinek and Jackson 2015). There has also been the suggestion of sequestering significant concentrations of HPEs into the core (Blanchard et al. 2017; Wohlers and Wood 2015).

In order to provide absolute constraints on these models, we turn to geoneutrino measurements of radioactive decay in the mantle, and high-pressure experiments of HPE partitioning between silicate and metals.

Geoneutrinos A potential additional constraint on radiogenic heat production in the Earth can be made from the geoneutrino flux. Geoneutrinos are generally electron antineutrinos, produced during beta-minus decay, where a neutron within a nucleus decays to a proton, electron and electron-antineutrino. Present detectors use proton collisions, where an incoming antineutrino collides with a proton to form a neutron and positron, a process known as inverse beta-decay. The reaction is captured in large underground scintillation tanks, and consists of sequential light flashes associated with the initial positron destruction, and a later neutron capture. This proton collision, however, requires > 1.806 MeV to proceed, meaning these tanks are only sensitive to high-energy antineutrinos. Only isotopes on the ^{232}Th and ^{238}U decay scheme produce antineutrinos of sufficient energy (e.g. ^{228}Ac, ^{212}Bi for the ^{232}Th chain, and ^{234}Pa and ^{214}Bi for the ^{238}U chain (McDonough 2016)). As a result ^{40}K (and ^{87}Rb) are not currently detectable, despite making up most of Earth's geoneutrino flux, but may be in future electron collision detectors (e.g. Dye 2012).

Gando et al. (2011) combined results from Borexino and KamLAND to estimate that mantle ^{232}Th and ^{238}U contribute 20.0 +8.8/-8.6 TW to Earth's heat flux. Results from Borexino alone have tended towards higher values (Agostini et al. 2019), and recently, the Borexino team (Agostini et al. 2019) estimated the total radiogenic heat of the Earth at 38.2 +13:6/-12:7 TW (confidence intervals are ±34%), and the total mantle heat contribution of 24.6 TW +11.1/-10.4 from ^{238}U and ^{232}Th. Therefore, even at the 95% confidence interval this estimate would only just be compatible with the largest radiogenic heat production values deduced from geochemistry. We can convert these contributions to mantle concentrations as follows. If we assume the mass of the mantle is 4×10^{24} kg, then a flux of 24.6 TW gives us a mantle heat production from these isotopes of 6.15×10^{-12} W/kg (range of

Table 4 Compilation of existing data on Earth's major geochemical reservoirs, and selected rock types. Drawn from existing compilations in O'Neill (2016), Turcotte and Schubert (2002) and Schubert et al. (2001)

Geochemical reservoir	Mass (kg)	U (ppb)	Th (ppb)	K (ppm)	Heat production (TW)
Continental sediments[1]	0.7	1730	8100	18300	0.3
Upper crust[1]	6.7	2700	10500	23200	4.2
Middle Crust[1]	6.9	970	4860	15200	1.9
Lower crust[1]	6.3	160	960	6500	0.4
Continental crust	20.6	1311	5612	15247	6.8
Oceanic sediments[1]	0.3	1730	8100	18300	0.1
N-MORB[2]	–	47	120	600	–
E-MORB[2]	–	180	600	2100	–
OIB[2]	–	1020	4200	12000	–
Oceanic crust[3]	6.3	20	52	280	0.03
Mantle (ocean crust source)[4]	–	4	10	60	–
Convecting mantle (chondritic)[4]	3942	15	55	181	13.9
Convecting mantle (non-chondritic)[4]	3942	4	11	47	3.2
Convecting fertile mantle (geodynamic)[5]	3942	31	124	310	–
BSE (chondritic)[6]	4060	22	85	260	21.4
BSE (non-chondritic)[7]	4060	11	43	130	10.8

[1]Huang et al. (2013), [2]Sun and McDonough (1989), [3]O'Neill and Jenner (2012), [4]O'Neill (2016), [5]Turcotte and Schubert (2002), [6]Palme and O'Neill (2014), [7]O'Neill and Palme (2008). Note that "Oceanic crust" is parental ocean floor basalt of O'Neill (2016), incorporating all groups of oceanic basalts, and mantle (ocean crust source) refers to the residue mantle after 20% melt extraction. The convecting mantle refers to the BSE minus continental crust/lithosphere contributions

3.55–8.93 $\times$ 10^{-12} W/kg). We can then use the relation (Turcotte and Schubert 2002):

$$H_0 = C_0^U \left(H^U + \frac{C_0^{Th}}{C_0^U} H^{Th} \right) \tag{2}$$

Here H denotes the heating rate of an isotope from Table 1 (H_0 is the mantle heating inferred above), and the ratio of Th to U is assumed to be ~3.9 (Gando et al. 2011; note from Table 1 the ratio of ^{232}Th:^{238}U is 4.0, and the uncertainty in this ratio is in excess of a correction for ^{235}U). This gives our current concentration of ^{238}U in the mantle to be 33.05 $\times$ 10^{-9} kg/kg (range 19.08–47.96 $\times$ 10^{-9} kg/kg), and the concentration of ^{232}Th to be 128.90 $\times$ 10^{-9} kg/kg (range 74.40–187.06 $\times$ 10^{-9} kg/kg).

These data may also be used to constrain nuclear activity within the core. An assessment of the viability of a natural nuclear reactor in the core limited core heat production from U and Th to 2.4 TW (KamLAND neutrino observatory; Agostini et al. 2019) and 3 TW (Borexino, which is further from any man-made reactors; Gando et al. 2011). Assuming a core mass of 1.883 $\times$ 10^{24} kg, and using Eq. (2) again gives a limit to the concentration of ^{238}U of 6.85 $\times$ 10^{-9} kg/kg, and a ^{232}Th limit in the core of 26.71 $\times$ 10^{-9} kg/kg.

Although argued by Agostini et al. (2019) to be marginally consistent with a geodynamic model for mantle heat generation, these values are not consistent with published chondritic or non-chondritic BSE compositions (Table 4). In particular, these results exclude the enstatite-chondrite or non-chondritic Earth models at a high degree of confidence and, thus, more work is required before geoneutrino constraints can be regarded as reliable.

High-Pressure Partitioning Experiments and the Core HPE Budget A recurrent trope in planetary geochemistry is whether K and sometimes also U but seldom Th are not completely lithophile during core formation in the Earth, with non-negligible abundances of K ($\pm$U) in the core (Corgne et al. 2007). This discussion has largely been motivated by the challenge of facilitating a geodynamo through time, and preventing over-growth of the inner core due to core cooling. As an example, U and Th may under reducing conditions with a high-S content partition into the metal phase (Wohlers and Wood 2015). Such conditions might occur in a Mercury-type or enstatite-chondrite type body, with high S content. Wohlers and Wood (2015) explored this behaviour and suggested that the impact of a Mercury type parent body 20% the mass of the Earth, with the proto-Earth, might have introduced up to 4-5 ppm of U into the Earth's core (and similar for Th). This value would be larger for bigger impactors, or assuming more generous Th/K ratios for the Earth, and Wohlers and Wood (2015) suggest these isotopes alone may have produced up to 2-2.4 TW of heat in the core, sufficient for a geodynamo.

All the metallic elements in the periodic table can be reduced to the metallic state given sufficiently reducing conditions (that is why they are classified as metals), and most can then form liquid alloys with liquid Fe, and those that are immiscible in liquid Fe, like Ag or Pb, are soluble in liquid FeS, a possible core constituent. But demonstrating this chemically commonplace in an experiment does not mean that it occurred in nature. To show that requires comparing the siderophile tendencies of K or U with those of other Refractory Lithophile Elements at the same conditions, and balancing these tendencies against whether these other elements are also depleted in the Bulk Silicate Earth by partitioning into the core (O'Neill 2016). In the case of U, its abundance in the BSE is constrained relative to Th by U-Th-Pb isotopic systematics. Th is one of the more difficult elements to reduce to the metallic state. A recent appraisal of the evidence concluded trenchantly that "Negligible Th/U fractionation accompanied accretion, core formation, and crust–mantle differentiation, and trivial amounts of these elements (<0.2 ng/g U) were added to the core and do not significantly power ($\sim$0.03 TW) the geodynamo" (Wipperfurth et al. 2018). In addition, Blanchard et al. (2017) argued that U metal partitioning depends strongly on temperature and oxygen in the metal. Under core-forming conditions, they found an upper limit to the U content in the core of 3.5 pbb.

The case for K in the core is not so easily dismissed because of the uncertainties in estimating the BSE concentration of this element. It has been argued that the incorporation of over 100 ppm K into the core early in its history may have generated sufficient heat to facilitate a geodynamo, in the absence of an inner core (Nimmo et al. 2004). K in the core has also been suggested as a partial resolution to its depletion in the BSE (e.g. Wohlers and Wood 2015). However, current estimates for the depletion of K in the BSE relative to the RLEs are broadly consistent with those of other moderately volatile elements without siderophile affiliations, such as boron and fluorine, and the cosmochemically abundant alkali metal sodium (Palme and O'Neill 2014). Significant Na in the core is not expected from considerations of BSE Mn/Na ratios (Siebert et al. 2018). Furthermore, as Na is a very light metal, significant Na in the core would have implications for the density deficit of the Earth's core compared to Fe-Ni alloy, although this is a complicated matter given the poor constraints on the amounts of the more plausible candidates: S, O, Si, H and C have all been suggested. Nevertheless, the margin of uncertainty in these considerations are such that minor amounts of K in the core cannot be excluded. Recent experiments (Blanchard et al. 2017), however, have suggested a limit to amount of K in the core of 26 ppm, which, together with their U constraints, seem to limit heat production as a viable driver for the early geodynamo.

5 Implications for the Long-Term Evolution of Planets

The variations in heat-producing elements documented here has implications for the thermal evolution of planetary bodies (Jaupart et al. 2007). We explore these potential consequences by employing thermal history calculations, and comparing the evolution of a bulk-silicate Earth thermal model, to alternative Earth-sized models with variable heat production.

The models use a parameterised convection approach outlined in Schubert et al. (2001) and Korenaga (2006), and details can be found there. Parameterised models utilise a well known relationship between convective vigour—reflected in the non-dimensional Rayleigh number (Ra), and the normalised heat flux, the Nusselt number (Nu). Boundary layer theory, laboratory, and numerical experiments have shown that the relationship between these terms follows a form

$$Ra \sim Nu^{\beta}$$

The exponent β is around $1/3$ for simple isoviscous systems (Turcotte and Schubert 2002), but has been argued to be slightly lower for mobile lid systems (β ~0.26, Moresi and Solomatov 1998), and significantly lower for stagnant-lid systems which lose heat inefficiently (β ~0.12, Christensen 1985). To avoid complexities around Earth's tectonic evolution (e.g. O'Neill et al. 2018), we have used these tectonic endmembers to bracket possible temperature evolution. The results are shown in Fig. 6.

Typically BSE heat production is greater than chondrites; this is largely due to the apparent enrichment of Earth in U and Th compared to many chondrite groups (Table 2 and 4). Whilst Earth is depleted in K compared to chondrites, this has less of an effect. The carbonaceous chondrites are somewhat 'diluted' in silicates due to the presence of other carbon and ice compounds, and all have not experienced core extraction, which has the effect of volumetrically enriching HPEs in the BSE. Nonetheless, the variation in HPEs between the Earth and chondrite group extremes could, for given end-members, result in internal temperature differences of up to 100K. This internal temperature divergence could also have important consequences for timing of tectonic transitions within planets, and thus have a non-linear effect on the final thermal state.

Whilst Earth and Mars have reasonable HPE constraints due to sample availability, Venus and Mercury do not, and their internal abundance must be estimated from gamma ray spectroscopy constraints. Our thermal history calculations for Earth-sized planets, with HPE abundances for Mercury, Mars and Venus (Table 3), are shown in Fig. 5c. Fortuitously our estimates for Venus and Mercury result in thermal histories that are bracketed by those of BSE and Mars. The variation in temperatures possible for a given tectonic regime are slightly less than 100 K (e.g. for the stagnant-lid end-member), but again, this divergent evolution could have larger effects if it affects the timing of tectonic transitions.

Finally, we have also plotted a chondritic BSE model against a non-chondritic BSE, and 'geodynamically constrained' BSE, in Fig. 6d. The latter uses present day heat flux, and argues (Turcotte and Schubert 2002) that secular cooling contributes around 20% to the present-day flux. However, this argument utilised convective relationships appropriate for simple convecting systems, heated solely from within, and does not consider convective lag-times between Ra and Nu, which may overestimate the efficacy of secular cooling (and thus overestimate HPE concentrations). The non-chondritic model, derived from consideration of impact-collision crustal loss on early planetary bodies, has much lower HPE abundances that the chondritic BSE. Unsurprisingly, its internal temperatures are much colder that the other more enriched models.

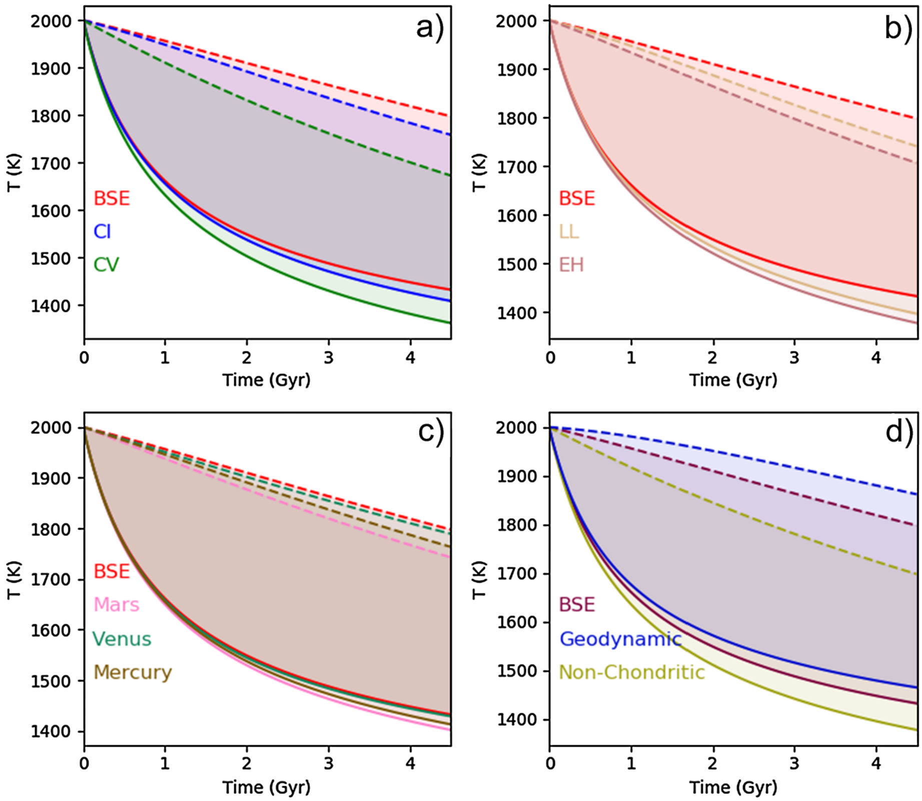

Fig. 6 Thermal evolution of Earth-sized planets for different abundances of heat-producing elements. The colour envelopes show the range of possible internal potential temperatures between a strict stagnant-lid regime (dashed lines), and a mobile lid regime (solid lines). (**a**) Difference in internal evolution between a bulk-silicate Earth model (see Table 4), and for an Earth with CI or CV chondrite HPE abundances (Table 2). (**b**) Comparison of BSE with LL ordinary chondrite and EH enstatite chondrite abundances (Table 2 and 4). (**c**) Comparison of BSE with estimated HPE abundances of Mars, Mercury and Venus (from Table 3). (**d**) Comparison of BSE based on chondritic abundances (red), non-chondritic estimates (brown) and geodynamic estimates (blue), from Table 4. Relevant physical parameters for the models are shown in Table 5

In order to assess the degree to which heat production may affect planetary tectonic regimes, and thus long-term evolution and habitability, we present a regime diagram (Fig. 7), showing the statistical likelihood for different tectonic regimes, depending on the magnitude of driving convective stresses compared to the retarding yield strength of the lithosphere.

Convective stresses are set by the mantle interior temperature through the exponential temperature-dependence of the mantle viscosity. In Fig. 7, the convective stress level for a mobile lid (plate tectonic) mode corresponds to a steady-state mantle interior temperature (yellow-filled black circles) that is given by the intersection (yellow-filled red circles) of a prescribed radiogenic heating power (dashed red lines) and mantle convective cooling power driven by three endmember mantle convective regimes (heavy red lines). In a probabilistic sense, the likelihood for a mobile lid- or episodic-style mantle convective regime is enhanced where the convective stress levels are within the lithospheric yield strength field. The yield strength is a wide field because this property evolves depending on the history of lithospheric damage and healing (e.g. Lenardic and Crowley 2012; Mulyukova and Bercovici 2018), as

Table 5 Parameters used to in the thermal history calculations of Fig. 6. For other details, see McNamara and Van Keken (2000), and Korenaga (2006)

Parameter	Value
Activation energy	300 kJ/mol
Density	4500 kg/m^3
Gravitational acceleration	9.81 m/s^2
Depth of convecting mantle	2890 km
Thermal conductivity	5.6 W/(m K)
Thermal expansivity	3×10^{-5} K^{-1}
Specific heat	1250 J/(kg K)
Reference viscosity	1×10^{21} Pa s

well as the thermal and volatile cycling history of a planet (Weller and Lenardic 2018; Lenardic et al. 2016). Lithospheric overturning in the presence of a water-rich atmosphere, for example, can cause the yield strength to decline over time through mineral hydration. Consequently, whether HPE concentrations permit a planet to enter into a mobile lid or intermittently mobile lid mode early in its evolution in the presence of a thick atmosphere can increase the likelihood that the planet will remain in a mobile lid regime. A similar early event in the presence of no atmosphere will induce a different evolutionary path.

In more detail, Fig. 7 enables a heuristic way to explore the sensitivity of Earth's (or any terrestrial planet's) current mode of plate tectonics to the HPE inventory. For example, if the present-day rate of internal heat production is increased by around a factor of 2, the mantle potential temperature increases to $\sim$ 1600 °C (red arrows). Critically, the corresponding convective stress level falls well below the yield stress field (black arrows) and the initial mode of plate tectonics is unstable to natural perturbations to this temperature (Lenardic et al. 2011) through their effects on the convective stress (green-filled circle). There is, in turn, a strong likelihood for a transition to a stagnant lid mode of tectonics and a different thermal evolutionary path (lower red curve and red-filled circle). Although the specifics of these tectonic transitions are subject to ongoing debate in the geodynamics community, it is abundantly clear that the internal heating rates, and the HPE budget of a planet, exert an absolutely fundamental control on planetary evolutionary paths.

6 Conclusions and Directions

Heat producing elements exert a basic control over planetary evolution, and yet their present concentration and distribution within planets are not well understood. Significant variations in HPEs exist between primitive chondrites, and terrestrial planets. Although progress is being made on the processes involved in their early re-distribution, efforts are hampered by a lack of evidence at key stages, such as disk condensation, and early planetesimal evolution. New technologies (e.g. geoneutrino detection) are providing potential insights into the internal distribution of HPEs within the Earth, but rather fundamental issues regarding even Earth's total budget remain, including tighter constraints on deep mantle and core HPE concentrations, and ^{40}K concentrations, which are currently unconstrained by current generation proton-collision geoneutrino detectors, but may be amenable to future electron-collision detectors (Dye 2012).

Our current best estimates of the mantle, lithosphere, and crust's radiogenic heat contribution from geochemical and cosmochemical estimates place the total BSE heat production at 21.4 TW for a chondritic Earth, or 10.8 TW for non-chondritic models. Using the most

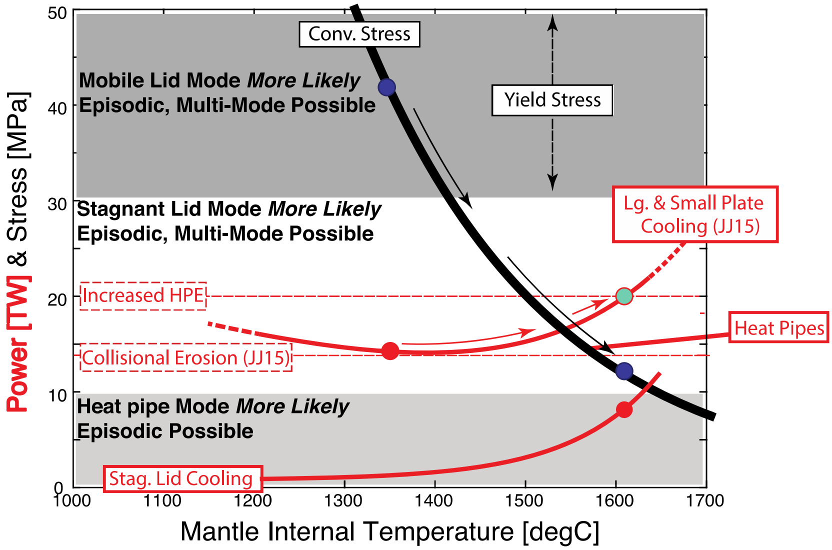

Fig. 7 Possible planetary evolutions (solid red lines) vs. tectonic endmember styles (shaded regions), as a function of the mantle convective stress imparted to the lithosphere (heavy black line) and HPE inventory expressed through present day radioactive heating power (dashed red lines) and mantle convective cooling regime (heavy red lines). This convective stress curve corresponds to the current "mobile lid" mode of plate tectonics and is governed by a strongly temperature-dependent mantle viscosity. Where stress levels are within the yield stress field, the likelihood for lithospheric failure and modern plate tectonics or episodic mantle convective regimes is increased in comparison to stagnant lid modes. For very low convective stress levels (below 10 MPa on this figure), lithospheric failure is impossible and the likelihood for cooling predominantly by mantle melting and magma transport to the surface in "heat pipes" is enhanced. The present-day convective stress level is well within the yield strength field (blue-filled circle)and corresponds to a mean mantle interior potential temperature (red-filled circle) given by the intersection of the non-chondritic "collisional erosion" radioactive heating power (dashed red line) and the cooling law for the "large and small plate regime" from Jellinek and Jackson (2015). This cooling law, which is consistent with Earth's current mode of plate tectonics and thermal history (Höink et al. 2013; van Summeren et al. 2012; Höink et al. 2013), reflects contributions to mantle cooling from large Pacific-sized (23%) plates, the motions of which are predominantly driven by plate buoyancy, and small Atlantic-sized plates (77%), the motions of which are mostly driven drag related to flow within an underlying asthenosphere. If the present day radiogenic heating power is increased to 20 TW, the interior temperature climbs to around 1625 °C (red arrows) and the corresponding convective stress drops well below the yield strength field (black arrows to blue-filled circle). This small- and large-plate solution for Earth's thermal history is consequently unstable (indicated by the green-filled circle). Natural fluctuations in the internal temperature and corresponding effects on the mantle convective stress will cause a transition to potentially a thermal evolution governed by the stagnant lid evolutionary path (filled red circle). See text

recent estimate for Earth's heat flux, 47 ± 1 TW (Davies and Davies 2010), then the implied Urey ratio is 0.45 or 0.23 respectively. The most recent heat production estimates from geoneutrinos is 38.2 +13.6/-12.7 TW, which would imply a Urey ratio of 0.81—though the uncertainties vary from 0.53 - 1.0. Uncertainties in geoneutrino estimates are large, as are variances between geochemical models, and the convergence of these approaches is critical to furthering models of Earth's internal HPE distribution.

The question of terrestrial exoplanet habitability—the long-term stability of surface conditions in the pressure-temperature window of liquid water—is closely tied to tectonic evolution and, thus heat production. These factors affect volcanic outgassing, and tectonically-associated in-gassing, and the major atmosphere gases associated with these processes (CO_2,

H_2O, SO_2, and noble gases) may be amenable to future spectroscopic measurements. With the next generation exoplanetary detection capability being able to detect Earth-sized planets, there is significant scope for refinement of our understanding of heat production variability within and beyond the solar system.

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