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Bicentennial Review

Hierarchical Earth accretion and the Hadean Eon

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Abstract: Geochemical traces from the Hadean Eon and terrestrial siderophile and volatile element data are discussed in the light of the standard, or hierarchical, model of planetary accretion, which envisages growth of the planets by collisions of progressively larger protoplanets. Siderophile element depletion patterns can be explained by partial inheritance from early stages of the process, when metal cores resulted from melting in collisions of small planetesimals. The abundances and isotope data for hydrogen and nitrogen suggest a chondrite-type source rather than nebular gas, in accord with atmosphere loss in the high-temperature aftermath of the Moon-forming Giant Impact, after which late accretion replenished the atmosphere. Lead isotope patterns and anomalous $^{142}\text{Nd}/^{144}\text{Nd}$ ratios in early Archaean metasediments and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of 3.7–4.4 Ga old detrital zircons point to a vanished crust that persisted through much of the Hadean Eon. A working hypothesis is proposed that links these observations. Following the freezing of a magma ocean caused by the Giant Impact, the mantle would be gravitationally unstable and an overturn would occur, leading to the formation of a huge mafic crust. After the overturn the mantle could be stable and inactive for hundreds of million years.

Two hundred years ago, when the science of Geology was young, it would have been unthinkable for a serious geological argument not to be based on solid evidence such as observations of an outcrop. Towards the end of the nineteenth century, this confidence in observation was put to the test by the purely physical modelling approach of Lord Kelvin, who had an equally unshakable belief in his cooling calculations that made geological time unacceptably short. Just a century ago the first mineral age calculations based on radioactive decay were made (Rutherford 1906). They yielded c. 400 Ma, which proved Kelvin's time scale to be wrong, and geological arguments were vindicated. The dilemma was solved by data from physics and chemistry: Joly (1903) had suggested that radioactivity could be an important source of terrestrial heat flow, and Strutt (1906) provided a quantitative basis for this idea.

Ever since that time, geochemistry and decay systems have provided hard data to anchor physical models to, in constructs that are now considered as robust as outcrops were 200 years ago (and still are). Among other things, geological time has acquired a beginning, even though its vestiges are in meteorites and the Moon rather than in terrestrial rocks. The oldest objects formed in the Solar System are 4570 ± 1 Ma (Lugmair & Shukolyukov 2001) or 4568 ± 1 Ma (Amelin *et al.* 2002) old, a very good agreement from very different dating approaches.

A great challenge for a constructive combination of geochemical data and modelling lies in the reconstruction of the Hadean Eon of the Earth, the first 700 Ma and arguably the most important part of its history. The processes and events that occurred in it set the scene for the subsequent history of the planet, in terms of both internal and surface processes. Yet there is no terrestrial rock record from this period, hence, it remains inaccessible to classical geological study. The approaches taken have been of three kinds. First, clues from the geology and

geochemistry of the earliest continental intracrustal and supracrustal rock units as well as from detrital zircons older than 4 Ga have been evaluated to derive a picture of the Hadean Earth. Second, marked terrestrial geochemical characteristics, such as the depletion in siderophile elements in the silicate Earth and the budget of volatile elements, have been evaluated to assess what processes could have brought them about. Third, physically *prima facie* plausible scenarios for such processes as the accretion of the terrestrial planets or atmosphere loss have been developed into numerical models and the thermal consequences of accretion events have been calculated. Thus the Hadean can be viewed from two perspectives: backwards, from terrestrial data, and forward, from meteorite data and accretion models.

In this review these two perspectives are taken. Some salient terrestrial data are first reviewed. These include: (1) evidence from the earliest sedimentary rocks and from detrital zircons; (2) the concentrations of siderophile elements in the silicate Earth; (3) the atmo-hydrosphere. Then, the hierarchical accretion scenario is sketched and its consequences, including a giant impact that gave rise to the Moon, are considered. These have a bearing on core formation, the question of whole-mantle melting (a magma ocean) in early Earth history, formation and loss of the atmo-hydrosphere, the question of the nature and quantity of the earliest crust, and the earliest climate history. These subjects are all related: the time scale of accretion determines what type of atmosphere (nebular-gaseous or meteorite-type) the planet could inherit, mantle melting could entail degassing and atmosphere formation, collisions in accretion could lead to atmosphere loss, and atmosphere–lithosphere interactions are important for palaeoclimate and the retention of the early atmosphere and ocean. From the bidirectional approach in time, a new working hypothesis for the internal dynamics and surface geology of the

Hadean Eon is then proposed, and its consequences are speculatively explored.

Most ancient crust material and inferences on the Hadean Eon

Clues from the earliest Archaean crust

The oldest contiguous continental crust province is located in southern west Greenland, in the Godthåbsfjord area north of Nuuk, and its westward continuation in Labrador. Here the tonalitic–trondhjemitic–granodioritic (TTG) Amitsoq Gneiss yielded a Pb/Pb whole-rock date of 3.62 ± 0.10 Ga (Black *et al.* 1971). Soon afterwards, banded iron formation (BIF) in the large iron deposit within the associated Isua Greenstone Belt was dated by Pb/Pb at 3.76 ± 0.07 Ga (Moorbath *et al.* 1973), defining the oldest metasedimentary sequence. Later, it was shown that there is a very extensive area of pre-3.7 Ga TTG, reaching from the area south of Isua with zircon U–Pb ages of 3.81–3.82 Ga (the Itsaq gneisses, Nutman *et al.* 1999; Kamber *et al.* 2003) to the Hebron–Saglek area of Labrador, where TTG units 3.73 Ga in age (Schiette *et al.* 1989) and a monzodioritic unit at least 3.81 Ga old (Collerson 1983; see also Kamber *et al.* 2003) occur. It is a convention to place the start of the Archaean era (and thus the end of the Hadean) at the age of these oldest rocks.

Many relatively small remnants of probable supracrustal rocks occur throughout this province, but the arcuate Isua Greenstone Belt is the only extensive assembly where all the different rock types (ultramafic, mafic and felsic metavolcanic rocks, BIF, siliciclastic sediments and possibly carbonate rocks) can be studied. Units in the greenstone belt range from 3700 to 3790 Ma in age (Nutman *et al.* 1997; Kamber *et al.* 2005) and have undergone medium-grade metamorphism. All contacts between it and the TTG rocks are sheared, so that the nature of a primary relationship, if any, cannot be established. Shear zones abound within the greenstone belt itself, and many rock units originally mapped as sedimentary rocks have later been identified as shear zones (Fedó *et al.* 2001; Myers 2001). A further problem is metasomatism. For instance, rocks originally mapped as limestones were mostly found to be metasomatized ultramafic rocks (Rosing *et al.* 1996). Nevertheless, careful study has allowed a reconstruction of the depositional environment from bona fide metasedimentary units, pillow lavas and pillow breccias: it was a sea floor, below wave base but with episodes of emergence (Fedó *et al.* 2001). The REE + Y abundance patterns of Isua BIFs clearly show an ocean water signature from uniform positive Y and La anomalies (Bolhar *et al.* 2004). The overall geochemistry of meta-siliciclastic units is similar to that of units in younger Archaean greenstone belts, and indicates a provenance from a mixture of ultramafic, mafic and felsic rocks, probably mostly volcanic. Further, many samples show relative depletion of Ca and Na, a clear sign of chemical weathering in the source area (Bolhar *et al.* 2005). Thus at 3.75 Ga there was TTG-type continental crust, an ocean, rain causing chemical weathering, and groundwater leaching, followed by runoff that could remove soluble cations from soil. This implies that the Urey cycle, removing CO₂ from the atmosphere by weathering and aqueous transport (and carbonate formation), was already operating. Fully unknown and controversial, meanwhile, are the temperatures of the land surface and the ocean water. The felsic gneisses, possibly the basement to the supracrustal rocks, are on the whole of TTG character, akin to those of later Archaean provinces (Kamber *et al.* 2003).

Extrapolations of known early Archaean features to the

Hadean Eon do, of course, not necessarily follow, but the TTG rocks and supracrustal rocks of West Greenland can nevertheless yield clues. One important observation is that some sedimentary rocks of the Isua Greenstone Belt are genetically unrelated to the TTGs in the same province. This is demonstrated by Pb isotopes (Moorbath *et al.* 1973; Kamber & Moorbath 1998; Kamber *et al.* 2003) using the $^{207}\text{Pb}/^{204}\text{Pb}$ v. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram, proposed by Holmes and Houtermans just over half a century ago (Fig. 1; Holmes 1949). Sediments (notably BIFs) and TTG gneisses both yield whole-rock isochron-type arrays giving mostly their age of origin (between 3.7 and 3.8 Ga), but the arrays for chemical sediments are offset to higher $^{207}\text{Pb}/^{204}\text{Pb}$ by *c.* 0.5. To generate such a relatively large difference in $^{207}\text{Pb}/^{204}\text{Pb}$ between these

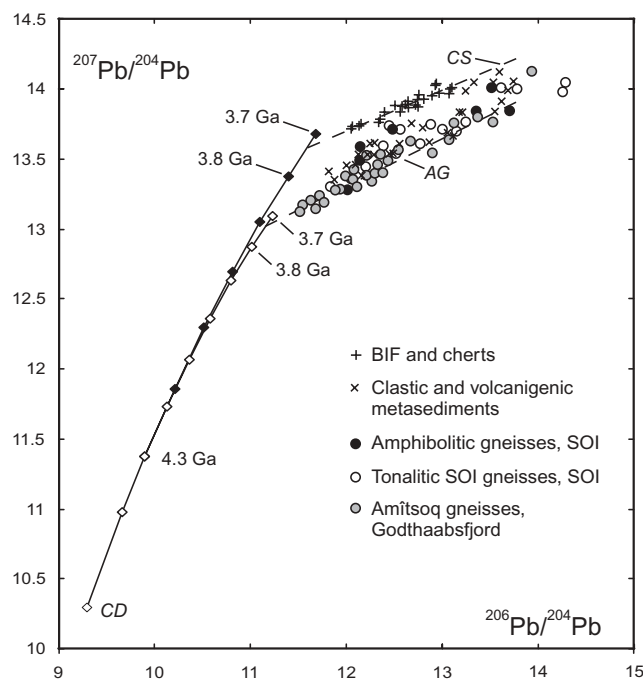


Fig. 1. Summary of the West Greenland early Archaean Pb isotope problem in the Holmes–Houtermans Diagram ($^{207}\text{Pb}/^{204}\text{Pb}$ v. $^{206}\text{Pb}/^{204}\text{Pb}$), and proposed solution. The figure shows data from Moorbath *et al.* (1973) and Kamber *et al.* (2003), and a model essentially the same as proposed and discussed by Kamber *et al.* (2003). Chemical sediments (BIFs and cherts) and the Amitsoq and South of Isua (SOI) gneisses form arrays in $^{207}\text{Pb}/^{204}\text{Pb}$ v. $^{206}\text{Pb}/^{204}\text{Pb}$ space that yield Pb/Pb errorchron ages close to 3.75 Ga (dashed reference lines: CS, chemical sediments; AG, Amitsoq gneisses). The lines are offset in $^{207}\text{Pb}/^{204}\text{Pb}$. In the simplified model shown, a system with $\mu = 7.7$ (where μ is equivalent to atomic $^{238}\text{U}/^{204}\text{Pb}$ ratio extrapolated to the present) starts with Canyon Diablo primordial Pb (CD) and accumulating radiogenic ^{206}Pb and ^{207}Pb from 4.55 Ga onward ($\diamond$, shown at 100 Ma intervals from 4.4 Ga). At 4.3 Ga there is a differentiation event and a subsystem with $\mu = 10.3$ is separated ($\blacklozenge$). $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios increase faster in this subsystem than in the original one. As ^{235}U (half-life 0.7 Ga with daughter ^{207}Pb) was abundant in early Earth history, the difference in $^{207}\text{Pb}/^{204}\text{Pb}$ is particularly pronounced. The main, not enriched system gives rise to the Amitsoq and SOI gneisses between 3.8 and 3.7 Ga, and the enriched system provides Pb to the chemical sediments. It should be noted that this solution is not unique: earlier differentiation times with correspondingly lower μ values of the enriched system also give fits. Kamber *et al.* (2003) argued that the enriched system is a Hadean protocrust.

rock units, they must have had precursors with very different U/Pb ratios over a time span of several hundred million years. This conclusion is highly robust: in $^{207}\text{Pb}/^{204}\text{Pb}$ v. $^{206}\text{Pb}/^{204}\text{Pb}$ space, Pb isotope evolution was steep in early Earth history, when $^{235}\text{U}/^{238}\text{U}$ was high, and flattened out rapidly with time, as ^{235}U decays more rapidly than ^{238}U . A steep precursor development as required by the Isua data in Figure 1 was possible only at *c.* 4 Ga or before. For example, Kamber *et al.* (2003) have modelled a history with two separate reservoirs going back to 4.3 Ga, for which the Pb isotope growth is illustrated in Figure 1. They proposed that the high U/Pb reservoir was a Hadean protocrust consisting of mainly mafic volcanic rocks, which survived for several hundreds of million years at the surface and was sampled by the sediments.

In a few Isua metasediment samples, values of $^{142}\text{Nd}/^{144}\text{Nd}$ significantly (10–20 ppm) above the average Earth have been detected (Harper & Jacobsen 1992; Boyet *et al.* 2003; Caro *et al.* 2003; Sharma & Chen 2004). The abundance of ^{142}Nd was augmented by the decay of extinct ^{146}Sm with a half-life of 103 Ma. Fractionation of the Sm/Nd ratio in magmatic processes (discussed further below) could have led to such detectable variations in $^{142}\text{Nd}/^{144}\text{Nd}$ ratios only in the lifetime of ^{142}Nd ; that is, in the first *c.* 300 Ma of Earth history. The silicate Earth is otherwise homogeneous in $^{142}\text{Nd}/^{144}\text{Nd}$. Thus early formed $^{142}\text{Nd}/^{144}\text{Nd}$ anomalies must generally have been wiped out by efficient mixing in the silicate Earth. The $^{142}\text{Nd}/^{144}\text{Nd}$ anomalies in the Isua metasediments show, however, that some matter older than about 4.2 Ga escaped such mantle stirring, and this is in accord with the Pb isotope evidence reviewed above.

Dated detrital zircons from Isua siliciclastic sediments show a narrow age range of 3.70–3.71 Ga with one outlier at 3.74 Ga; they are identical in age and geochemistry to zircons in felsic volcanic rocks of the Isua Belt, and are thus probably derived from such units (Kamber *et al.* 2005; note that older volcanic units >3790 Ma also exist in the Isua Belt, Nutman *et al.* 1997). The voluminous adjacent Itsaq and Amitsoq gneisses, with older zircon ages (see Nutman *et al.* 1999), thus hardly feature in the sedimentary record of the time, in accord with the Pb isotope data. Kamber *et al.* (2005) interpreted this as a result of intensive volcanic resurfacing, preventing the exposure and erosion of basement material.

No continental crustal material older than about 3.8 Ga has been found on Earth that is coherent beyond the scale of a zircon grain. The Acasta Gneiss outcrops in the Slave Craton, northern Canada are orthogneisses with amphibolite lenses; they contain zircons 4.0 Ga in age as well as younger generations (Bowring & Williams 1999). The Sm–Nd systematics of these rocks were completely reset by an event at 3371 ± 59 Ma (Moorbath *et al.* 1997). This resetting has been so complete that the $^{143}\text{Nd}/^{144}\text{Nd}$ v. $^{147}\text{Sm}/^{144}\text{Nd}$ whole-rock data array is almost an isochron (MSWD = 9.2). It is generally accepted that only extensive remelting can produce such resetting at the outcrop scale. Nevertheless, the evidence of a 4.0 Ga old protolith remains, and this has at least in part a granitoid composition.

Evidence from detrital Hadean zircon grains

Detrital zircons in quartzites from the Beartooth Mountains in the Archaean Wyoming Province have ages ranging from 3.7 to 4.0 Ga (Mueller *et al.* 1998) and the Jack Hills metaconglomerates and quartzites in the 3.73 Ga Narryer granite–gneiss terrane of the NW Yilgarn Craton, Australia, have yielded zircons in which many secondary ionization mass spectrometry (SIMS) U–Pb dates up to 4.3 Ga and some up to 4.36 Ga have

been determined (Wilde *et al.* 2001; Harrison *et al.* 2005; Nemchin *et al.* 2006). Although the source province of these very ancient zircons has not been found, the grains themselves yield much information. Its interpretation is controversial in all cases.

The presence of zircon in itself (indicating Zr supersaturation of a magma) with appreciably high U contents (up to *c.* 500 ppm), and the REE patterns of these zircons (with Nd contents up to $200 \times \text{C1}$), were seen by Wilde *et al.* (2001) as evidence for a highly evolved magma as a source of the detrital grains. Whitehouse & Kamber (2002) questioned the REE evidence. They noted a highly inconsistent partitioning behaviour of REE in early Archaean zircons and their magmatic host rocks, possibly pointing to inclusions. However, they concurred with Wilde *et al.* (2001) on the Zr and U arguments for a differentiated magma source.

Further, the >4 Ga detrital zircons have yielded $\delta^{18}\text{O}$ values between 5 and 7.5‰ (SMOW) (Peck *et al.* 2001; Valley *et al.* 2005), a range extending significantly above the mantle value (5‰). Continental crust of all ages is variably enriched in ^{18}O relative to the mantle, and this is interpreted as a signal inherited (via subduction fluids) from oceanic crust alteration, or attributed to magmatic assimilation of sediments or altered volcanic rocks, or both. The elevated $\delta^{18}\text{O}$ values in the ancient detrital zircons, together with their indications for an evolved source, have led to the proposal (Peck *et al.* 2001; Valley *et al.* 2005) that the source provinces of these ancient zircon grains were equivalent to modern continental crust, and had originated in subduction zones. This would imply that liquid water was present and probably abundant as far back as 4.3 Ga, and that plate tectonics already operated at that time. However, Nemchin *et al.* (2006) studied truly pristine, magmatic zircons of the detrital population, and only found values close to 5‰ in these. They disputed the use of $\delta^{18}\text{O}$ values as evidence for subduction-related petrogenesis, and implied that post-magmatic processes (e.g. metamorphism) may have caused the higher $\delta^{18}\text{O}$ values found by others.

Evidence for an evolved magma source of these zircons need not imply a continental crust environment. As an alternative scenario, Kamber *et al.* (2005) proposed that differentiated melts could form part of an accumulating Hadean volcanic crust. They also noted that radioactive heat production of all rock types was between 3 and 4.5 times higher in the Hadean than today, and calculated that partial melting of basalt, or gabbro, at depths between 20 and 40 km would have been possible. Remelting and magmatic differentiation could have produced magmas highly enriched in incompatible elements. If there was a hydrosphere, volcanic rocks could have interacted with this between resurfacing episodes, so that hydrous rocks could exist at depth without subduction. Solidus temperatures would be considerably lowered, making remelting more likely. It has been demonstrated that melting of gabbros under hydrous conditions can yield plagiogranitic magmas (Koepke *et al.* 2004). Explaining early Hadean magmatic petrogenesis is thus made easier by invoking a hydrosphere, although this does not constitute hard evidence.

Another important archive contained in these most ancient zircons lies in their Lu–Hf isotope systematics. These are highly relevant to the early fractionation of the silicate Earth and the possible formation of large amounts of crust in its early history. To the question of how the amount of continental crust grew through geological history, many approaches have been applied, among them considerations of age distributions (e.g. Hurley & Rand 1969; Taylor & McLennan 1995), the continental freeboard argument (Armstrong 1981), back-extrapolation of present-day

continental growth rates (Reymer & Schubert 1984), forward global isotope modelling (Kramers & Tolstikhin 1997) and initial Nd and Hf isotope compositions of ancient rock provinces (Bennett *et al.* 1993; Bowring & Housh 1995). Again, there is anything but a consensus on this issue. Here only the question of total crust mass in the Hadean is addressed, to which only the last of the above approaches is applicable. The use of initial $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios in early Archaean rocks is based on the fractionation of the Sm/Nd ratio during melting in the mantle: The residue is left with much lower REE concentrations but an increased Sm/Nd ratio, whereas the melt (and, ultimately, the continental crust) has a lower ratio. In contrast to the $^{146}\text{Sm}-^{142}\text{Nd}$ system (see above), the $^{147}\text{Sm}-^{143}\text{Nd}$ decay has a very long half-life (106 Ga) and the Sm/Nd fractionation results in a secular increase of $^{143}\text{Nd}/^{144}\text{Nd}$ ratio heterogeneity in the silicate Earth: the residual mantle $^{143}\text{Nd}/^{144}\text{Nd}$ ratio increases faster than that of the bulk silicate Earth (BSE). A wide scatter of initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in both the Amitsoq Gneisses of west Greenland (Bennett *et al.* 1993) and the Acasta Gneisses of northern Canada (Bowring & Housh 1995) has been claimed to signal that much highly evolved matter (such as a continental crust) had evolved very rapidly after Earth accretion. However, the observation that the Sm–Nd systematics of these rocks were reset at later dates (Moorbath *et al.* 1997; see above) means that the true initial ratios cannot be reconstructed, and the Nd isotope data therefore cannot be used to infer large-scale early terrestrial differentiation.

Lu–Hf systematics operate similarly to Sm–Nd, as residual mantle has higher Lu/Hf and hence faster growth of $^{176}\text{Hf}/^{177}\text{Hf}$ than the bulk silicate Earth, and the inverse applies to evolved melts and continental crust. Compared with Sm–Nd, however, Lu–Hf systematics offer a much more robust approach to earliest differentiation events, as Hf is built into zircon at the per cent level, being the geochemical twin of Zr. Because zircons are much less enriched in REE than in Hf, their Lu/Hf ratios are extremely low and the $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of the parent magma at the time of their crystallization can be readily determined. Zircon crystals are a very good archive, as recrystallization (and thus open-system behaviour for Hf) would be betrayed by a younger U/Pb age. The Hf isotope approach can be applied to detrital and *in situ* zircons alike.

In Figure 2 the current database of initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of mid-Archaean to Hadean zircons (Amelin *et al.* 1999, 2000; Harrison *et al.* 2005) is plotted against the respective zircon U–Pb ages. Mid- and early Archaean zircons plot close to the bulk silicate Earth development line (derived from chondrite data and representing an undepleted, or primitive, mantle reservoir), indicating that they probably crystallized from juvenile, average-mantle derived magmas. The zircons from the Acasta Gneisses and the detrital Jack Hills population show a much greater scatter. In the older ranges of the Jack Hills suite, there are some values lying above the BSE line, mostly within, but in one case significantly outside experimental error, as found by Harrison *et al.* (2005). Those workers interpreted this as evidence for a strongly depleted mantle reservoir, resulting from the formation of a massive continental crust as early as 4.4 Ga ago. This is not, however, borne out by the vast majority of the data, and this single grain may also stem from a depleted reservoir of a local nature, or even from lunar meteoritic material incorporated in these sediments. On the whole, the data plot below the bulk silicate Earth line, and thus reflect long-lived enriched (melt-type) sources, rather than depleted (residual) ones. A further distinction can be made, illustrated by the two dashed arrows drawn for reference through the Jack Hills population in Figure

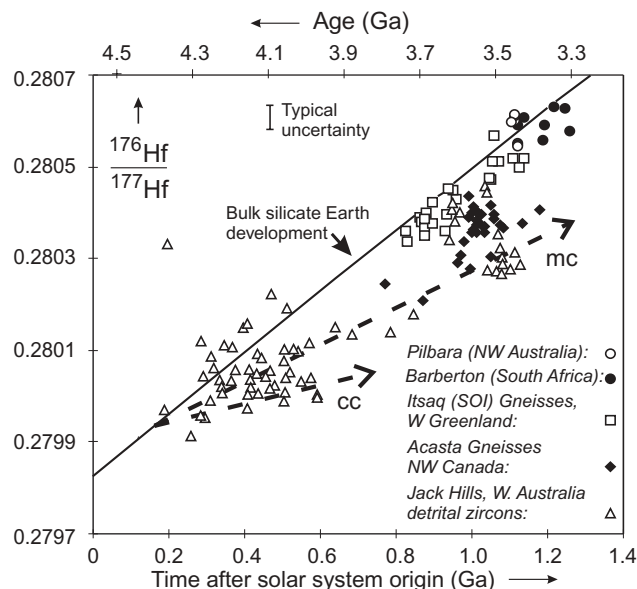


Fig. 2. Initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of Archean and Hadean zircons plotted against their U–Pb ages. Data from Amelin *et al.* (1999, 2000) and Harrison *et al.* (2005; ICP-MS data). Bulk silicate Earth development line is based on a ^{176}Lu decay constant value of $1.86 \times 10^{-11} \text{ a}^{-1}$ and a chondritic $^{176}\text{Lu}/^{177}\text{Hf}$ ratio (0.03615). Dashed arrows, drawn in for reference, represent $^{176}\text{Hf}/^{177}\text{Hf}$ development in a mafic crust (mc) with $^{176}\text{Lu}/^{177}\text{Hf} = 0.021$ and an average continental crust (cc) with $^{176}\text{Lu}/^{177}\text{Hf} = 0.012$, both generated at 4.4 Ga.

2. Continental crust type rocks have on average a very low Lu/Hf ratio and their $^{176}\text{Hf}/^{177}\text{Hf}$ ratio evolves as arrow 'cc'. The average Lu/Hf ratio of mafic (oceanic) crust is intermediate between that of continental crust and the bulk silicate Earth, and evolves as shown by arrow 'mc'. It can be seen that on shorter time scales, both mc and cc (and indeed, bulk silicate Earth) development models are compatible with the Jack Hills zircon data. However, on a longer time scale (1 Ga) only the mafic crust model is appropriate. A viable interpretation is that these zircons reflect the Hf isotope development of a rock province that was generated by partial melting in the mantle at *c.* 4.5–4.4 Ga and remained isolated since its formation but underwent internal differentiation, leading to the scatter. The same may apply to the Acasta population, with a province generated at *c.* 4.1 Ga. We are reminded of the model of Kamber *et al.* (2005), which invoked remelting of a thick, long-lived mafic crust. Localized remelting of such a crust from time to time would result in the Hf isotope pattern seen in Figure 2 for the Jack Hills as well as the Acasta zircons.

Thus a number of lines of evidence point to a long-lived protocrust having existed during the Hadean Eon. With the possible exception of the Acasta Gneisses, which are intracrustal and may represent a reworked remnant of such a protocrust, this has fully disappeared, leaving only isotope signatures and detrital zircon grains as traces. This disappearance would point to it having been mainly mafic, allowing bulk subduction at some stage. Yet all available evidence points to it having been stable at the Earth's surface for hundreds of millions of years, much longer than present-day oceanic crust. In most geologists' world view, geodynamics in the Hadean, with much higher radioactive heat production than today and residual heat from accretion,

would have been more vigorous than at present. The notion of a long-lived Hadean mafic protocrust is therefore paradoxical, or at least counter-intuitive.

Siderophile elements and core formation

A number of aspects of the chemistry of the Earth that are difficult to explain by simple mechanisms and a source of chondritic composition have been reviewed by Drake & Righter (2002). They include, in particular, the abundance pattern of the siderophile elements and the deficiency of Si. The cause of the depletion of the siderophile elements in the silicate mantles of planets is their preferential incorporation of metal that formed their cores. Siderophile element abundance patterns are important because they can give information on the mode of core formation processes, which are associated with planetary accretion in a broad sense. They thus represent a rare direct window on the accretion of the Earth.

The main peculiarity of the BSE siderophile element abundance pattern is that it does not reflect equilibrium partitioning between a silicate and a metallic melt for the individual elements, at least not at low pressure, but that it has a broadly stepwise shape, with a division into three groups, or steps (See Fig. 3). The relative depletion of these element groups as a whole broadly follows their metal–silicate partition coefficients, with the platinum group elements (PGE) being the most depleted and the weakly siderophile elements Mn, V and Cr the least. Thus the abundance pattern reflects partition coefficients in broad terms, but not in detail. The near-chondritic relative abundance pattern of the PGE is particularly striking, in view of their highly variable partition coefficients (Fig. 3). There is a further

discrepancy: whereas the PGE are all over-abundant relative to low-pressure equilibrium partitioning, the weakly siderophile elements V, Cr and Mn are all under-abundant, and the intermediate group is divided. The under-abundant elements are mostly those with multiple valence states, for which the metal–silicate partition coefficient increases strongly with decreasing oxygen fugacity.

To account for this set of observations, a number of scenarios have been put forward. Wänke *et al.* (1984) proposed heterogeneous accretion with an early, reducing stage, followed by accretion of progressively more oxidizing material, culminating in a ‘late veneer’ of almost metal-free, carbonaceous chondrite-like material. Righter *et al.* (1997) and Righter (2003) have shown that metal–silicate equilibrium at high pressure may reproduce some of the observed abundances, and have proposed a deep region in a terrestrial magma ocean as the locus of siderophile element depletion on Earth. Morgan *et al.* (2001) have examined the ‘late veneer’ hypothesis in connection with the observed late Lunar Cataclysm, and found that a terrestrial counterpart to this event would be insufficient to refill the Earth’s mantle with PGE. Azbel *et al.* (1993) and Kramers (1998) have modelled terrestrial siderophile element depletion on the basis that core formation occurs in successive events (‘continuously’) concurrently with accretion. This continuous core formation modelling follows two simple principles. First, the equilibrium depletion of a siderophile element in metal–silicate fractionation is given by $C_{\text{silicate}}/C_0 = 1/[(1 - F_{\text{metal}}) + DF_{\text{metal}}]$, where C_0 is its concentration in the mantle prior to the fractionation event, F_{metal} is the fraction of metal melt in molten silicate–metal mixture, and D is the metal–silicate partition coefficient. Thus, as the metal fraction in the mantle decreases by core formation, the weakly and moderately siderophile elements are progressively left in the silicate fraction during melting events where metal equilibrates with silicate, as $DF_{\text{metal}} < 1$. After the metal fraction reaches the per mil level, only the PGE (with D values > 1000) are further depleted. Second, as accretion continues, the siderophile element content of newly arriving matter is diluted by the siderophile element-depleted resident silicate mantle. The results of high-pressure fractionation and continuous core formation modelling are both shown in Figure 3.

It appears that none of these approaches on its own can readily explain the siderophile abundance pattern. The ‘late veneer’ hypothesis requires an addition amounting to only *c.* 0.3% of the mass of the silicate Earth to replenish it to the observed PGE abundances after hypothetical depletion by a bulk low-pressure metal–silicate fractionation event (lines a and b in Fig. 3), but this amount is wholly insufficient for Ni, where about 8% addition would be required (line c in Fig. 3). The high-pressure approach requires highly specific P – T conditions for equilibrium in a deep magma ocean in an almost completely formed Earth; the mechanics of this process are problematic (Rubie *et al.* 2003). In the continuous core formation models, the under-abundance (relative to low-pressure equilibration) of elements such as V, Mn and W (Fig. 3), for which the siderophile character is very strongly dependent on oxygen fugacity, can be explained only if it is assumed that earliest metal segregation occurred in an extremely reducing environment, rendering these elements siderophile. Alternatively, they might have been incorporated in Fe metal that condensed directly from a reducing vapour phase (Larimer 1967; Grossman & Larimer 1974), either in interstellar episodes, or after flash heating events in the early solar nebula that led to the formation of chondrules (Connolly & Love 1998). The continuous core formation model thus requires heterogeneous accretion with increasing oxygen fugacity to be successful,

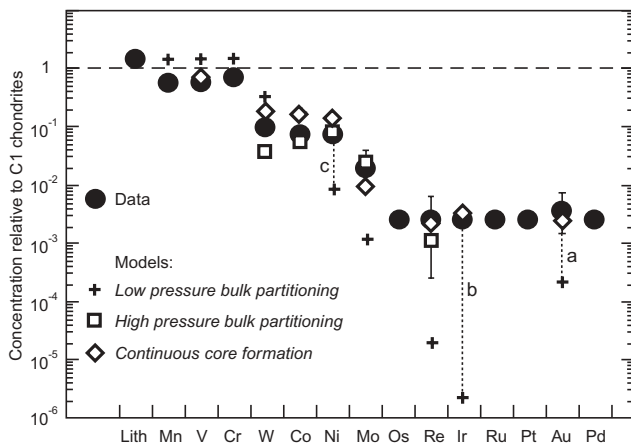


Fig. 3. Depletion of refractory siderophile elements in the bulk silicate Earth relative to C1 chondrites. Modified and expanded from Drake & Righter (2002). Elements are arranged from left to right in order of increasing siderophile behaviour. Lith, lithophile refractory elements (enriched in BSE because not incorporated in core). (For high-pressure modelling, see Righter *et al.* (1997) and Righter (2003).) Continuous core formation modelling shown uses decreasing Fe content and hence increasing oxygen fugacity of accreting matter, leading to better fit of V, W and Mo than in earlier versions (Kramers 1998, and unpubl. data). The lengths of vertical dashed lines a, b and c give examples of the amount of late chondritic veneer that should be added to replenish the siderophile element contents to observed levels in a silicate mantle depleted by low-pressure metal–silicate partitioning: a and b (noble metals) about 0.3%, c (Ni) about 8%.

and its late stage is not highly different from a late veneer accretion as envisaged by Wänke *et al.* (1984).

A chronometer based on the decay of extinct ^{182}Hf (half-life 9 Ma) to ^{182}W is relevant to the time scale of planet formation (Kleine *et al.* 2002; Schoenberg *et al.* 2002; Yin *et al.* 2002). W (see above) is siderophile under reducing conditions, and therefore in the course of segregation of metal (by whatever process) an increase in Hf/W ratio in the non-metal fraction (whether it be vapour, melt or solid silicate) results. If this happens in the lifetime of ^{182}Hf , it results in an enhanced growth of the $^{183}\text{W}/^{182}\text{W}$ ratio of the differentiated material relative to undifferentiated Solar System solid matter (carbonaceous chondrites). For instance, silicate fractions of ordinary chondrites have higher $^{182}\text{W}/^{183}\text{W}$ ratios, and metal fractions lower ones, than their bulk material (e.g. Lee & Halliday 2000; Kleine *et al.* 2002; Yin *et al.* 2002). The bulk silicate Earth, depleted in W (Fig. 3), has higher Hf/W and $^{182}\text{W}/^{183}\text{W}$ ratios than carbonaceous chondrites as shown in Figure 4. In this extinct isochron diagram, the slope of an isochron signifies a ratio of radiogenic $^{182}\text{W}^*$ to ^{180}Hf . As the $^{182}\text{W}^*$ represents ^{182}Hf that has fully decayed, this is equal to the ratio $^{182}\text{Hf}/^{180}\text{Hf}$ at the time (or average time) of differentiation. This ratio in turn is dependent only on time, and the data in Figure 4 permit estimation of the time interval between solar nebula formation and the Hf/W enrichment of the average silicate matter in the Earth. This average time is 29.5 ± 1 Ma if a value of $(1.0 \pm 0.08) \times 10^{-4}$ is used for the initial $^{182}\text{Hf}/^{180}\text{Hf}$ ratio of the Solar System, as suggested by the chondrite data shown in Figure 4 (Kleine *et al.* 2002; Yin *et al.* 2002). The precise meaning of this time interval is model dependent and will be discussed further below.

A further isotope system that has been frequently used in attempts to constrain accretion and core formation time is U–Pb, via arguments on the Pb isotope composition of the bulk silicate Earth. Pb is slightly volatile and is also siderophile at high pressure (Oversby & Ringwood 1971), and therefore planetary accretion with collisions (leading to volatile loss) and core formation would both lead to an increase of the U/Pb ratio in the silicate Earth. This would have been recorded in terrestrial Pb isotopes. Attempts to constrain core formation time by Pb isotopes were initiated by Allègre *et al.* (1982), based on the observation that Pb isotope ratios of the mid-ocean ridge basalt (MORB) source mantle and average upper continental crust (as represented by pelagic sediments) both appear to plot to the right of the meteoritic isochron in the $^{207}\text{Pb}/^{204}\text{Pb}$ v. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram. Further discussions have followed (e.g. Galer & Goldstein 1996; Wood & Halliday 2005), but have not yielded highly meaningful results. The reason is that the Pb isotope composition of the bulk silicate Earth is very poorly known, because of the large heterogeneity of the continental crust in particular (see database of Kramers & Tolstikhin 1997). Thus Pb isotopes, in many other instances a powerful tracer and chronometer, are a blunt instrument with regard to the timing of terrestrial core formation.

The Earth's atmo-hydrosphere and its possible sources

Possible sources

The atmosphere of a planet like the Earth could have stemmed from gravitational attraction of nebular gas by planets or their predecessors, and/or from outgassing of accreted volatile-rich solid material, in particular carbonaceous chondrite-type matter or comets. As shown below, these possible atmosphere components have different chemical and isotopic signatures and there-

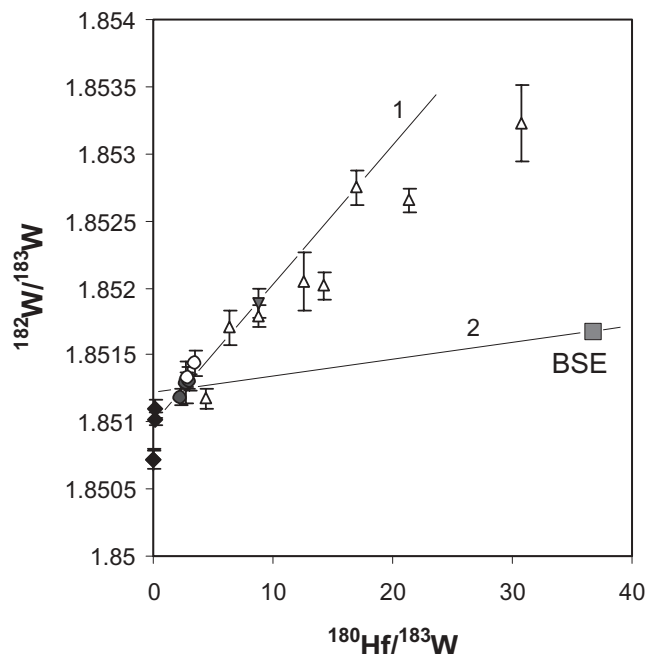


Fig. 4. $^{182}\text{W}/^{183}\text{W}$ v. $^{180}\text{Hf}/^{183}\text{W}$ 'extinct isochron' diagram showing chondrite data and bulk silicate Earth (BSE). ●, carbonaceous chondrite whole rocks (Allende and Murchison); ▼, calcium–aluminium inclusion (CAI), Allende; ○ ordinary chondrite whole rocks; ◆, ordinary chondrite metal fractions; △, ordinary chondrite non-metal fractions. Data from Yin *et al.* (2002) and Kleine *et al.* (2002). The chondrite metal fractions are in the same $^{182}\text{W}/^{183}\text{W}$ range as iron meteorites. In this diagram the slope of an extinct isochron, $\Delta^{182}\text{W}/\Delta^{180}\text{Hf}$, drawn through cogenetic samples is equal to the $^{182}\text{Hf}/^{180}\text{Hf}$ ratio at the time of their Hf/W differentiation. This $^{182}\text{Hf}/^{180}\text{Hf}$ ratio is dependent only on time. Line (1), through carbonaceous chondrites and Allende CAI, gives a value of $(1.0 \pm 0.08) \times 10^{-4}$ for the $^{182}\text{Hf}/^{180}\text{Hf}$ ratio at the time when the earliest Solar System objects formed ('initial' ratio). The scatter of chondrite silicate phases suggests a time span of c. 3 Ma for chondrite-forming processes. Line 2, through average carbonaceous chondrites and the bulk silicate Earth, gives a $^{182}\text{Hf}/^{180}\text{Hf}$ ratio of 1.1×10^{-5} for the time when the BSE obtained its present Hf/W ratio (through W depletion, mixing, etc.). The time difference required for this ^{182}Hf decay is 29.5 Ma. It should be noted that this is only a maximum limit for the time interval of core formation (see text and Yin *et al.* (2002) for a discussion).

fore, like siderophile element patterns, the Earth's volatile element abundances can give us clues to the planetary formation process.

In chondrites, major volatiles reside in different phases. H is primarily hosted in hydrous silicate minerals ('clays'), and to some extent in tarry carbonaceous matter. C and N occur in this same tarry matter, and C also as carbonate. For both C and N there is further a small, variable pre-solar grain contribution (graphite and diamond in the case of carbon). In addition to these 'native' volatiles, meteorite matter and, in particular, dust contain volatile elements in the form of surface-implanted solar wind.

Figure 5 summarizes isotope ratios of H, C and N in the terrestrial planets and possible sources. D/H ratios and $\delta^{15}\text{N}$ values of planets and chondrites are very significantly above the solar neighbourhood value. The D/H ratios in the Earth and

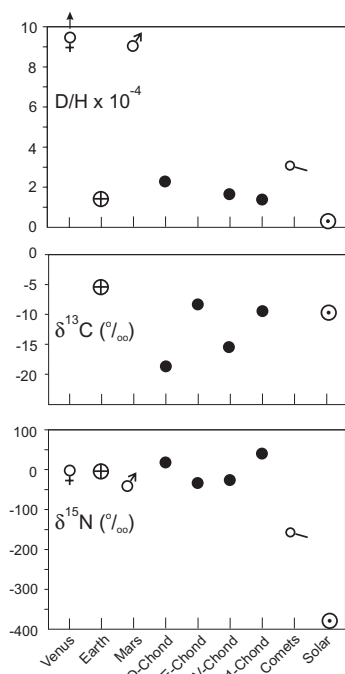


Fig. 5. Comparison of hydrogen, carbon and nitrogen isotopic compositions of the Earth, Venus, Mars, three chondrite types, comets and the values for the solar nebula (for hydrogen this is obtained from nearby interstellar clouds and the atmosphere of Jupiter, as the sun has produced deuterium). δ values for C and N are relative to terrestrial standards: PDB and atmospheric N. Data from Deloule & Robert (1995), Deloule *et al.* (1998), Owen & Bar-Nun (2001) and Grady & Wright (2003). (See discussion in the text.)

chondrites group are somewhat variable, but are all by a factor of >4 higher than the value in interstellar hydrogen ($c. 2.6 \times 10^{-5}$), which is similar to that in Jupiter's atmosphere and thus probably corresponds to the solar neighbourhood hydrogen 4.5 Ga ago (Mahaffy *et al.* 1998; Morbidelli *et al.* 2000). Similarly, $\delta^{15}\text{N}$ values in chondrites vary by $\pm 40\%$ from the terrestrial standard, and there is a large (400%, or almost a factor of two) offset from the solar neighbourhood value, which, also in this case, is the same as that of Jupiter's atmosphere (Owen & Encrenaz 2003). The inference that the major volatiles H and N on Earth are predominantly derived from a chondritic, rather than from a nebular gas source, is very strong.

The striking differences between the chondritic and solar neighbourhood (and protosolar) values of D/H and $\delta^{15}\text{N}$ can be explained by different ultimate sources: hydrogen and nitrogen incorporated in chondrite parent bodies could be derived from interstellar ice grains, organic matter and other presolar grains, whereas the solar value represents the (dominant) gas in the solar neighbourhood. Under the low P – T conditions reigning in a presolar molecular cloud, fractionation is expected to result in heavy isotope enrichment in interstellar grains (Drouart *et al.* 1999; Robert *et al.* 2000; Millar 2003). The isotopic character of the major volatiles in the Earth's atmosphere is thus, surprisingly, a window on presolar events.

Figure 6 shows solar-normalized abundances of major volatiles and noble gases. The chondritic abundance patterns of H, C and N, as well as those for the noble gases, differ strongly from solar values. From Ar to Xe the C1 chondrite pattern in Figure 6 is

identical to the so-called 'Q' component (Ozima *et al.* 1998), which, like C and N, appears to reside in carbonaceous matter (Verchovsky *et al.* 2002). For He and Ne, which in 'Q' are extremely depleted, a solar-implanted component dominates the C1 abundances. Atmospheric data have the advantage that comparisons can be made between Earth, Mars and Venus, and Figure 6 shows that there are great differences in both absolute and relative abundances between the three. Both Earth and Mars have noble gas patterns similar to C1 up to Kr, but show a relative depletion in Xe (the missing xenon problem; see Tolstikhin & O'Nions 1994). Venus has higher heavy noble gas abundances and a solar-like pattern for Ar, Kr and Xe. Its ^{36}Ar abundance is super-chondritic (Fig. 6), showing that the Venusian atmosphere must have a significant solar nebula component. On the other hand, Ne is more depleted in Venus' than in the Earth's atmosphere.

The decoupling of major volatiles from noble gases in chondrites and planetary atmospheres compared with the solar abundances is obvious from Figure 6. It is readily quantified by the atomic $\text{N}/^{36}\text{Ar}$ ratio. Its solar value is 40, and carbonaceous chondritic ratios, although variable, average about 2×10^5 . The terrestrial ratio is 5×10^4 , much closer to chondritic than to solar values. The same applies to Mars ($c. 10^4$) and Venus (2×10^3) (Porcelli & Pepin 2003). Clearly, accreting chondritic material could deliver a dominant contribution of H, C and N to a growing planet, and its accompanying contribution of light noble gases could at the same time be insignificant. The irregular abundance patterns for H, C and N in the planets can be related to planetary atmosphere loss processes, to be discussed further below.

There is evidence for almost pure solar-type light noble gases in the deep Earth. In some plume-derived rocks and fluids, $^4\text{He}/^3\text{He}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ ratios are much lower than those in MORB (e.g. Dixon *et al.* 2000; Tolstikhin & Hofmann 2005). Modelling of light noble gas characteristics of the upper mantle has generally made use of the concept of influx from a large reservoir, the lower mantle (O'Nions & Oxburgh 1983; Kellogg & Wasserburg 1990; Porcelli & Wasserburg 1995). However, this is now problematic in view of mounting evidence for whole-mantle convection (Christensen 1995; Van der Hilst *et al.* 1997; Van Keken & Zhong 1999). Tolstikhin & Hofmann (2005) and Tolstikhin *et al.* (2006) presented the proto-oceanic crust D' hypothesis as an attractive alternative. Their scenario involves the formation of earliest oceanic crust by a partial melting process, and loading of this crust with a terrestrial regolith of chondritic composition (a 'late veneer') with a light noble gas composition dominated by previous solar wind implantation of the matter that then accumulated in the regolith. Slabs of the crust and dense regolith would sink through the mantle, and ultimately reside at the core–mantle boundary where small portions of it, entrained in mantle convection, would 'leak' small amounts of solar He, Ne and Ar, noticeable against the extremely low mantle background of these gases. This scenario requires such a crust to be stable at surface in earliest Earth history long enough to collect the regolith, and such a long residence is in accord with the interpretation of Kamber *et al.* (2003, 2005) of the Isua Pb isotope data and the Hf isotope data for most very ancient detrital zircons (see above).

Evidence for atmosphere loss, and its time scale

Xe has a radiogenic isotope, ^{129}Xe , which is the daughter of extinct ^{129}I decay (half-life 15.7 Ma). The initial ratio of $^{129}\text{I}/^{127}\text{I}$ is reasonably well constrained from meteoritic data ($c. 0.0001$,

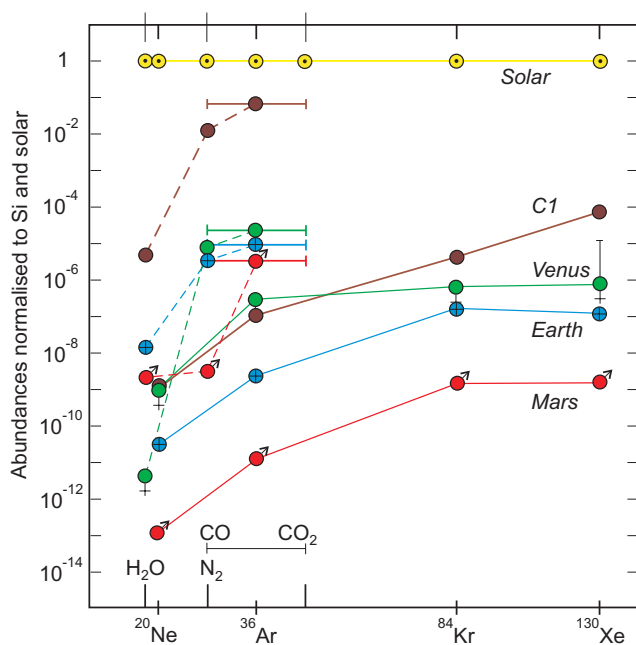


Fig. 6. Solar-normalized atomic abundances of primordial noble gases and major volatiles H, C and N in C1 chondrites and three terrestrial planets, plotted against the atomic or molecular masses (molecular weight can be an important factor in some types of gas loss from the atmosphere; see text). Noble gas patterns are connected with continuous lines, major elements with dashed lines. C is plotted at mass 36, intermediate between CO and CO₂. H and C budgets for planets include ice caps, oceans, permafrost and sedimentary matter where applicable. Molecular masses for H, N and C naturally do not apply to chondrites (or solar) but for unity of presentation they are plotted similarly. From Ar to Xe the C1 noble gas pattern is identical to 'Q' (see text); in Ne and He the implanted component is dominant. Expanded from Hunten (1993).

Swindle & Podosek 1988). Together with the bulk terrestrial I content (between 4 and 10 ppb; see Muramatsu & Wedepohl 1998) this permits estimation of the amount of ¹²⁹Xe that should exist on Earth (or, in a closed-system atmosphere). The amount observed is, however, only between 1 and 3% of what it should be from these *a priori* data, documenting a great loss of highly volatile elements. This loss process could not have ceased earlier than *c.* 50 Ma after the formation of the Solar System, or further ¹²⁹I decay would have replenished the Earth with radiogenic ¹²⁹Xe. From ¹²⁹Xe alone there is no maximum constraint on that time interval. This is provided by fissionogenic contributions, notably ¹³⁶Xe, from both ²³⁸U and extinct ¹⁴⁴Pu (half-life 80 Ma) (see Azbel & Tolstikhin 1993; Tolstikhin *et al.* 2006). In spite of uncertainties, particularly regarding the initial amount of ¹³⁶Xe on Earth, it can be reliably estimated that at least 40% of the fissionogenic ¹³⁶Xe(Pu) produced in the Earth is still in the atmosphere. Thus major losses occurred before all ¹⁴⁴Pu was decayed. From the combined ¹²⁹Xe(I) and ¹³⁶Xe(Pu) systematics it follows that the last major loss of Xe (and therefore of bulk atmosphere) from Earth occurred no later than 200 Ma after the formation of the Solar System, a much longer time scale than that obtained from the Hf–W system (Fig. 4) but within the Hadean Eon.

We now leave the data pertaining to the Hadean Eon and Earth

accretion, and in the following section turn to an accretion model and its predicted consequences.

Hierarchical accretion and the Giant Impact

Brief review, physical models and time scales

The standard model of planetary formation (so called because there is now general consensus about this model) originated at the Vernadsky Institute in Moscow (e.g. Vityazev & Majeveva 1977; Safronov & Vityazev 1986) and has been further developed with numerical simulations by Wetherill (1990), Weidenschilling (2000), Chambers & Wetherill (2001), and others (for a review, see Chambers 2004). It differs from earlier solid-matter accretion models, for example, that of Urey (1962), according to which the planets were accreted directly from dust, in that it involves three stages, each plausible within its own, separate physical parameters. These are: (1) orderly growth (the formation of thousands of planetesimals, all approximately the same size); (2) runaway growth (promoting the growth of large ones at the cost of small ones within one narrow circular-orbit 'feeding zone'); (3) planetary accretion (via excentric orbits that cross over different feeding zones). The term 'hierarchical' captures the nature of the model with its sequence of accretion processes, involving collisions of ever larger bodies.

The solar nebula formed as a disc-shaped cloud consisting of gas and dust. The dust in the nebula is not synonymous with condensate, but may have been partly presolar: even in the terrestrial feeding zone this cannot be excluded (see Fig. 5 and above discussion on the isotope ratios of major volatiles). It was already recognized half a century ago (Wood 1962) that chondrules, spherules formed from droplets of silicate melt and the building blocks of chondritic meteorites, are not a direct condensate from hot nebular gas, but products of some secondary heating process. At the start of the hierarchical accretion process, chondrules and their fragments are a component of the dust, which is therefore heterogeneous in origin and character.

The nebula was stabilized against accreting into the nascent Sun mainly by its orbital motion, and to a much smaller extent by a gas pressure gradient towards the Sun, a direct consequence of the Sun's heat. This dust–gas mixture controlled the first stages of accretion, as it caused differential velocities between particles. The larger a particle, the less it was supported by the pressure gradient of the gas, and the more it had to approach a Kepler orbit: in real terms, fall towards a lower orbit where it then moved faster than the ambient gas and small particles. Such differential speeds led to accretion by gathering. As long as gravitational attraction is insignificant compared with the relative velocities in controlling the gathering, the relative rate of growth of a particle is not determined by its mass. Modelling of this 'orderly growth' predicts metre-sized bodies to have become dominant within 2000 years, with some kilometre-sized ones already in existence (Weidenschilling 2000). These have their own significant gravity fields, and this leads to the process of 'runaway growth' in which largest bodies within a limited orbital zone gather up all the mass remaining in orbit. Tens of bodies with mass around 3×10^{26} g could have formed in this way in the terrestrial planet region in the first million years. The third stage, 'planetary accretion', the formation of bodies up to the mass of the Earth (6×10^{27} g) or larger, requires the disturbance of orbits and large collisions. Orbits are disturbed by gravitational interaction as well as by collisions, and modelling predicts that between *c.* 20 and *c.* 100 Ma is required for this process to

lead to a long-lasting configuration of a few planets in stable, non-crossing orbits (Wetherill 1990; Chambers 2004).

For the third stage, this model thus predicts that giant collisions of nascent planets should occur as stochastic events. Strong evidence for this lies in the very different axes and speeds of rotation of the planets. Depending on the masses, energy and angle of impact, such collisions could lead to fragmentation and dispersion of the fragments, or to the colliding bodies merging into one. The latter is much more likely. In the early part of the collision stage, as bodies are relatively small and escape velocities are low, much of the collision energy appears to be spent in mechanical disaggregation, not acceleration, so that not much mass escapes (Nolan *et al.* 2001). As the mass of a growing planet increases, material ejected by a collision mainly falls back onto it (e.g. Benz & Cameron 1990). One example of a late-stage collision, expected in the framework of hierarchical accretion, is the Giant Impact, an excentric collision between the >70% formed Earth and an approximately Mars-sized other planet, that is generally considered to have led to the formation of the Earth's Moon (e.g. Benz *et al.* 1989; Canup & Asphaug 2001; Canup 2004). Apart from generating the Moon, this event profoundly affected the later history of the Earth, as discussed further below.

The time scales that result from modelling the stages of the hierarchical process agree well with observations. Calcium–aluminium inclusions (the ‘hottest’ objects in the Solar System), chondrules and most iron meteorites give radiometric ages within *c.* 1 Ma of each other by various methods (Lee & Halliday 2000; Lugmair & Shukolyukov 2001; Amelin *et al.* 2002; Yin *et al.* 2002), in accord with the short orderly and runaway growth timing. Differentiation of the parent body of angrite achondrites occurred some 14 Ma later (Lugmair & Galer 1992), recording collision heating, and shock metamorphism in chondrites (e.g. Brazzale *et al.* 1999; Goepel *et al.* 1994) covers a similarly long time scale. Lastly, the *c.* 30 Ma *prima facie* Hf–W time interval for average silicate Earth formation (Fig. 4) is well within the planet formation time scale given by numerical models (Wetherill 1990; Chambers & Wetherill 2001).

Consequences for siderophile elements and the meaning of the Hf–W time scale

Hierarchical accretion, involving collisions of ever larger planetary bodies over a long period of time, necessarily leads to extensive impact-induced melting within growing planets, and thus gravitational metal segregation and core formation. How much equilibration of trace elements between metal and silicate melts and solids occurs in these processes depends on drop or grain sizes and the duration of the coexistence of the phases. These are related, and it is clear that equilibration is not favoured in collisions of bodies that already have cores: metal and silicate domains are expected to be large. Therefore, first, surface to volume ratios are small, limiting equilibration, and, second, segregation by gravity will be rapid. This has been shown convincingly in Giant Impact simulations (e.g. Canup & Asphaug 2001; Canup 2004), where cores are seen to merge relatively rapidly. On the other hand, equilibration is expected to occur if undifferentiated, chondritic matter with micron-scale metal grains is involved in a collision that causes melting.

Thus, in hierarchical accretion, planetary differentiation and core formation can be seen as the result of many parallel and successive catastrophic events in different planetesimals, involving merging of pre-existing metal cores and silicate mantles as well as adding to these from undifferentiated matter, or generat-

ing new ones. At early stages, with relatively low gravity, no high pressure is expected. At late stages, the merging of already formed cores should have dominated. Therefore high-pressure magma ocean core formation as envisaged by Richter *et al.* (1997), Richter (2003) and Rubie *et al.* (2003) is not predicted by the hierarchical scenario. On the other hand, the continuous core formation models of Azbel *et al.* (1993) and Kramers (1998) could describe a process collectively occurring on many planetesimals equally well as on a single planet. Further, hierarchical accretion provides a natural explanation for the low abundance of the slightly and moderately siderophile elements Mn, V, Cr and W in the silicate Earth, compared with what is expected from their measured silicate–metal partition coefficients (Fig. 3). The partitioning of these elements into metal is highly redox dependent; if the earliest metal segregation occurred in redox equilibrium with the solar nebula, these elements would have been considerably more siderophile than shown in experiments involving terrestrial silicate mantle-type material. Thus the depletion in these elements could have been inherited from early stages of the accretion process. The process is mimicked by continuous core formation with increasing fO_2 , which yields reasonable fits for these element concentrations on Earth (Fig. 3).

It has been argued (Jacobsen 2005) that the 30 Ma Hf/W time scale for the silicate Earth (Fig. 4) gives the time of the Giant Impact. This is incorrect unless that event involved a rehomogenization of the core and mantle of the whole Earth, which is not shown by models (see Canup 2004). A hierarchical accretion scenario with a continuous core formation model allows a different interpretation. This involved mixing as well as fractionation. If W partitioning into metal was mainly an early stage, low fO_2 process, then the silicate mantles of early planetary embryos had low W contents, and rapidly developed high $^{182}W/^{183}W$ ratios. However, the terrestrial W isotope signature is heavily influenced by undifferentiated ‘chondritic’ matter being added to the Earth or its predecessors at later stages of accretion, when W was no longer siderophile. This matter would have a high W content and low $^{182}W/^{183}W$, and thus would have lowered the $^{182}W/^{183}W$ ratio of what was to become the bulk silicate Earth. The 30 Ma time scale (Fig. 4) gives the interval between Solar System formation and the time when the silicate matter that is now on Earth (but was then probably still on different precursors) acquired on average its present Hf/W ratio by these different processes. It therefore does not date any event, but is intermediate between the shorter time scale for collective core formation and the longer one for Earth accretion. Shorter time scales for core formation derived from forward modelling of Hf–W systematics (e.g. 11 Ma; Yin *et al.* 2002), are not at all in conflict with a longer time scale for the planetary accretion process itself.

Consequences for the atmo-hydrosphere

The timing of the hierarchical accretion model provides only a narrow window of opportunity for a growing planet to obtain an atmosphere by attracting solar nebula gas. The time scale for dispersal of solar nebula gas in the zone of the terrestrial planets has been reviewed by Podosek & Cassen (1994) and estimated to be up to several million years but <10 Ma. It was thus most probably present in this zone during orderly and runaway growth, but is unlikely to have existed at the time when large planetary bodies formed. Nebular gas therefore never coexisted with large planets and their massive gravitational attraction, at least not in the terrestrial planets zone. In the atmospheres of planetary

embryos, gravitationally captured nebular gas could have formed an important component, but whether this could have been inherited by larger planets depends on atmosphere retention during and following collisions. In contrast, volatiles in chondrite-type matter, such as Q-gases, or cometary contributions, could be delivered to a planet at any time during its accretion and history, up to the present. In the case of major volatiles, the chondrite component must pass through a planetary interior and processes of metamorphism, melting and degassing, before it can form part of the atmo-hydrosphere as water, CO₂ and N₂.

The survival to the full planetary stage of nebular atmospheres captured by planetary embryos in the first 10 Ma of Solar System history depends on gas loss associated with collisions, an interplay of kinetic energy from various sources and the escape velocity, $v_{\text{esc}} = \sqrt{2GM/r}$. Here G is the gravitational constant, M the mass of the planetary body, and r is the radius from which upward movement is unimpeded (the exobase). The square-root proportionality of v_{esc} to M means that atmosphere retention is not the privilege of massive planets.

Two studied processes of atmosphere loss could be directly connected to the shock of a collision. First, a shock wave directly from the impact site itself could propel a plume of vapour with a velocity greater than v_{esc} (impact-side blowoff) and second, a seismic shock could accelerate the antipodal atmosphere upwards, also leading to escape (antipodal blowoff). A third process, thermal escape, does not have to be related to a collision, but occurs in any situation where the thermal velocity of molecules in the exobase layer of the atmosphere can exceed v_{esc} .

Impact-side blowoff appeared, from early modelling, to be a highly effective atmosphere loss mechanism ('hemispheric blow-off', Melosh & Vickery 1989). This has not been confirmed by later work (Newman *et al.* 1999; Pierazzo & Melosh 1999). Rather than expanding sideways and blowing away a wide swathe of atmosphere, the superheated impact plume is seen to be deflected upwards in a kind of chimney, and entrain only a small atmospheric section, albeit at very high velocity. Likewise, antipodal blowoff (Chen & Ahrens 1997) may be much less significant than first thought. Genda & Abe (2003) found that, in the Moon-forming Giant Impact, only about 26% of the atmosphere would be lost by this process. They also noted that the model estimates are maxima, as irregularities such as turbulence and rock fracturing are not taken into account. Scaling in the models of Genda & Abe (2003) is independent of planetary size. However, they found that in collisions of same-size planetary bodies a larger portion, up to 65%, of the combined atmosphere may be lost. In small planetesimals of *c.* 10 km radius and possibly up to the size of Vesta, internal fracturing and disruption by impacts destroys elasticity (Nolan *et al.* 2001). Therefore antipodal atmosphere blowoff would not occur from such small bodies.

Thermal escape or 'Jeans escape' occurs if the temperature at the exobase is sufficiently high for the upward velocity of molecules as a result of their kinetic energy to occasionally exceed v_{esc} . As $T \propto E_{\text{kin}} = \frac{1}{2}mv^2$, this process is strongly mass dependent. Escape rates are proportional to $e^{(-GMm/kT)}$, where G is the gravitational constant, M and m are the masses of the planet and the molecule, k is Boltzmann's constant, and T and r are the temperature and radius of the exobase (see Hunten 1993). The lightest molecules, H₂ and He, can escape from the terrestrial atmosphere at today's exobase temperature.

If sufficiently intense, such a light molecule flux can drag heavier molecules up to v_{esc} by repeated collisions, and this process is known as hydrodynamic escape. Jeans escape and

hydrodynamic escape are thus related. A governing parameter in the latter is ϕ , the ratio of factors favouring escape to those inhibiting it (equation (22) of Zahnle & Kasting 1986): $\Phi = \phi_s r^2 kT / GMmb_s$. Here ϕ_s is the flux of the dragging light gas s , and b_s is the binary diffusion coefficient of the molecule with mass m in medium s . It can be seen that stronger outflow occurs at lower gravity, higher temperature of the exosphere, or a stronger H₂ flux. The escape rate is proportional to $1/m$, hence mass fractionation is much smaller than in the case of Jeans escape.

Thus, significant portions of solar nebular atmospheres captured by planetesimals in the first few million years of Solar System could well be retained throughout the hierarchical accretion process. The real danger of atmosphere loss lies in giant impacts with long, hot aftermaths, causing Jeans and hydrodynamic escape. Benz & Cameron (1990) have found that, after the Giant Impact that formed the Moon, the re-accretion of matter onto the Earth caused surface and upper atmosphere temperatures as high as 16 000 K, thus, an atmosphere of silicate vapour mixed with gases. The top of this atmosphere continued to be heated for thousands of years by continuous accretion from a disc, and thus no strong convective cooling is expected to have occurred during this time. Given the high temperature, it is expected that all light gases would be lost by thermal escape. Even heavy gases (xenon being the most extreme example) would probably be mainly lost in this event. The time scale given by Xe isotopes, discussed above, does not contradict an association of major atmosphere loss with the Giant Impact.

After accretion of the disc ended, a convective cooling regime would set in, silicate vapour would rapidly condense and fall to Earth, and only a thin atmosphere, if any, would be left. Subsequently, the atmosphere could have been replenished by the accretion of carbonaceous chondritic matter. The most successful and detailed models of the Giant Impact and Moon formation (Canup & Asphaug 2001; Canup 2004) leave room for up to 5% further Earth accretion after the event. Modelling has shown that gravitational disturbances by the giant planets probably caused the outer asteroid belt, home to most asteroids of carbonaceous chondritic character, to lose the bulk of its mass towards the end of planetary formation, and it is thus likely that most bodies striking the Earth at this late stage would have originated in this zone (Morbidelli *et al.* 2000; Chambers & Wetherill 2001). The content of H, C and N in C1 chondrites is more than 200 times higher than that of the Earth (Fig. 6), and a C1-type accretion amounting to just 0.5% of the Earth's mass would therefore provide more than the Earth's budget of these major volatiles. For a mixture of different types of carbonaceous chondrite matter, 1–2% of such late accretion would suffice. This would, however, deliver insufficient light noble gases, as illustrated by the atomic N/³⁶Ar ratios (5×10^4 for the Earth and 2×10^5 for carbonaceous chondrites; see above). Later degassing of a small remnant of trapped gases from the mantle, or an implanted solar wind component in the accreting material, or both, could have supplied the bulk of terrestrial light noble gases. Subsequent preferential loss of light gases by hydrodynamic escape could have modified the abundance patterns of both major and noble gases (Zahnle & Kasting 1986; Kramers 2003).

This scenario readily predicts the dual nature of the Earth's atmosphere as outlined above, and it could also provide an explanation why heavy noble gases are so much more abundant in the atmosphere of Venus than on Earth, and have a solar relative abundance pattern (Fig. 6). If Venus did not suffer a Giant Impact of the same magnitude as the Earth, it could have retained much of its primordial solar atmosphere. Subsequent

hydrodynamic escape (driven by solar-type hydrogen) would then have depleted the light gases, including water, in particular. In the light of that possible scenario it could be speculated that the Giant Impact could have ultimately saved the Earth from the fate of Venus

Consequences: silicate Earth physiology

A Giant Impact of a Mars-sized body would in the first instance utterly destroy the physiognomy of one terrestrial hemisphere (Canup & Asphaug 2001; Canup 2004). More long-term melting of, possibly, the whole mantle would occur as a consequence of the core of the impactor sinking through the Earth's mantle, its gravitational potential energy being converted to heat. Then the mantle would be heated from below by this core-accretion process, and initially, from the top, by the disc accretion sketched above. The modelling of Benz & Cameron (1990) predicts superliquidus temperatures in excess of 6000 K for the whole mantle, with the upper mantle having temperatures of 10 000 K or above. As in the atmosphere, convection would initially not take place under these conditions.

Arguments against there ever having been a very deep (up to whole mantle) silicate magma ocean on Earth have centred on the trace element differentiation that would have resulted from fractional crystallization within it, particularly with respect to Sm–Nd and Lu–Hf systematics (Kato *et al.* 1988). Liquidus silicate phases at high pressure would have a perovskite-type structure and would strongly fractionate REE and high field strength elements, including an extreme fractionation of the Lu/Hf ratio that would have left a trace in the form of great $^{176}\text{Hf}/^{177}\text{Hf}$ heterogeneities in the mantle. There is no evidence for this. However, such arguments do not preclude a sequence of events as predicted by the modelling of Benz & Cameron (1990). The fates of the earliest atmosphere and the mantle are intimately connected in the post-Giant Impact era. At first the magma ocean, blanketed by a superheated atmosphere, would be wholly superliquidus and thus no fractionation would occur. As disc accretion ceased and the surface cooled after the loss of the thick atmosphere, vigorous magma ocean convection would rapidly set in. Tonks & Melosh (1990) have argued that this convection, although cooling the mantle, would actually prevent chemical fractionation within it. They estimated the Rayleigh number of a deep terrestrial magma ocean, cooled at the top, to be in excess of 10^{24} , so that highly turbulent convection would be expected. They showed that on Earth (unlike the Moon with its lower gravity) a melt descending along an adiabat in deep magma convection would enter the solidus–liquidus interval at some depth, but subsequent convective upwelling would be so vigorous that no crystal settling could result. High-pressure phases formed at great depth would be entrained in the convection and redissolve in the melt at shallower depth. This concept may probably be extended to the lowermost mantle, as adiabats are consistently steeper than the liquidus and solidus, down to the core–mantle boundary (Boehler 2000). As the convecting mantle cooled, it would freeze from the bottom up as dictated by solidus temperatures. In this process the growing crystals form a framework that ‘locks up’ the solid–melt mixture close to the solidus, when the melt fraction is about 30%, and therefore little or no fractionation occurs. Thus, complete mantle melting could have occurred leaving few, if any, geochemical traces at all. Meanwhile, it could provide a neat explanation for the initial geochemical and isotopic homogeneity of the Earth's mantle.

A working hypothesis for the Hadean Eon

Armed with the predictions from modelling the consequences of hierarchical accretion, we can address the observations on the Hadean Eon described above. These include a separate, long-lived reservoir at the surface, as required by Pb isotopes of the earliest supracrustal rocks, ^{142}Nd anomalies, and detrital zircon ages and Hf data, as well as the possible formation at depth of a separate long-lived reservoir that ‘leaks’ solar-type noble gases. In its lifetime, a mantle-deep magma ocean would prohibit all these features, but exploring its aftermath may be less contradictory.

As the mantle adiabat of a deep magma ocean is steeper than its liquidus and solidus curves in the P – T diagram (see Fig. 7a), it is inevitable that it will freeze from the bottom up. As a result of this, the mantle will have a solidus-determined geotherm after freezing. This is much less steep than the solid-mantle adiabatic geotherm. Regarded on a short time scale, the mantle represents a system in which internal heat generation is unimportant and in such a case the deviation of the temperature gradient from the adiabatic one, $\Delta T = \Delta T_{\text{system}} - \Delta T_{\text{adiabat}}$, is a linear factor in the Rayleigh number. In a solidus-determined mantle geotherm, using an adiabatic gradient of 0.3 K km^{-1} and a lowest-mantle solidus temperature of 4300 K (Boehler 2000) $\Delta T \approx 2000 \text{ K}$, this (and therefore the Rayleigh number) is at least an order of magnitude higher than today's value. The solidus-determined mantle would therefore be gravitationally unstable, and mantle overturning would be expected (Boss & Sacks 1984).

It is suggested that the consequences of this would be twofold. First, widespread decompression remelting would occur within the upper mantle; the melt would carry away excess heat and form a huge mafic–ultramafic crust. Second, the overturn would result in a curious thermal mantle structure, with uppermost mantle temperatures close to the peridotite solidus (i.e. up to 2000 K at 100 km depth) and a relatively cool lower mantle, as sketched in Figure 7b. Convection in the upper part of the mantle could continue, with further decompression melting, to lead to a gravitationally stable mantle structure as sketched qualitatively in Figure 7b. The lowest mantle would, however, still be sub-adiabatic, although at higher temperatures than today. There would then be no significant heat-driven mantle dynamics and associated melt production, until the top had cooled, and/or radioactivity and latent heat from core processes would have raised lower mantle temperatures sufficiently to restart some form of mantle convection. Apart from disturbance by further impacts, the mantle would be quiet.

In principle, the mantle overturn might therefore be able to produce a vast mafic crust above a mantle that was stable and non-convecting for some time. The time scale for stability is, of course, of interest, but there are many variables, and short of detailed modelling only rough estimates can be made, concerning the cooling rate of the uppermost mantle and the heating rate of the lower mantle.

The protocrust, enriched in heat-producing elements, would provide an outer blanket for which variable geotherms have been estimated by Kamber *et al.* (2005). If the peridotite mantle below this initially had a geotherm close to the solidus as shown in Figure 7b, a large part of the temperature gradient in the mantle would be located in the uppermost 200 km, and this would be the layer in which convection would be most likely to set in. For a non-internally heated layer the Rayleigh number is proportional to the cube of its depth. For the uppermost 200 km, with a ΔT value of *c.* 600 K, the Rayleigh number is of the order of 10^2 – 10^3 , which means that convection is likely to be extremely

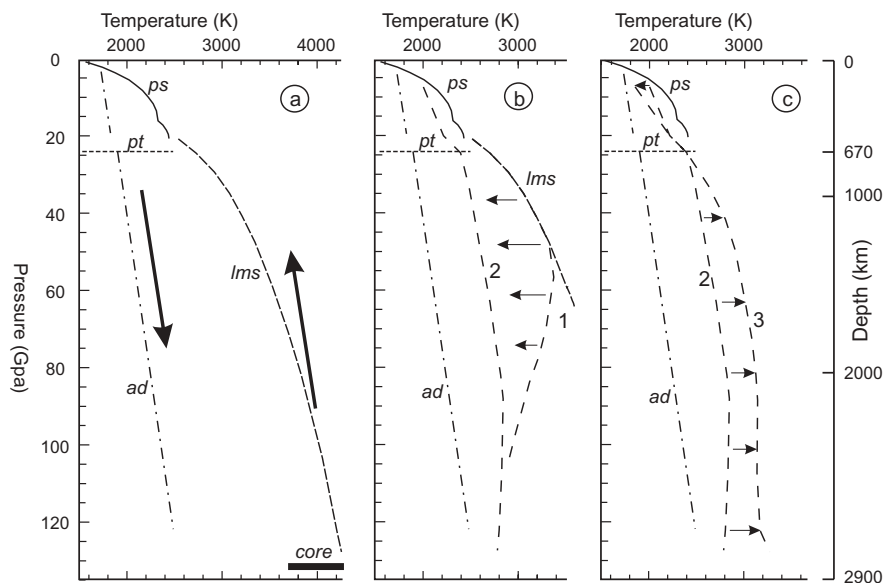


Fig. 7. P - T diagrams to 135 GPa, the pressure at the core-mantle boundary, sketching in a qualitative way the thermal scenario suggested for the Hadean mantle. Frame adapted from Boehler (2000). Dot-dash line *ad*, present-day mantle adiabat for reference; *pt*, phase transitions at 670 km (at present 'lower-upper mantle boundary'); *ps*, peridotite solidus; *lms*, lower mantle solidus upper limit from Boehler (2000); *core*, core temperature range at core-mantle boundary. (a) Situation following the rapid freezing of a mantle-depth magma chamber after the Giant Impact. The mantle geotherm is considered to be described by the solidus curves and is superadiabatic. The resulting overturn is indicated by the arrows. (b) Relatively rapid processes after overturn. Geotherms are shown as dashed lines. (1) Lower mantle is subadiabatic and thermal bulge in mid-mantle is limited by solidi. Convection could cool this region (arrows) to adiabatic geotherm (2). (c) Slow processes after this convection ceases, shown by arrows: conductive cooling of upper mantle and radioactive heating of the lower mantle with core contribution to heating in lowermost mantle (curve 3). It should be noted that the lowermost mantle stays subadiabatic.

sluggish in this layer. The rate of a thermal adjustment by conduction to a new situation is a function of the thermal diffusivity κ and the heat capacity of the rock, as well as the length scale. For silicate rocks, $\kappa \approx 10^{-6} \text{ m}^2 \text{ s}^{-1}$. The time scale t (seconds) for the decay of a thermal anomaly of length scale l (metres) is approximately $t \approx l^2 / \kappa$. The length scale of the 'bump' centring on 200 km depth in Figure 7c is *c.* 150 km, and this corresponds to a smoothing time scale of *c.* 700 Ma.

After the overturn, the lower mantle temperature would initially have been predicted from the low-pressure dry peridotite solidus and adiabatic heating to be *c.* 2800 K (Fig. 7b and c). Heating of the lower mantle by radioactivity would occur as sketched in Figure 7c. The rate of this can be estimated. From chondrite data, present-day Th, U and K concentrations of the bulk silicate Earth are derived (96 ppb Th, 18.3 ppb U, 250 ppm K; see Kramers & Tolstikhin 1997). At 4.5 Ga, the average heat production of the BSE would then be $2.3 \times 10^{-14} \text{ W g}^{-1}$, roughly 4.5 times the present value (see equation (1) of Kramers *et al.* 2001). The heat capacity of silicate rocks is *c.* $0.3 \text{ cal g}^{-1} \text{ K}^{-1}$ (*c.* $1.25 \text{ J g}^{-1} \text{ K}^{-1}$). At 4.5 Ga, primitive mantle material would heat itself at the rate of *c.* 0.6 K Ma^{-1} and this rate decreased rapidly during the Hadean, as ^{235}U (with half-life 0.7 Ga) is initially the main contributor. It would require about 500 Ma to heat the mantle by 200 K. Heating by the core would contribute in the lowermost mantle. As a result of the cooling at the top and this heating, a stronger thermal gradient in the uppermost mantle would first stimulate convection there, whereas the lower half of the mantle would still remain subadiabatic as heating was uniform throughout it. Convective cooling in the upper part of the mantle would then displace the gradient downward, ultimately leading to whole mantle convection. It should be noted that after the quiescent Hadean period, convec-

tion would resume at a mid-mantle temperature at least 400 K higher than today. This is in keeping with considerations from Archaean komatiites (Campbell & Griffiths 1992).

The time scale estimates, although crude, appear to indicate that, after overturn, the mantle could have remained quiescent for approximately the duration of the Hadean Eon. Obviously, detailed modelling would be required to test the concept further. This would be worth while, as the hypothesis resolves an apparent paradox: it predicts a massive, mafic crust that would be very long-lived during the Hadean, but could nevertheless wholly disappear afterwards. Invoking such a crust helps to explain the baffling Hadean features listed at the start of this section.

This scenario also allows some tentative predictions about the climate during the Hadean Eon. If, as argued above, the major components of our present atmosphere essentially accumulated via post-Giant Impact accretion, then after the Impact and its aftermath the Earth's surface, under a 30% weaker Sun and with at most a very thin atmosphere, would first have become extremely cold (Kasting & Ackerman 1986). Release of H, C and N from impacted chondritic matter into the atmosphere relies on high-temperature processes: metamorphism, melting or evaporation. For large bodies these can result from the impact itself, but in the case of small impactors the volatiles could remain locked up in solids until the temperature was raised by a large impact (stochastic), burial (slow) or tectonics. If the Hadean mantle was stagnant, the wait for tectonics could be long and the atmosphere would be built up more slowly than the rate of late accretion itself.

It would contain carbon mainly as CO , CO_2 and (non-biogenic) CH_4 , of which the last in particular is a strong greenhouse gas and could have been present at a volume fraction

$>10^{-5}$ in an early, anoxic atmosphere (Kasting *et al.* 1983). As atmosphere and surface temperatures would rise, oxidation caused by photolysis of H_2O and escape of H_2 would lead to a dominance of CO_2 . Even without CH_4 , the greenhouse effect from 1 bar of CO_2 would suffice to prevent the Earth from freezing at a solar luminosity 30% lower than the present one (Kasting & Ackerman 1986). In comparison, the amount of carbon at present in sedimentary rocks, if put back into the atmosphere, would amount to at least 30 bar as CO_2 . An important question is how efficiently CO_2 could have been removed from the atmosphere.

The main abiotic process for this is the Urey cycle, operating via silicate weathering on land and transport of bicarbonate to the sea, followed by carbonate precipitation. On a Hadean Earth with an inactive mantle, the required silicates for weathering could be supplied by newly accreted matter or impact ejecta. The mechanism includes a thermostat, as it requires a water cycle with both liquid oceans and rain. As an alternative without a thermostat, Sleep & Zahnle (2001) have proposed the carbonation of oceanic basalt and subsequent recycling of carbonate into the mantle by subduction as an efficient mechanism to reduce atmospheric CO_2 in the Hadean. This could, however, not operate with a quiescent mantle. The Urey cycle is therefore required. This suggests that, after the buildup of an atmosphere, the Hadean climate would have become temperate or even hot.

Concluding remarks

The highly diverse datasets reviewed in this paper, traces from Archaean rocks, siderophile and volatile element data, have one thing in common: they can be explained by aspects of the hierarchical accretion model and its possible or putative consequences. Via this powerful model, internal and surface processes are related and predictions can be made that can be tested by detailed modelling of, for instance, the thermal behaviour of the mantle after freezing of a magma ocean.

It is admitted that this paper has in part acquired the character of a planetary just-so story, possibly lacking scientific rigour. An important aspect of the hierarchical model is, however, that its late stages involve stochastic events that have very important consequences for the planets involved. When chance events can have such diverse outcomes, reverse modelling becomes impractical. As seen in the case of numerical simulations of planetary formation and the Giant Impact, diverse lines of evidence that qualitatively converge can point the way to forward modelling that reproduces observations. In a sense, this tradition is 200 years old and, following it, we can get closer to understanding why the Earth evolved in the way it did.

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