Earth formation: Combining physical models with isotopic and elemental constraints

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Models of Earth formation have undergone substantial refinement in recent years, although their basic characteristics differ little from the “classic” views of Safronov and Wetherill. In these models, Earth accumulation can be mostly completed in 10 Ma but may extend out over tens of millions of years and the source material for Earth is derived from a fairly wide range of circumsolar distances of condensation or first accumulation. Both of these conclusions may still undergo revision as dynamicists seek a better understanding of the role of small bodies and dissipation in the formation process. But it seems unavoidable that giant impacts occurred and these events are likely to set the stage for lunar formation and the initial state of Earth, including much of the physics that governs core formation, initial core temperature, siderophile abundances in the mantle, possible differentiation of the mantle into a layered structure and formation of Earth’s initial atmosphere and hydrosphere. I will focus here on some recent efforts to understand Hf-W and what this may tell us about core formation (both timing and process). I will also talk about oxygen isotope puzzle: Why is Earth and Moon so similar. I will argue that the Hf-W story does not require early (~10 Ma) earth formation because it tells core formation time and this process may have taken place in large part in precursor bodies rather than Earth itself. I will also argue that the oxygen isotopic similarity may be an out come of a giant impact scenario in which the lunar-forming disk equilibrates isotopes with Earth on a timescale ~100 years, even though the Mars-mass projectile might have had a Mars-like isotopic character.

The oxygen isotope composition of the Sun

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The oxygen isotope composition of the Sun is one of the outstanding issues in cosmochemistry. Refractory inclusions show up to 6% enrichment in $^{16}$O relative to terrestrial which was originally ascribed to a nucleosynthetic input to the solar system. With the discovery of non-linear fractionation in the Earth’s atmosphere it appears more likely that a chemical mechanism is responsible. Clayton (2002) has proposed that photochemical predissociation and self shielding lead to preferential enrichment of $^{16}$O in CO gas, and $^{17}$O, $^{18}$O-rich water ice. Recently Yurimoto and Kuramoto (2004) have proposed that the $^{16}$O anomaly is inherited from the molecular cloud precursor. In both of these models, the Sun will have a composition that is $^{16}$O-rich, in this case, at least as $^{16}$O-rich as refractory inclusions.

We have measured the oxygen isotopic composition of solar wind in lunar metal grains (Ireland et al., 2004). The oxygen implanted in the grains is depleted in $^{16}$O by $54 \pm 5$‰ relative to terrestrial oxygen. Rather than having the $^{16}$O-enriched composition of refractory inclusions, the Sun is depleted in $^{16}$O, and does not match any prior prediction.

If the Sun is depleted in $^{16}$O, it cannot be reconciled with a solar nebula predissociation model, but can be accommodated in a model of molecular cloud inheritance. Specifically, removal or partial removal of the C$^{16}$O gas in the star-forming region will move the nebula to a heavier oxygen isotope composition.

If molecular cloud inheritance is the source of the oxygen isotopic systematics observed, it has profound implications for our view of the early solar system. Thermal processing in the early solar system simply unmixes the refractory $^{16}$O-rich components from the molecular cloud dust. Refractory inclusions cannot be direct solar condensates, rather they must be predominantly remelted residues of dust from the molecular cloud, potentially with recondensation of evaporated material. Fractionation of volatile elements may take place in the star-forming region leading to abundance differences between dust in the accretion disk and in the Sun.

References
CO self-shielding and oxygen isotopes in the solar nebula

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The recent suggestion\(^1\) by Clayton that CO photodissociation is the source of the oxygen isotope anomaly measured in meteorites\(^2\) offers an opportunity to relate a longstanding and fundamental problem in meteoritics to the far-ultraviolet (FUV) environment in which the solar nebula formed. Presently, three locations for CO photodissociation are being considered in models: the X-point region of the solar nebula\(^1\), the surface of the nebula\(^3\), and the parent cloud from which the nebula was formed\(^4\). The surface disk and parent cloud models require a greatly enhanced FUV radiation field, \(\sim 1000\) times the local interstellar medium (ISM) field, consistent with solar system formation in a star-forming region.

A key test of CO photodissociation as the source of anomalous oxygen isotopes in CAIs is that nebular H\(_2\)O (produced from product oxygen atoms) has the \(\delta^{17}\)O/\(\delta^{18}\)O value measured in CAIs. Figure 1 demonstrates that CO photodissociation in the presence of abundant H\(_2\) produces nebular H\(_2\)O with \(\delta^{17}\)O/\(\delta^{18}\)O \(\sim 1.0\) (solid curve), similar to measured values, whereas photodissociation of pure CO produces a ratio \(\sim 1.1\) (dotted curve). This suggests that CO self-shielding in an H\(_2\)-rich environment is in fact a viable mechanism for explaining oxygen isotopes in CAIs.

References

\(^2\) Clayton R.N. et al. (1973), Science 182, 485.

Early solar system timescales

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From our present perspective, in many respects it is useful to think of the formation of the solar system as an event, a singular occurrence that happened a long time ago. The current best estimate for the absolute age of that event is usually taken to be 4.567 Ga [1], but in fact the absolute age of the formation of the solar system has been known for more than a generation with sufficient precision and robustness to satisfy any legitimate curiosity.

There is greater interest in viewing the formation of the solar system as a process, a series of events linked by cause and effect, extending over some finite time. The events of interest are chiefly dynamical, but dynamical theory is not yet able to predict a robust complete history. Appeal must therefore be made to an empirical history based on geochemical events caused by the dynamic processes, datable by geochronological techniques based on radioactive decay.

For quite some time, the class of refractory-element-rich objects called CAIs has been esteemed the first solid material to have formed in the solar system (e.g. [2]), on the basis of chemical characteristics, stable isotope anomalies that suggest primitiveness, the initial presence of some short-lived (now extinct) radionuclides, and of course on the absence of greater known ages than for any other objects. Typically, the “age of the solar system” means the isotopic closure age of CAIs.

There are two other kinds of geochemical events often thought to date solar nebula processes – the formation of chondrules, and the chemical differentiation by which planetary materials were extracted from a source of cosmic composition. Chondrules (like CAIs) were once thought to have formed in the very earliest stages of nebular history, but are now thought to have formed later and over an extended timescale, a few Ma after CAIs. The chemical compositions of the differentiated meteorite parent bodies are also thought to have been formed a few to several Ma after CAIs.

Recent results [3] for the $^{182}$Hf-$^{182}$W system are reported to indicate chemical events a few Ma before formation of CAIs. If this conclusion is substantiated, much of the current picture of what happened in the early solar system will have to be rethought.

References

U-Pb dating of meteoritic perovskite

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Perovskite (CaTiO3) is a minor but important oxide in Ca-Al-rich inclusions (CAIs) and is a particularly useful mineral for precise geochronology as it can contain significant concentrations of U and Th. Ireland et al. (1990) investigated U-Pb systematics of perovskite from Allende and Murchison CAIs using SHRIMP and obtained a 207Pb/206Pb age of 4565 ± 34 Ma for Allende. Here we report new TIMS and ion-probe data with significantly improved precision on perovskite grains from an Allende CAI.

The CAI, referred to as 134-1, is a large elongate (1.8 cm x 0.9 cm) Compact Type-A inclusion composed of melilite with minor amounts of spinel and perovskite. It also has a very thick (>1 mm) multi-layered rim sequence surrounding the coarse grained interior. Perovskite occurs as small (~<50 µm) rounded grains scattered throughout, but is more abundant towards the core. It occurs as both interstitial grains and as inclusions in melilite.

Nine (~1µg) fractions of perovskite were separated and analysed via TIMS. Fractions were washed in acid to reduce surface contamination. The residues yielded low 206Pb/204Pb ratios between 43.5 to 167.5. Seven points define a Pb-Pb isochron indicating a 207Pb/206Pb age of 4568.3 ± 2.4 Ma (MSWD = 1.3). This age is consistent with other studies on Allende CAIs. Two analysis are lower than the line space, which minimizes noise-induced correlations between variables. We then assumed that the sample is a mixture of radiogenic (*) and common lead and used the intercept of the residue-leachate array in the 207Pb/206Pb-204Pb/206Pb plot to estimate the 207Pb/206Pb ratios. Full error propagation inclusive of blank contribution (0.01-0.9% of the total Pb contents) required the development of a specific correction scheme. We find that whole-rocks yield ages clearly less reliable than those of chondrules. Chondrules from Ste Marguerite (H4) give an age of 4563.4 ± 0.6 Ma indistinguishable from the phosphate age of 4562.7 ± 0.7 Ma (2). These values are also indistinguishable from the age of the chondrules from Nadiabondi (H5) (4562.5 ± 0.9 Ma), whereas the phosphates give a younger age of 4555.6 ± 3.4 Ma [2]. The oldest age is obtained for Forest City (H5, 4567.8± 0.7 Ma). The chondrules from Tuxua (LL5) are 4559.9 ± 0.5 Ma old, again older than the phosphates (4543.6 ± 2.1 Ma) [2]. Overall, the ages of L OC are younger than those of H and LL OC. Cooling rates may be estimated using the data of [4] on Pb diffusion in rock-forming minerals: a fast cooling rate (~300°C/My) is inferred for Ste Marguerite, whereas Nadiabondi (~40°C/My) and Ausson (L5; 10°C/My) appear to have cooled much more slowly. The age of Ste Marguerite is therefore the closest to the temperature peak. Assuming that the dominant heat source was 26Fe (T1/2 = 1.5 My), this places the age of the protoplanet at 4567 ± 1 Ma, which is similar to the age of the CAI of [1].

Pb-Pb geochronology of the early solar system

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We report high-precision Pb isotope data by MC-ICP-MS on whole-rocks and chondrule separates from ordinary chondrites (OC). Compared with literature CAI and mineral separate data [1-3], the ages obtained for OC throw new light on the timescale for the formation and cooling of planetary bodies in the early Solar System.

All age calculations were done in 207Pb/206Pb, 206Pb/204Pb, 204Pb/206Pb space, which minimizes noise-induced correlations between variables. We then assumed that the sample is a mixture of radiogenic (*) and common lead and used the intercept of the residue-leachate array in the 207Pb/206Pb-204Pb/206Pb plot to estimate the 207Pb/206Pb ratios. Full error propagation inclusive of blank contribution (0.01-0.9% of the total Pb contents) required the development of a specific correction scheme. We find that whole-rocks yield ages clearly less reliable than those of chondrules. Chondrules from Ste Marguerite (H4) give an age of 4563.4 ± 0.6 Ma indistinguishable from the phosphate age of 4562.7 ± 0.7 Ma (2). These values are also indistinguishable from the age of the chondrules from Nadiabondi (H5) (4562.5 ± 0.9 Ma), whereas the phosphates give a younger age of 4555.6 ± 3.4 Ma [2]. The oldest age is obtained for Forest City (H5, 4567.8± 0.7 Ma). The chondrules from Tuxua (LL5) are 4559.9 ± 0.5 Ma old, again older than the phosphates (4543.6 ± 2.1 Ma) [2]. Overall, the ages of L OC are younger than those of H and LL OC. Cooling rates may be estimated using the data of [4] on Pb diffusion in rock-forming minerals: a fast cooling rate (~300°C/My) is inferred for Ste Marguerite, whereas Nadiabondi (~40°C/My) and Ausson (L5; 10°C/My) appear to have cooled much more slowly. The age of Ste Marguerite is therefore the closest to the temperature peak. Assuming that the dominant heat source was 26Fe (T1/2 = 1.5 My), this places the age of the protoplanet at 4567 ± 1 Ma, which is similar to the age of the CAI of [1].

References
From dust to planets: Time scales of accretion and differentiation in the early solar system

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In recent years, several chronometers based on the decay of short-lived radionuclides have been applied towards obtaining high-resolution time constraints for events in the early solar system (e.g. [1]). However, it is still a matter of debate whether many of these extinct radionuclides may be applied as chronometers since their origin and initial distribution in the early solar system are not yet well constrained. Nevertheless, several recent studies have demonstrated that high precision absolute (U-Pb) ages obtained for some meteoritic materials are concordant with relative high-resolution ages obtained from the application of the \(^{26}\)Al-\(^{26}\)Mg (half life ~0.72 My) and the \(^{57}\)Mn-\(^{57}\)Cr (half life ~3.7 My) chronometers [2,3,4]. Specifically, it has been shown that the earliest solids in the solar nebula (i.e., Ca-Al-rich inclusions) were formed at 4567.2 ± 0.6 Ma [3]. Furthermore, our recent work on U-Pb, \(^{26}\)Al-\(^{26}\)Mg and \(^{55}\)Mn-\(^{55}\)Cr systematics in the eucrite Asuka 881394 suggests that some asteroidal bodies had accreted and differentiated within ~3 My of CAIs [4].

We have recently also applied the \(^{182}\)Hf-\(^{182}\)W (half life ~9 My) and \(^{146}\)Sm-\(^{142}\)Nd (half life ~103 My) systems to the shergottite-nakhlite-chassignite (SNC/martian) meteorites to constrain the timing of metal segregation and silicate differentiation on Mars [5]. This work demonstrates that major silicate differentiation on Mars occurred well within ~50 My of solar system formation. Specifically, the mantle source reservoir of the shergottites was established at 4525 ± 20 Ma, while that of the nakhlites was likely established prior to ~4542 Ma.

References

The formation of the solar system: New constraints from the \(^{247}\)Cm-\(^{235}\)U chronometer

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The \(r\)-process only nuclide \(^{247}\)Cm decays to \(^{235}\)U with a characteristic half-life of ~16 million years. \(^{247}\)Cm is presently extinct, but offers potential as a short-lived \(r\)-process chronometer, providing constraints on the time interval between the last \(r\)-process nucleosynthetic event and the formation of the solar system. The existence of “live” \(^{247}\)Cm in the early solar system should be observed today as variations in \(^{238}\)U/\(^{235}\)U, provided Cm/U fractionation occurred. The Cm-U system also has a direct bearing on the U-Pb cosmochronometer, which currently assumes no Cm effects in early solar system material.

Using a Nu Instruments NuPlasma and new techniques in MC-ICPMS, we are able to resolve variations in \(^{238}\)U/\(^{235}\)U at the two epsilon level (2σ\(r\)) on sample sizes consisting of <20 pg of \(^{235}\)U. Because no long-lived isotope of Cm exists, our study uses Nd as a chemical proxy for Cm. Thus, additional concentration data for \(^{144}\)Nd, \(^{147}\)Sm and \(^{238}\)U were acquired by MC-ICPMS using techniques in isotope dilution. Uranium isotopic measurements and Nd/U values for a suite of bulk meteorites show no well-resolved excursions in \(^{235}\)U/\(^{238}\)U from the terrestrial value at the ~2 epsilon level. These data provide an upper limit on \(^{247}\)Cm/\(^{235}\)U at the start of the solar system of \(1 \times 10^{-4}\), assuming Nd is a suitable proxy for Cm and the Nd/U ratios have not been significantly modified (Stirling et al., in press, GCA).

We have extended the search for “live” \(^{247}\)Cm in the early solar system to small samples from mineral phases in primitive objects that are likely to display strong Cm-U fractionations. Uranium isotopic measurements have been acquired on acid-etched leachates for a suite of chondritic meteorites, and for a suite of minerals separated from early-formed carbonaceous chondrites and angrites. Some of these phases show significant \(^{238}\)U excesses with respect to the bulk chondritic value, although no correlation with Nd/U is observed. These data may indeed reflect \(^{247}\)Cm effects. The suitability of Nd as a chemical proxy for Cm, however, may require revision. These new results have important implications for the \(^{247}\)Cm-\(^{235}\)U cosmochronometer and the timing of \(r\)-process nucleosynthesis relative to the formation of the first solar system materials.
**The Hf-W isotopic system and the origin of the Earth and Moon**

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The Earth has a radiogenic W-isotopic composition compared to chondrites, demonstrating that it formed while $^{182}$Hf (half-life 9 Myr) was extant in the Earth and decaying to $^{182}$W. This implies that the Earth underwent early and rapid accretion and core formation, with most of the accumulation occurring in $\sim$10 Myr, and concluding about 30 Myr after the origin of the solar system. The Hf-W data for lunar samples can be reconciled with a major Moon-forming impact which terminated the terrestrial accretion process $\sim$30 Myr after the origin of the solar system. The suggestion that the proto-Earth to impactor mass ratio was 7:3 and occurred during accretion is inconsistent with the W isotope data. The W isotope data is satisfactorily modeled with a Mars-sized impactor on proto-Earth (proto-Earth to impactor ratio of 9:1) to form the Moon at $\sim$30 Myr.

**Magnesium isotope composition of chondrites, achondrites and the Earth-Moon system**

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We have measured $^{24}$Mg, $^{25}$Mg, and $^{26}$Mg abundances of chondrites, achondrites, lunar and terrestrial rocks and minerals using Nu1700 a high mass resolution MC-ICPMS. Mg-isotopes of terrestrial and meteorite samples fall on a single mass dependent fractionation line. This provides evidence that inner solar system objects were derived from a well mixed reservoir. In contrast to Fe isotopes [1], Mg isotopes show very limited mass-dependent variation. The Mg isotopic composition ($\delta^{26}$Mg) of mantle olivines, enstatites and Cr-diopsides average at -0.07±0.02‰, -0.08 ±0.11‰, and +0.05±0.02‰ (2 s.d.) relative to DSM3, respectively. Based on these data we estimate a $\delta^{26}$Mg between -0.1‰ and 0.0‰ for Earth. Terrestrial volcanic rocks average at $\delta^{26}$Mg=-0.15±0.14‰. Eucrites (n=9) and Martian meteorites (n=4) have a mean of -0.06±0.14‰ and -0.12±0.11‰ respectively, overlapping with terrestrial mantle minerals and volcanic rocks. In contrast, 12 analyses of 7 carbonaceous and ordinary chondrites yield an average of -0.35±0.08‰ (2s.d.). Preliminary data for lunar rocks and minerals vary between chondritic values and DSM3 and are therefore slightly heavy relative to terrestrial values. The overall range of $\delta^{26}$Mg for planetary bodies in the inner solar system is <0.5‰. The homogeneity among chondritic meteorites is surprising because large isotopic variations have been reported for Ca,Al-rich inclusions and to a lesser extent chondrules e.g. [2,3]. The small $\delta^{26}$Mg range requires that, whatever produces the oxygen isotope heterogeneity in chondrites involves processes that cause little mass-dependent Mg isotope fractionation. This is consistent with a recently published model of mass-independent fractionation of oxygen at mineral surfaces during condensation of the solar nebula [4] but seems to be in conflict with the self-shielding model [5].

References

Ag isotope variations in the Earth

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The short-lived radionuclide $^{107}$Pd decays to $^{107}$Ag with a half-life of 6.5 Myrs. Pd is more siderophile than Ag and therefore partitions more strongly into the core thereby allowing this system to place chronological constraints on core formation processes.

Preliminary results on terrestrial samples revealed Ag isotopic variations on the order of $-1.1\epsilon$ to $5.3\epsilon$ (relative to the SRM 978a standard) for ore samples and slightly smaller variations for basalts from the Hawaiian volcanoes Kilauea and Mauna Loa (Haury et al., 1999). Basalts from Mauna Loa have been shown to have radiogenic $^{186}$Os, from the decay of $^{190}$Pt, which may be a signature of core-mantle interaction on the Earth (Brandon et al., 1998). These basalts are therefore promising samples to search for Ag isotopic anomalies due to the extinct nuclide $^{107}$Pd. However, this task requires precise and accurate Ag isotopic measurements, which has proven difficult because Ag has only two naturally occurring isotopes that can easily experience mass fractionation during chemical processing and analysis (Carlson et al., 2001, Woodland et al. 2003). We have improved the chemical separation procedure in order to obtain a better separation of Ag from Ti. This is essential for basalt analyses because of matrix effects related to Ti during ICP analysis. First results for the Steens Mtn. flood basalt CH83-55 yield an average Ag isotopic composition of $-1.6 \pm 1.6 \epsilon$, indistinguishable from the SRM 978a standard. Analyses of a more comprehensive set of Hawaiian basalts and chondrites are underway. We also reanalyzed the native Ag metals derived from globally distributed ores and previously investigated with a VG Plasma 54-30. The new measurements, performed with an Axiom, confirm the previously reported Ag isotopic variations in the range of $-1.1\epsilon$ to $5.3\epsilon$.

References

Timing, mechanisms and conditions of terrestrial planet accretion and early differentiation

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Over the past few years there have been major advances in our understanding of both the timescales and processes of terrestrial planet accretion, primarily as a result of $^{182}$Hf-$^{182}$W chronometry. The accretion of Mars would appear to have been extraordinarily fast, providing evidence of runaway growth. The current best estimates for some martian reservoirs would imply that they formed within the first 1 or 2 million years of the solar system. Mars differentiation appears incomplete and lacks the uniform and well-mixed W depletion found on Earth. Although accretion may have been rapid the timescales for early metal segregation in the source for Nakhla for example could be more than 20 Myrs. In contrast, the final stage of Earth accretion – the Moon-forming collision (or Giant Impact) between the Earth and another planet “Theia”, took place 40 to 50 million years after the start of the solar system. Comparisons between the results of $^{182}$Hf-$^{182}$W chronometry and more traditional systems like $^{235/238}$U-$^{207/206}$Pb indicate that the models used to define these timescales are over-simplified. With the age of the Moon well-constrained the W isotopic data for the Earth provide evidence for minor amounts of incomplete mixing during accretion. For example, the degree of equilibration of W between the core of Theia and the silicate Earth during the Moon-forming Giant Impact could have been as little as ~30%. This cannot explain the discrepancy between Hf-W and U-Pb timescales. A change in U/Pb in the silicate Earth during accretion and differentiation is the best explanation. However, the mechanism for this is unclear.
The implications of the Hf and Nd isotopic records for the early history of the silicate Earth

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The Sm-Nd and Lu-Hf isotope systems have been valuable tools in trying to understand the differentiation and evolution of bulk silicate Earth (BSE). Together these systems help constrain evolution of the crust and mantle and provide a basis for quantifying bulk Earth isotopic mass balance. Linking these systems is especially important for constraining the history of the early silicate Earth as they provide independent records in rocks with long and complex tectono-thermal histories. Ultimately, the utility of these systems will depend on how well we know the $^{176}$Sm and $^{176}$Lu decay constants as well as the Lu-Hf and Sm-Nd isotopic composition of BSE.

Recent work on the $^{176}$Lu decay constant by cross-calibration of U-Pb and Lu-Hf isotope systems on mineral isochrons in terrestrial rocks [1,2] have determined values ($1.867 \times 10^{-11} \text{y}^{-1}$) 3-4% lower than the values in use for the last two decades and ~6% lower than the value determined from meteorites [3]. The terrestrial value, if true, would result in predominantly negative initial $\varepsilon_{\text{Hf}}$ values for the oldest terrestrial rocks and zircons, indicating they were derived from a source with a prior crustal history. In contrast, a faster decay constant would result in more positive $\varepsilon_{\text{Hf}}$ values and indicate derivation from a depleted mantle source. The chondritic Lu-Hf parameters, while still a matter of debate [4], will have little effect on $\varepsilon_{\text{Hf}}$ values in the early Earth because plausible increases in the $^{176}$Hf/$^{177}$Hf BSE value are linked to higher $^{176}$Lu/$^{177}$Hf values, based on Lu-Hf systematics in chondrites.

The Nd isotope record for the early Earth is broadly characterized by positive $\varepsilon_{\text{Nd}}$ values. Thus, if the terrestrial $^{176}$Lu decay constant is correct, there appears to be a fundamental conflict between the Nd and Hf isotopic records for the Earth's oldest rocks with Nd indicating a depleted mantle source and Hf a crustal source. In light of large amounts of new Hf data emerging for early Archean rocks and zircons, and the implications of that data for early crust on the Earth, this apparent conflict between the Nd and Hf isotopic records needs to be resolved.

References

Early terrestrial mantle dynamics from the $^{143}$Nd isotopic record of 3600 Ma to >3850 Ma mafic and felsic rocks

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Mantle isotopic evolution for $^{143}$Nd/$^{144}$Nd is frequently depicted as linearly increasing from a chondritic primitive mantle composition at 4.56 Ga to modern MORB compositions. This implies a progressive depletion of the mantle and a continuity of rates and processes from ancient to modern Earth. The test of these concepts relies on clarifying and extending the isotopic record by finding the oldest, least altered mantle-derived rocks, providing them with age and geologic context and determining accurate initial compositions. Our continuing field and laboratory investigations have identified the islands near Nuuk, SW Greenland, including Qiangarsuit and Innersuaat, as having the most extensive record of early (3800-3850 Ma) Earth chemistry. Six oldest orthogneisses, with SHRIMP zircon dates of 3850-3840 Ma provide minimum ages for varied mantle derived mafic/ultramafic rock sequences. Initial $\varepsilon_{\text{Nd}}$ (3850Ma) from >30 mafic samples are in a narrow range of $+2$ to $+4$ ($\pm 0.5$), providing a robust control on early mantle depletion. No negative $\varepsilon_{\text{Nd}}$ values have been determined. Assuming depletion occurred at 4.56 Ga, these data require a minimum average $^{143}$Sm/$^{144}$Nd=0.224 in the pre-3850 Ma upper mantle. The apparent Nd isotopic homogeneity at 3850 Ma contrasts with the more extreme depletion and large range of positive and negative $\varepsilon_{\text{Hf}}$ measured in >4.0 Ga detrital zircons from Western Australia (Harrison et al., this volume). The oldest felsic suites from SW Greenland provide no evidence for pre-existing felsic crust in the form of either inherited zircons, or Nd and Hf isotopic compositions.

The emerging global Nd and Hf isotopic patterns reveal a increasingly detailed picture of rapid and extreme early planetary differentiation, likely associated with accretionary processes, followed by partial re-homogenisation of the mantle before 3.9 Ga. For at least the next billion years (3.9 Ga to <2.7 Ga) $\varepsilon_{\text{Nd}}$ and $\varepsilon_{\text{Hf}}$ isotopic compositions were near constant, indicating rapid crustal recycling timescales (100-300 Myr) and/or reservoir mixing. Long held views of simple, linearly evolving mantle depletion need to be revised in recognition of the isotopic record of punctuated mantle evolution.
Early differentiation of terrestrial reservoirs and extinct radioactivities

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The formation of the core, the atmosphere and the isolation of the first proto-crust in the Earth seem to have taken place in the first hundred million years after the beginning of the Solar System. Yet, these timescales of these events are probably overlap and hence, the isotopic systems that are used for the respective chronology are not independent. For example, it has been argued that core formation requires a partially molten mantle and crust formation could result from the late stage of magma ocean crystallization.

The timescale of the first crustal extraction (4,460±115 Ma) as evidenced by recent measurements of $^{142}$Nd anomalies in Isua rocks (Caro et al. 2003), is not very precisely defined but if it predates 4.48 Ga, then this event could have affected Hf-W systematics in the silicate Earth and should be taken into account for assessing the age of core formation. Crustal extraction is also likely to affect I-Xe systematics since I is efficiently extracted during in melts.

In this contribution, we examine with a three-box model including accretion (with equilibration) how an early crustal growth would affect Hf-W systematics. An early crustal formation could result in Hf/W fractionation in the crust-mantle system and W anomalies detectable in Archean rocks.

Reference

Remains of an enriched Hadean protocrust in modern mantle

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Applications of short-lived $^{146}$Sm-$^{142}$Nd (half-life of 103 Ma) and long-lived $^{147}$Sm-$^{143}$Nd (half-life of 106 Ga) coupled isotope systems in early Archaean rocks have indicated that mantle differentiation occurred 50 to 200 Ma after the formation of the earth and produced depleted silicate reservoirs with high Sm/Nd ratios. The nature and fate of the protocrust, with complementary low Sm/Nd ratios, is unknown. Two relevant models are: (1) a stagnant lithospheric lid of the magma ocean consisting dominantly of depleted mafic-ultramafic lithologies. This model proposes that the low Sm/Nd protocrust did not form and therefore no terrestrial sample should display a deficit in $^{142}$Nd. (2) Burial of early enriched (low Sm/Nd) crust into the deep mantle. This model suggests that early crust was foundered into the lower mantle leaving behind a depleted upper mantle. If protocrust is preserved in the lower mantle some of the lower mantle derived plume material should possess negative $^{142}$Nd anomalies.

Here, we present ultraprecise measurements of Nd isotopes in 65 Ma old Deccan Traps lavas, which sample the deep mantle, the asthenospheric mantle and the subcontinental lithospheric mantle. We show that samples representing magma from deep mantle plume give no evidence of the existence of the protocrust at the core-mantle boundary and that the samples with lithospheric component give a negative $^{142}$Nd anomaly with $\mu^{142}$Nd $=\frac{(^{142}$Nd$^{144}$Nd)$_{nD}\ -1]}{(^{142}$Nd$^{144}$Nd)$_{nD}\ -1]}\times10^6$ values ranging from -10 to -12 ppm. It follows that if the Deccan starting plume was isotopically homogeneous, a portion of Hadean protocrust resided in the ancient Indian subcontinental lithospheric mantle.
Heterogeneous Hadean hafnium: Evidence of continental crust by 4.5 Ga?

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The paradigm for continent formation long favoured by isotope geochemists is that growth began at ~4 Ga and was ~80% of its present mass by 2.5 Ga. This view reflects the absence of a >4 Ga rock record and the systematic post-4 Ga evolution of depleted mantle $^{143}$Nd/$^{144}$Nd and $\delta^{176}$Hf/$\delta^{177}$Hf. The observations of some early Nd and Hf isotopic heterogeneities leave open the possibility of earlier global fractionations and a minority view has persisted that continental crust was widespread in the early Hadean (e.g., Armstrong, 1981; Reymer and Schubert, 1984). In this regard, the relative lack of evidence for earlier depletions (from a magma ocean or continent formation) reflects remixing of these heterogeneities. Detrital zircons from Jack Hills, Australia, with 4.0-4.4 Ga U-Pb ages transcend this ambiguity as they represent pieces of crust that have been sequestered for up to ~4.4 Ga. Zircons have very low Lu/Hf and thus record near initial $\delta^{177}$Hf/$\delta^{176}$Hf at the time given by the U-Pb age. Amelin et al. (1999) used Jack Hills zircons as old as 4.14 Ga to investigate early crustal evolution and inferred the existence of re-melted Hadean crust. We have carried out $\delta^{176}$Hf/$\delta^{177}$Hf analyses by both solution and laser ablation MC-ICPMS on over 70 Jack Hills zircons ranging in age from 3.96 to 4.35 Ga. These results indicate very large positive and negative $\delta^{176}$Hf deviations from CHUR ($\Delta^{176}$Hf = 0.01867/Ga; $\Delta^{176}$Hf/$\Delta^{177}$Hf = 0.282772; $\Delta^{176}$Lu/$\Delta^{177}$Hf = 0.0332). Negative values of $\delta^{176}$Hf equivalent to $\Delta^{176}$Hf/$\Delta^{177}$Hf $\times$ 1.5 observed between 4.35 and 4.2 Ga are consistent with development of a Lu/Hf = 0 reservoir by 4.5 Ga. Positive $\delta^{176}$Hf deviations in the same age interval imply a depleted reservoir with Lu/Hf up to 0.08. We interpret these results as indicating either 1) that the remains of original mantle heterogeneities from accretion were not yet well mixed by mantle convection by 4.35 Ga, or 2) that significant continental crust had formed by ~4.5 Ga. The latter interpretation is consistent with inferences from $\Delta^{143}$Nd systematics (Caro et al., 2003; Boyet et al., 2003).

Crystallization temperatures of Hadean zircons: Plate tectonics at 4.35 Ga?

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As the sole known survivors from the Hadean Eon, the detrital zircons of Western Australia’s Narryer Gneiss Complex have already provided intriguing glimpses into the state of the very early Earth. Given the significance of the chemical and isotopic information these crystals contain, it is crucial to understand the circumstances under which they grew. Knowledge of their crystallization temperatures, in particular, would place useful constraints on the types of magmas being produced during the Hadean. Toward this goal—and to provide information on zircons of all ages—we have calibrated a new thermometer based on the concentration of Ti in zircons coexisting with rutile, using both high P-T experiments and analyses of natural zircons of well-constrained provenance. Zircon Ti content varies by three orders of magnitude over the temperature range ~600°–1450°C, and is insensitive to changes in pressure. In applying this new thermometer to zircons removed from their original context (such as detrital Hadean zircons), coexistence with rutile cannot be assumed. However, thermodynamic considerations show that TiO$_2$ activities generally range from 0.5 to 1.0 in igneous and metamorphic systems capable of crystallizing zircon. That range of TiO$_2$ activities affects calculated temperatures by only a few 10’s of °C. Sixty-eight analyses of 55 Jack Hills zircons from 4.0 to 4.35 Ga in age yield temperatures ranging from 791 °C to 659°C (710±32°). This range is indistinguishable from that expected of granitoid zircon formation today, and strongly suggests a limited range of regulated mechanisms producing zircon-bearing rocks during the Hadean. Combined with the suite of mineral inclusions observed by previous workers, these temperatures substantiate the existence of wet, minimum-melting conditions within 200 m.y. of solar system formation. They further suggest that by 4.35 Ga, the Earth had settled into a pattern of crust formation, erosion, and sediment recycling similar to that produced during the known era of plate tectonics.
A lower age limit for the Archean based on $\delta^{18}$O of detrital zircons

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A lower boundary for the Archean Eon is proposed based on changes in magma chemistry due to interaction with liquid water at the Earth’s surface. The $\delta^{18}$O of detrital igneous zircons from Jack Hills, Western Australia, record the changing surface environment during the onset of ‘cool early Earth’ conditions. Mildly elevated $\delta^{18}$O for igneous zircon occurs as far back as 4325 Ma, however a later rise of ~1‰ in $\delta^{18}$O to 7.3‰ provides strong evidence for the recycling of supracrustal rocks into magmas, and the first evidence for the presence of liquid water on Earth (Cavosie et al., 2005). This boundary may also signify the stabilization of continental crust, as evidenced by the formation of supracrustal rocks. Rare and scattered geologic occurrences (e.g. 3850 Ma metasediments, 4030 Ma gneisses, or a 4400 Ma detrital zircon) are merely ‘snapshots’ in a fragmentary rock record, and do not define boundary conditions, as some have speculated. Such occurrences, no matter how significant, should not be used to define eon boundaries. The earliest eon (before Cool Earth conditions) encompasses accretion, differentiation, and the early meteorite bombardment of Earth (including Moon formation). The naming of the earliest eon (e.g. Hadean, Priscoan, etc.) requires further international discussion, as chronostratigraphic principles cannot be applied where superposition is unknown due to the lack of a preserved intact rock record. The published $\delta^{18}$O of dated zircons suggest that the onset of cool Earth conditions was at ca. 4200 Ma, which is here proposed as the beginning of the Archean Eon.

Hf and Nd isotope evolution of lithologies from the 3.8 Ga Nuvvuagittuq Sequence, northern Superior Province, Canada

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The 3.8 Ga Nuvvuagittuq volcano-sedimentary sequence in the Inukjuak Domain of the Superior Province in northern Quebec lies on the coast of Hudson Bay. The Nuvvuagittuq sequence consists of volcanic and sedimentary units as well as tonalitic gneisses and pegmatites. The volcanic units include mafic amphibolites with associated intermediate volcanic horizons. The sedimentary rocks consist largely of iron formation that vary from iron oxide dominated facies to silicate (quartz-amphibole) dominated facies. One particular silicate facies forms a dominant and persistent horizon that can be followed throughout much of the sequence. The volcano-sedimentary units are intruded by layered ultramafic sills that vary from dunite and pyroxenite to gabbrro compositions. The bulk of the supracrustal sequence forms a semi-oval structure that is cored and enveloped by ca 3.6 Ga tonalitic gneisses.

The tonalitic gneisses range from granodiorite to tonalite and granite in composition and interleave with amphibolite and ultramafic units along the outer margin of the sequence. The TTG suite is characterised by heavy rare earth element (REE) depletion compared to light REE. Hf and Nd isotope analyses of the tonalites yield negative initial epsilon values suggesting that the tonalites have recycled significant amounts of older ca 3.8 Ga crust.

The volcanic units range from basaltic to dacitic in composition with the amphibolites yielding flat to slightly light REE enriched profiles and the dacitic compositions yielding light REE enriched and heavy REE depleted profiles. Hf and Nd isotope data from the volcanic lithologies range from slightly depleted initial epsilon values (+2 for Nd, +3 for Hf) to slightly negative values (-1 for Nd and -4 for Hf). Comparison with geochemical data suggests that the Hf isotope system has been perturbed in the volcanic lithologies whereas Nd has been more robust. Comparison of the Nuvvuagittuq Nd and Hf isotope data with that of West Greenland localities suggests that the mantle source for the Nuvvuagittuq lithologies was less depleted than that of West Greenland.

References
Platinum-Osmium isotope evolution of the Earth's mantle

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Extraction of metal-rich core likely resulted in strong depletion of the silicate portion of Earth in highly siderophile elements (HSE), including Re, Os, and Pt. Replenishment of HSE through a 'late veneer', or high-pressure equilibrium between metal and silicate have been proposed to explain the excess of HSE relative to that expected from core extraction at lower pressures. To address these issues on core extraction, late accretion and terrestrial mantle evolution, 30 Os-rich alloys from upper mantle peridotites, and 13 samples of carbonaceous, enstatite and ordinary chondrites, were measured for high-precision Os isotopic compositions on the JSC Triton. Two of the Os-rich alloys with present-day ¹⁸⁷Os/¹⁸⁸Os of 0.1095 and 0.1096 have ¹⁸⁶Os/¹⁸⁸Os of 0.1198320 and 0.1198329, respectively. They have ¹⁸⁷Os model ages of 2.8 Ga. The measured ¹⁸⁶Os/¹⁸⁸Os for these two samples are within uncertainty of the initial ratio of 0.1198323±0.09 for 2.7 Ga Pyke Hill komatiites and constrains the Pt-Os upper mantle evolution curve. The remaining 28 Os-rich alloys with ¹⁸⁶Os/¹⁸⁸Os from 0.1167 to 0.1596 have a range in ¹⁸⁶Os/¹⁸⁸Os from 0.1198352 to 0.1198408, with an average of 0.1198382±0.02 (σ). Carbonaceous chondrites have ¹⁸⁶Os/¹⁸⁸Os of 0.1198352 (n=3). Ordinary chondrites have ¹⁸⁶Os/¹⁸⁸Os from 0.1198345 to 0.1198408 (n=7), and enstatite chondrites from 0.1198335 to 0.1198401 (n=3), with averages of 0.1198387±0.02, and 0.1198374±0.004, respectively. The enstatite and ordinary chondrite time evolution curves match those for the Pyke Hill komatiites and the 2.8 Ga Os-rich alloy mantle sources. These ¹⁸⁶Os/¹⁸⁸Os relationships between Os-rich alloys and enstatite and ordinary chondrites are consistent with previous arguments based on ¹⁸⁷Os/¹⁸⁸Os systematics for a late veneer of similar types of materials controlling the HSE budget of the upper mantle. Unless liquid metal/silicate melt partition coefficients for Pt and Os are within about 10% of each other, a high pressure core extraction model will not alone explain these ¹⁸⁶Os/¹⁸⁸Os compositions.

Pt-Re-Os isotope and HSE systematics of 2.8 Ga komatiites

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If coupled ¹⁸⁶Os,¹⁸⁷Os enrichments in Archean komatiites reflect addition of a core component, the Os isotopic compositions could be used to infer the timing of the onset and the rate of inner core crystallization. Here, Pt-Re-Os isotope and highly siderophile element (HSE) abundance data for 2.8 Ga komatiites at Kostomuksha are presented. The Pt-Os data for seven komatiitic samples define an isochron with an age of 2816±190 Ma and an initial ¹⁸⁶Os/¹⁸⁸Os of 0.1198340±0.00067. Corresponding Re-Os data yield an isochron age of 2880±83 Ma and an initial ¹⁸⁷Os/¹⁸⁸Os of 0.10916±0.00067. These Os isotopic compositions characterize those of the komatiite mantle source and are 64±17 ppm and 1.8±0.6% more radiogenic, respectively, than those of the contemporary convecting upper mantle or chondritic references. The calculated komatiite source had absolute HSE abundances similar to those of the Abitibi komatiite and an average depleted spinel lherzolite. The coupled ¹⁸⁶Os-¹⁸⁷Os enrichments in the komatiite source are best explained via derivation of the Os largely from the outer core. If this interpretation is correct, the komatiite data provide minimum constraints on the Os isotopic composition of the outer core at 2.8 Ga. The existing models of core crystallization based on experimentally determined partition coefficients for Pt, Re, and Os between solid metal and liquid metal can adequately explain the Os isotopic composition of the Kostomuksha komatiite source, although require the onset of inner core crystallization at 3.5 Ga at the latest. The results of this study indicate that core-mantle interaction might occur in the form of isotopic exchange without significant mass transfer from the core to the mantle, and that at least some komatiites originated from mantle plumes that rose from the core-mantle boundary.
δ\(^{37}\)Cl values of the solar system

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Multiple sodalite grains within altered CAIs in Allende (CV3) were analyzed for their chlorine isotopic composition using \textit{in situ} ion microprobe analysis. δ\(^{37}\)Cl values range from –0.39 to –2.09 ‰, averaging to –1.33 ± 0.55‰ (n = 10). Isotopic variation within individual CAIs and among the inclusions is within external reproducibility over the analytical session (±0.25‰), indicating that sodalite formed from a homogeneous reservoir.

Published δ\(^{37}\)Cl values fall in two distinct clusters (Fig. 1).

![Fig. 1. δ\(^{37}\)Cl values of meteorites. Sodalite in Allende (black box; this study); Water-soluble extracts (circles; Bridges et al., 2004); Bulk carbonaceous chondrites (triangles; Magenheim et al., 1994, 1995); Bulk meteorites (dashed box, Bonifacie et al., 2004); terrestrial seawater is 0‰.]

These clusters have been used to argue for two distinct reservoirs in the early solar system: an isotopically light parent body brine and heavier chondrite silicate solid (Bridges et al., 2004). If a significant portion of the CI in Allende is hosted in sodalite, then our data contradict the earlier reported ~4‰ value, a conclusion supported by Bonifacie et al. (2004). We conclude that the solar system average, and by extension, the bulk Earth, have δ\(^{37}\)Cl values ≤–1‰.

References
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Uncoupled C and S biogeochemical cycling in the Neoproterozoic from the Huqf Supergroup, Oman

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Huqf Supergroup strata [~715 – 540 Ma] have been analyzed for organic and carbonate δ\(^{13}\)C, as well as δ\(^{34}\)S from anhydrite and carbonate-associated sulfate (CAS). The Huqf contains a negative excursion in carbonate δ\(^{13}\)C of ~13‰ in the Shuram Formation. This “Shuram” excursion extends through >500m of section, suggesting a long term perturbation to the C cycle.

Sulfate δ\(^{34}\)S shows little variability throughout the period of the Shuram excursion. There is no indication of a correlation between δ\(^{34}\)S and carbonate δ\(^{13}\)C during the Shuram excursion, indicating that the oxidation of depleted carbon responsible for the Shuram δ\(^{13}\)C excursion was not accompanied by significant oxidation of sulfide. Together, these data are best explained by the oxidation of a vast reservoir of dissolved organic carbon in the deep ocean.

Following the Shuram excursion, sulfate δ\(^{34}\)S climbs sharply over 6 Myr, reaching a maximum of ~41‰ just before the Precambrian/Cambrian boundary. This is followed by a slight decrease in δ\(^{34}\)S in the overlying earliest Cambrian strata. There is no appreciable change in carbonate δ\(^{13}\)C coincident with or subsequent to the ~20‰ increase in sulfate δ\(^{34}\)S. This observed rate of change in sulfate δ\(^{34}\)S (~3‰/Myr) indicates low Neoproterozoic sulfate concentrations. The decline in sulfate δ\(^{34}\)S following the Precambrian/Cambrian boundary suggests a progressive increase in the concentration of seawater sulfate. These data indicate a massive Neoproterozoic reorganization of the global C-S biogeochemical cycles, likely due to oxygenation of the deep ocean.
Was there voluminous ancient (>4.0 Ga) sialic crust? Implications from the Hf composition of detrital zircons

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We report LA-MC-ICPMS Hf isotope results of ancient detrital zircon from two locations in the Canadian Shield. Quartzite, deposited prior to 2.3 Ga in the Beaverlodge Belt, Rae Province, contains zircon entirely >3.6 Ga old. Metagreywacke from the Assee Lake Area, western Superior Province, was deposited ca. 3.2 Ga and contains predominantly Paleoarchean zircon. The U-Pb and Lu-Hf isotope characteristics from these locations indicate that significant Paleoarchean crust was exposed at the time of sediment deposition, and crustal growth/rewiring occurred between 3.7 and 3.86 Ga (Figure 1). Do to the extremely negative εHf of much of the zircon, some of the reworked crust must have been ≥4.0 Ga. However, the only presently known location of ≥4.0 Ga crust, the Acasta Gneiss, Canada, does not have a significant 3.7 to 3.86 Ga component.

Occurrence of a 4.2 Gyr old zircon in the Acasta Gneiss Complex of northwestern Canada

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The recognized terrestrial materials more than 4.1 Gyr old have been restricted to detrital zircons within metasediments and a xenocrystic zircon within granitic gneiss in the Narrey Gneiss Complex of Western Australia. Consequently, knowledge of crustal evolution and surface environment in the early Earth is based on mainly the chemical and isotopic signatures of the zircons. Here we report a further occurrence of a very old zircon grain in the Acasta Gneiss Complex of northwestern Canada, a locality which contains the oldest crustal rocks as old as 4.03 Gy. The zircon grain was separated from 3.9-Gyr-old tonalitic gneiss and has a xenocrystic core with an U-Pb age of 4,203 ± 58 Myr (Fig. 1). The trace element composition of the core shows that it crystallized from granitoid magma. These data therefore indicates wide presence of continental crust on the Earth by 4.2 Gy ago and subsequent reworking of them in the early crustal evolution.

Figure 1: 176Hf/177Hf vs Age plot of ancient detrital zircons.

Fig.1 Cathodoluminescence image of zircon crystal AC012/1-12.
A $^{15}$N-enriched Archean atmosphere

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Introduction

The origin and evolution of nitrogen in Earth’s atmosphere is controversial. Earlier results on Archean cherts and BIF show a range of $\delta^{15}$N from –6 to 30‰. Given temporal and spatial association of chert-BIF with volcanic sequences erupted from mantle plumes, we selected blacks shales distal to these systems of the 2.6 Ga Kolar gold province, E. Dharwar craton, that proxy for average crust, are enriched at 14 to 21‰, which are also consistent with other late Archean gold provinces, confirming that the N-budget of the hydrothermal fluids is dominated by sedimentary rocks.

Results

Kerogen in metashales from the 2.7 Ga Sandur belt, E. Dharwar craton, is characterized by $\delta^{15}$N 13.1 ± 1.3‰, and C/N 303 ± 93. Kerogen from 1.7 Ga carbonaceous shales of the Cuddapah basin average 5.0 ± 1.2‰, close to the mode at 3 to 4‰ for kerogen and bulk rock of Phanerozoic sediments. Hydrothermal micas from late-metamorphic quartz-vein systems of the 2.6 Ga Kolar gold province, E. Dharwar craton, that proxy for average crust, are enriched at 14 to 21‰, which are also consistent with other late Archean gold provinces, confirming that the N-budget of the hydrothermal fluids is dominated by sedimentary rocks.

Discussion and Implication

Enriched values in Precambrian rocks cannot be caused either by N-isotopic shifts due to metamorphism or Rayleigh fractionation, or by long-term preferential diffusional loss of $^{14}$N. It is possible that the $^{15}$N-enriched values stem from a different N-cycle in the Archean, with large biologically mediated fractionations, yet the magnitude of the fractionations between atmospheric N2 and organic nitrogen observed exceeds any presently known. We attribute the $^{15}$N-enriched reservoir to a secondary atmosphere derived from CI-chondrite-like material and comets with $\delta^{15}$N of +30 to +42‰. Shifts of $\delta^{15}$N to its present atmospheric value of 0‰ can be accounted for by a combination of early growth of the continents with sequestration of atmospheric N2 into crustal rocks, and degassing of mantle N ~ -5‰.

References


Experimental study of sulfur isotope fractionation associated with pyrite oxidation by H$_2$O$_2$

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Radiolysis of water can accelerate water/rock interaction through production of radicals (e.g., H$,^\cdot$, HO$,^\cdot$, OH$^-$) and reactive molecules (e.g., H$_2$, H$_2$O$_2$, O$_2$). Radiolytic oxidation can be observed in modern groundwater associated with uranium ore bodies and can be inferred for ancient groundwater. Prior to development of an O$_2$-rich atmosphere on Earth, radiolytically generated oxidants could have reacted with pyrite and provided local sources of partially to fully oxidized sulfur species suitable for microbial metabolism.

We evaluated sulfur isotope effects associated with reactions between pyrite and radiolytic oxidants using a series of sealed-quartz-tube experiments run with 60 mg of acid-cleaned pyrite, 10 ml of deoxygenated water, and concentrations of H$_2$O$_2$ at micromolar levels. Experiments ranged in temperatures from 4 to 150ºC and had durations from 1 to 10 days.

In initial experiments, primary oxidation products were dissolved sulfate, elemental sulfur, iron sulfate minerals, and iron oxyhydroxide minerals. X-ray diffraction patterns and images from scanning electron microscopy reveal anhedral to subhedral hydrated iron sulfates in globular clusters of about 10-30 µm in diameter forming on pyrite surfaces. $\delta$S$^{34}$ was 0.5-1 permil and $\Delta$sulfate-pyrite was 1-2 permil. Our results indicate that pyrite oxidation by H$_2$O$_2$ induces greater fractionation that has been recognized in previous studies. Although $\Delta$ values for sulfates and elemental sulphur are not large, compensating depletion of $^{34}$S in undetected products could be substantial if the proportional yields are small. Preliminary isotope results from high-temperature experiments indicate that the $^{34}$S-depleted fraction might be held in iron sulfate and/or iron oxyhydroxides.
Carbon isotope variations of carbon deposits synthesized in the laboratory by arc discharge

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Carbon has many allotropes such as diamond, graphite, fullerene, etc. Such carbon allotropes are important in the noble gas study because they could be good noble gas carriers in meteorites. In fact, the presolar diamond (host phase of HL noble gas component) and Q (host phase of normal noble gas component) are carbon phases. Heymann (1986) also suggested that fullerene could be a noble gas carrier in carbonaceous chondrites. Thus, it is very important to study the trapping efficiency of noble gases in carbon at the syntheses. The isotope effect of carbon itself should be also very important.

Thus we newly set up a new apparatus to synthesize the carbon deposit including fullerene under noble gas atmosphere. The method is so-called “arc method” which is widely used to make fullerene. We use graphite as electrodes and apply 0-30V and 0-170A electric power to have an arc discharge. The graphite of anode is vaporized by the bombardment of electrons, and deposits on the cathode and the discharge. The graphite of anode is vaporized by the bombarding of electrons, and deposits on the cathode and the surrounding wall as soot under noble gas atmosphere. We collect carbon soot from the wall for our experiment. We made these syntheses under various experimental conditions, and measured carbon isotopic ratios and the trapping efficiency of noble gases in the carbon soots.

The interesting result is obtained in carbon isotopes. Our preliminarily results suggest that there were about several permil difference of carbon isotopes between the carbon soots deposited at the different place inside the apparatus. We had thought that there should be no isotope difference for the sample that was vaporized at such high temperatures. There might be some isotopic effect at the deposition or during the frying of vaporized carbon. It is likely that light carbon flies in the long distance inside the apparatus.

Reference


Lu-Hf systematics of the earliest crust in Antarctica: The Napier Complex of Enderby Land

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We have conducted Lu-Hf systematics of mineral separates and whole-rock samples from the Napier Complex of the East Antarctic Shield in order to constrain Archean crustal and mantle evolution and to assess the robustness of Lu-Hf isochrons during UHT metamorphism. Evidence that at least portions of the Earth’s mantle were already chemically depleted before formation of the oldest surviving crust comesfrom Sm–Nd isotopic data However, doubts have arisen because the Sm-Nd system can be perturbed by younger events. Our measurements on individual zircon grains have yielded a remarkably uniform range of initial $^{176}$Hf/$^{177}$Hf values between 0.280399 ± 5 and 0.280469 ± 7. Because the samples were collected from different localities and in different rock types, it had been assumed that they would have a wide range in isotopic compositions, indicating a complex history of mantle melting and crustal recycling. Instead, these results now indicate that the source of the crustal materials that formed the Napier Complex at 3.8 Ga were depleted relative to the chondritic uniform reservoir, or CHUR. Moreover, the results demonstrate that even the silicic rocks in the Napier Complex are juvenile products of mantle melting or are remobilized crustal materials recycled on a very short timescale.

Measurement of Lu-Hf isotopic compositions for garnet, opx, sapphire, omulite, rutile and whole rock samples from several localities in the Napier Complex have yielded isochrons with ages between 2459 ± 23 Ma and 2173 ± 37 Ma with rather uniform initial ratios between 0.280876 and 0.280884. Although the calculated errors are larger than those often obtained from zircon U-Pb dating, it should be noted that they are only slightly larger than one percent. Besides producing isochrons, one major contribution of this work has been demonstration of what happens to the Lu-Hf system at the mineral and whole-rock scale during ultra high temperature (UHT) metamorphism. The main rock-forming minerals record an initial Hf ratio acquired during metamorphism while zircons “see through” this event and record the initial ratio of the rocks acquired at the time of crystallization.
Rare earth elements in the core?

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Introduction

It was traditionally assumed that all REE are in the silicate geosphere only and that in Sm-Nd system the Bulk Earth corresponding to chondrites is identical to the Bulk Silicate Earth (BSE). But these assumption have never been proved. The objective of this study was to check them and find out if the Earth core can contain REE.

Results

The mantle xenoliths which judging by HREE concentrations, Al₂O₃/MgO and CaO/Al₂O₃ in them are identical to chondrites, and hence to a primitive mantle, were studied. Model Pb-Pb isotope ages (TCHUR) of such xenoliths correspond to 4510±30 Ma. At the same time εNd and ⁸⁷Sr/⁸⁶Sr in these xenoliths are typical of the MORB source.

Discussion

The results evidence that the MORB source composition in not really identical to DM but to BSE or, which is the same, to per geochemically primitive mantle. It means that deficit of LREE in the MORB source displayed by the value εNd=+10 arose at the earliest stage of the planet evolution and is not connected with formation of the crust or EM, as it was traditionally assumed. Accordingly, all kinds of the mantle material having εNd < +8 have to be considered as an EM. The DM (εNd=+12) is petrogenetically fruitless, has no volcanic derivatives and is represented only with xenoliths. Moreover, if the ratios of refractory elements such as REE, in initial planetary material in reality corresponded to those in chondrite one, just kipping the balance requires that deficient LREE in BSE be concentrated in the Earth core as a complementary reservoir. It is supported by the presence of phosphates and phosphides enriched with REE in irons [1]. So, the most probably the core is not an inert reservoir for REE.

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Reference


NANO-SIMS U-Pb dating of monazite

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We have developed ²³⁸U-²⁰⁶Pb and ²⁰⁷Pb-²⁰⁶Pb dating method of monazite by using a NanoSIMS NS 50 ion microprobe installed at Ocean Research Institute, The University of Tokyo. A ~4 nA O primary beam was used to sputter a 5-µm-diameter crater and secondary positive ions were extracted for mass analysis using a Mattauch-Herzog Geometry. Multi-collector system was modified to detect ¹⁴⁶Ce, ²⁰⁴Pb+, ²⁰⁶Pb+, ²³⁸U⁺, and ²⁰⁸Pb⁺ ions at the same time. A mass resolution of ~5500 at 10% peak height was attained with a flat peak top, while the sensitivity of Pb was about 4 cps/1nA/ppm. A monazite from North-Central Madagascar with a U-Th-Pb chemical age [1] of 525.2±8.2 Ma (2σ) obtained by EPMA was used as the standard for Pb/UO²⁻ - UO₂⁻/UO²⁻ calibration. There is a positive correlation between the Pb/UO²⁻ and UO₂⁻/UO²⁻ ratios of the standard. A simple linear regression was more appropriate than the quadratic relation to fit the trend. The ²⁰⁶Pb/²⁰⁴Pb ratios were measured by a magnet scanning.

U-Pb ages of 44 monazite grains extracted from a sedimentary rock in Western foothills of Taiwan were analyzed. Observed ages were compared with the U-Th-Pb chemical ages of the same sample [2]. ²³⁸U-²⁰⁶Pb ages agree well with those of the chemical except for a few samples. The discrepancy may be due to common Pb effect by an over-estimation of radiogenic Pb by the chemical age. The ²⁰⁷Pb-²⁰⁶Pb ages also agree with the chemical age while there are a few discordant samples in addition to several samples with common Pb signature. Taking into account of concordant samples, there are three main age groups, 230Ma, 440Ma and 1850Ma. The age distribution suggests that the provenance of detrital monazites is possibly North China Craton [3,4].

References

Comparative stable Fe isotope systematics of terrestrial and meteoritic materials

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Thus far, variations in $\delta^{56}$Fe values reported for chondrules from carbonaceous and ordinary chondrites (Zhu et al., 2001) and between bulk samples of HED meteorites, chondrites, Mars, Moon and Earth (Poitrasson et al., 2004) were interpreted by a number of different processes. These include Fe isotope fractionation through partial Fe evaporation and condensation, physical metal-silicate differentiation, and low-temperature aqueous alteration on the parent bodies. The aim of this study was to investigate (1) to what extent intra-planetary and inter-planetary processes may be responsible for the variability of Fe isotope signatures of planets and planetesimals and (2) whether trace element patterns of chondrules and CAIs that are related to condensation correlate with their Fe isotope variabilities.

A comprehensive set of new high-precision Fe isotope data (Schoenberg et al., 2005) of 15 bulk chondrites, 15 iron meteorites, 8 eucrites, 20 terrestrial rocks as well as chondrules and CAIs from carbonaceous and ordinary chondrites will be presented. Within student-t test limits the three chondrite groups remain indistinguishable from each other and have an average $\delta^{56}$Fe value of $-0.023\pm0.104\%$ (2 S.D.) relative to the IRMM-014 Fe standard. However, student-t statistics also reveal that chondrites, eucrites ($-0.002\pm0.024\%$), iron meteorites ($+0.035\pm0.078\%$), and terrestrial silicate rocks ($+0.085\pm0.080\%$) analysed here have discernible, different Fe isotope compositions at a high level of confidence. The meteorite data suggest that preferentially heavier Fe isotopes were incorporated into metal cores during metal-silicate differentiation. Therefore, this process cannot be the cause for the slightly elevated $\delta^{56}$Fe values of terrestrial silicate rocks compared to bulk chondrites. We reproduce the wide Fe isotope fractionation in CAI and also show that chondrules form different chondrites are variably fractionated in Fe. Trace element data for chondrules and CAI show that those with the most anomalous refractory element abundances tend to also be strongest fractionated in Fe.

References