Heterogeneous Hadean Hafnium: Evidence of Continental Crust at 4.4 to 4.5 Ga

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The long-favored paradigm for the development of continental crust is one of progressive growth beginning at ~4 billion years ago (Ga). To test this hypothesis, we measured initial 176Hf/177Hf values of 4.01- to 4.37-Ga detrital zircons from Jack Hills, Western Australia. ε176 (deviations of 176Hf/177Hf from bulk Earth in parts per 10^4) values show large positive and negative deviations from those of the bulk Earth. Negative values indicate the development of a Lu/Hf reservoir that is consistent with the formation of continental crust (Lu/Hf = 0.01), perhaps as early as 4.5 Ga. Positive ε176 deviations require early and likely widespread depletion of the upper mantle. These results support the view that continental crust had formed by 4.4 to 4.5 Ga and was rapidly recycled into the mantle.

A fundamental question of Earth’s evolution is: When did the growth of continental crust begin? One model is that the first crust formed after 4 Ga and grew slowly until the present day (1, 2). This view reflects the absence of a >4-Ga rock record (3) and the broadly coherent post-4 Ga evolution of depleted mantle 143Nd/144Nd (4) and 174Hf/177Hf (5). Long-standing observations of early Nd (6) and Hf (7, 8) depletions, however, leave open the possibility of even earlier global frac-tionations. Another view (9, 10) is that continental crust was widespread during the Hadean Eon [the first 500 million years (My) of Earth history]. In such a scenario, the lack of direct evidence of earlier depletion events reflects subsequent remixing. Detrital zircons from Jack Hills, Western Australia, with 4.0- to 4.4-Ga U-Pb ages (11–13) represent pieces of crust that have been sequestered for up to ~4.4 Ga. Hf isotopic compositions vary because of radioactive decay of 176Lu, and such variations in zircons constitute an excellent tracer of Earth’s crust/ mantle differentiation. This is because zircons have very low Lu/Hf ratios and thus record near-initial 176Hf/177Hf at the time given by their U-Pb age. Amelin and co-workers (14) investigated Hf isotopes in Jack Hills zircons as old as 4.14 Ga and inferred the existence of reworked Hadean crust. We have now extended this application by undertaking Lu-Hf analyses of grains ranging in age up to 4.37 Ga, thereby narrowing the gap to less than 200 My from the end of Earth’s accretion to the first mineral record. We document significant Hf isotopic heterogeneity during the early Hadean and conclude that major differentiation of the silicate Earth, possibly the formation of continental crust with a volume similar in magnitude to the present day, may have occurred by 4.4 to 4.5 Ga.

Using the multicollector Sensitive High Resolution Ion Microprobe Microscope, we have surveyed the radiogenic 207Pb/206Pb (207Pb/206Pb*) ratio

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References and Notes
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of over 50,000 Jack Hills zircons separated from a large conglomerate sample (JH992) obtained from the original locality of Compston and Pidgeon (11). Hadean grains thus identified were dated by the U-Pb method (11–13). Zircons between 4.01 and 4.37 Ga were then analyzed for Lu/Hf and Hf isotopic composition (tables S1 and S2). Although 207Pb/206Pb* ages can be variable within Hadean zircons (11–13), it is rarely the case (15) that an individual grain exhibits more than two generations of crystal growth. In the cases of concordant or nearly concordant (<12% discordant) results, we assume that the 207Pb/206Pb* age records the time of crystallization, which we then use to calculate e_Hf(T), where T is age. For grains that showed evidence of zoning or yielded apparent e_Hf(T) values that strongly deviated from those of bulk Earth, we undertook additional ion microprobe dating investigations to assess whether multiple generations of zircon growth were present (table S2 and fig. S2).

Of the 104 multicollector–inductively coupled plasma–mass spectrometry (MC-ICP-MS) zircon 176Hf/177Hf results we present, 44 were measured by solution MC-ICP-MS (table S1) (16) and 60 by laser ablation MC-ICP-MS (table S2) (16). We deliberately used both approaches, because each has potential limitations that are in part compensated for by the other. Solution MC-ICP-MS provides a bulk Hf isotopic composition, but does not suffer from isobaric interferences on 176Hf from Yb and Lu. Although laser ablation MC-ICP-MS measurements require peak stripping to correct for Yb and Lu interferences on 176Hf, they allow spatially resolved analysis using spots of 60 to 80 μm in diameter, which facilitates the identification of zircons zoned with respect to 176Hf/177Hf. Because these analyses retain some of the zircon under analysis, subsequent ion microprobe investigations of potential age heterogeneity are possible.

We calculated e_Hf(T) using the “terrestrial” 176Lu decay constant (λ176) of 1.867 ± 0.008 × 10^-11 year^-1 ([17] and references therein) and the present day chondritic parameters 176Lu/177Hf = 0.0332 ± 0.0002 and 176Hf/177Hf = 0.282772 ± 29 (18) [λ176] and solar system initial 176Hf/177Hf deduced from meteorite Lu-Hf isochrons appear to reflect irradiation effects in the solar nebula (19). Using the chondritic averages of Patchett and co-workers (20) instead would not significantly change our calculated values of e_Hf(T) because their 176Hf/177Hf and Lu/Hf values all fall on the same 4.5-Ga isochron as those in (18).

Our data (tables S1 and S2) show a high degree of Hf isotope heterogeneity, with variation in e_Hf(T) values at 4.2 Ga of over 20 ε units. Before we examine the geological significance of these data, we investigate possible artifacts of combined interpretation of Lu-Hf and U-Pb systematics in a complex zircon population that could lead to incorrect inferences of early deviations from chondritic evolution. A key link in using zircon to assess initial Hf isotopic ratios is that the age ascribed accurately reflects the time at which the Hf isotopic composition was incorporated into the zircon. In the case of a zircon zoned in U-Pb age, relating an older age component to the bulk Hf isotope composition could result in an incorrect estimate of e_Hf(T).

For example, consider the case of grain CU05 8.5, which yields an ion microprobe age of 4123 ± 18 Ma and age-corrected solution MC-ICP-MS 176Hf/177Hf = 0.280415 ± 0.000015 (2 SE) (table S1), corresponding to an apparent e_Hf(T) = +10.7 ± 0.5. However, because the bulk solution ICP-MS 207Pb/206Pb* age is only 3624 Ma (21), we infer that this grain is substantially heterogeneous with respect to age and that the 4.1-Ga ion microprobe date represents only a small portion of the total U-Pb system. If we instead use the bulk 3.62-Ga age, the apparent e_Hf drops to a near-bulk Earth value of +1.2 ± 0.5. We thus eliminated this sample from further consideration.

Less obvious is that mixtures of concordant components with contrasting U concentrations each plotting on bulk Earth could also yield substantial positive and negative deviations in e_Hf(T). This is because of the strongly nonlinear relationship between 207Pb/206Pb* (or Pb/U) and age, whereas the long half-life of 176Lu resulted in essentially linear growth in 176Hf/177Hf over the past 4.56 Gy. To assess this effect, we developed a model in which concordant core (T1) and rim (T2) ages are characterized by e_Hf(T) at T1 and T2, respectively. If the bulk age of this composite is characterized by a U-Pb date obtained by ion microprobe spot analysis in the core, but associated with a 176Hf/177Hf ratio that is a mixture of the two end-members, the potential exists for incorrect e_Hf values to be calculated. More surprising is that in the case where U-Pb age and Hf isotopes are measured on the same spot overlapping these two zones, aberrant values result, as shown in the mixing curves.
For many grains analyzed by laser ablation MC-ICP-MS, further age investigations are possible, because the method is not completely destructive, compared with solution chemistry. Grains with calculated $\varepsilon_{180}$ that differ from bulk Earth by more than 5 $\varepsilon$ units were, where sufficient sample remained, redated near their rims to assess age homogeneity. In the majority of cases, $^{206}\text{Pb}/^{206}\text{Pb}^*$ ages were reproduced at a satisfactory level (table S2). In one case (RSES17 2.9), we were able to resolve a time-dependent $^{176}\text{Hf}/^{177}\text{Hf}$ signal that dropped by 4 $\varepsilon$ units upon penetrating a 3469 $\pm$ 12-Ma rim from a 4127 $\pm$ 64-Ma core, yielding $\varepsilon_{180}(13 \text{ Ga}) = 10 \pm 1.3$ (table S2 and fig. S1).

Where rims are demonstrably younger than core ages, we were able to rule out mixing between domains by the lack of a time-resolved variation in the $^{176}\text{Hf}/^{177}\text{Hf}$ signal and by visual evidence from imaging studies. Even where mixing may have occurred below our ability to resolve time variations in $^{176}\text{Hf}/^{177}\text{Hf}$, we have shown that the relationship between U concentrations in the core [82 parts per million (ppm)] and rim (440 ppm) would likely increase the estimated value of $\varepsilon_{180}$ if a portion of the rim had inadvertently been included in the analysis. Thus, the value of $\sim$ +15 is a minimum estimate of the true $\varepsilon_{180}$ of the grain core.

In four cases, measured $^{174}\text{Hf}/^{177}\text{Hf}$ and $^{178}\text{Hf}/^{177}\text{Hf}$ were outside accepted values (16), and these data were eliminated from consideration. Figure 2 shows the results for which we are confident that all the aforementioned effects have not affected the true $\varepsilon_{180}$ values. Concordant or near-concordant results are shown as solid symbols, whereas $\sim$12% discordant results are shown as open symbols. The diagonal line extending into the negative $\varepsilon_{180}$ field from an age of 4.5 Ga, labeled Lu/Hf $= 0$, demarcates the “forbidden region,” corresponding to Lu/Hf $< 0$. Data plotting near this line must have been derived from an environment in which Lu was essentially completely fractionated from Hf shortly after Earth formation. If that event was the formation of continental crust, then the average continental crust $^{176}\text{Lu}/^{177}\text{Hf}$ value of $\sim$0.01 (23) is a more appropriate comparator. The many results that plot along this line require formation of an enriched reservoir by 4.4 to 4.5 Ga.

Positive $\varepsilon_{180}$ deviations observed in the same age interval have not previously been documented (14) and imply derivation from reservoirs with high Lu/Hf ratios. These data almost surely reflect the rapid development of depleted mantle with single-stage $^{176}\text{Lu}/^{177}\text{Hf}$ ratios within the possible range of values (0.05 and 0.2) for rocks residual from mantle melting (24). Whereas the depleted signature we observe is roughly symmetrical with the enriched reservoir (Fig. 2), negative $\varepsilon_{180}$ values outnumber positive $\varepsilon_{180}$ by 2.5:1. This is in part expected, because rocks originating from a source with a depleted signature are less petrogenetically suited to crystallizing zircon.

Most models for the growth of continental crust have emphasized delayed, slow growth (1, 2, 4). The existence of Hadean Jack Hills zircons has been known for 20 years (11) but has been largely considered as a curiosity rather than a fundamental record of the origin of continental crust (25). Investigations of Jack Hills zircons ($^{88}\text{O}$, inclusion assemblages, zircon thermometry (12, 13, 26–28)) indicate that the vast majority formed in a continental environment (26) characterized by two forms of convergent margin magmatism (crustal anatexis and calcalkaline magmatism at or close to water saturation) throughout the Hadean. Together, these data indicate that Earth was experiencing continental crust formation during the Hadean and that a mature sediment recycling system similar to that of the known era of plate tectonics had developed by $\sim$4.4 Ga.

Jack Hills zircons are largely of continental origin (12, 13, 26–28), and our preferred interpretation of the variation of $\varepsilon_{180}$ (Fig. 2) is that a major differentiation event occurred at 4.4 to 4.5 Ga, producing continental crust and a complementary depleted mantle reservoir. Because the production of modern continental crust is intimately connected with orogenic magmas, our interpretation implies that plate boundary interactions may have begun within the first $\sim$100 My of Earth history. If the relative fraction of depleted versus enriched samples (Fig. 2) is representative of the general ongoing process, the volume of depleted mantle must have been a substantial fraction of the silicate Earth.

Positive $\varepsilon_{180}$ deviations of $+15$ at $\sim$4.2 Ga imply a reservoir with Lu/Hf of $\sim$0.1 (Fig. 2). This extrapolates to $\varepsilon_{180}$ of over $+200$ today, whereas values as negative as $\sim$7 at 4.2 Ga project to $\varepsilon_{180}$ of about $-100$. No evidence for these reservoirs has yet been recognized in the post-Hadean rock record (5, 29). Although it is conceivable that such reservoirs exist but have remained hidden for 4 Gy (30), their disappearance is well explained by the recycling of continental crust during the Hadean at rates $\sim$10 times greater than those at present (9, 31), coupled with vigorous stirring in a hotter and thus less-viscous mantle.

Armstrong (9) emphasized that all large terrestrial planets, including Earth, must have immediately differentiated into relatively constant volume core, depleted mantle, enriched crust, and fluid reservoirs. Recent investigations of $^{142,143}\text{Nd}/^{144}\text{Nd}$ variations indicate that a major silicate differentiation event occurred within 50 to 150 My (32, 33), and possibly even...
within 30 My (30) of Earth’s formation. Our results support the view that continental crust was at least a component of the enriched counterpart that formed at ~4.5 Ga, but this original crust was largely recycled back into the mantle by the onset of the Archean (<4 Ga).

References and Notes
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X-ray Structure of the EmrE Multidrug Transporter in Complex with a Substrate
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EmrE is a prototype of the Small Multidrug Resistance family of efflux transporters and actively expels positively charged hydrophobic drugs across the inner membrane of *Escherichia coli*. Here, we report the x-ray crystal structure, at 3.7 Ångstrom resolution, of one conformational state of the EmrE transporter in complex with a translocation substrate, tetrathenylphosphonium. Two EmrE polypeptides form a homodimeric transporter that binds substrate at the dimerization interface. The two subunits have opposite orientations in the membrane and adopt slightly different folds, forming an asymmetric antiparallel dimer. This unusual architecture likely confers unidirectionality to transport by creating an asymmetric substrate translocation pathway. On the basis of available structural data, we propose a model for the proton-dependent drug efflux mechanism of EmrE.

A major obstacle to effective treatment of bacterial infections is the emergence of strains that are resistant to available antibiotics. Of particular concern are multidrug-resistant strains that cause common diseases such as tuberculosis, gonorrhea, and hospital-acquired staphylococcal infections (1). Multidrug resistance arises, in part, through the action of integral membrane proteins called multidrug transporters (1, 2). Each of these transporters can actively expel a wide variety of drugs and toxic compounds from the cell. There are two broad classes of transporters: ATP-binding cassette (ABC) proteins directly couple drug efflux to adenosine 5’-triphosphate (ATP) hydrolysis, whereas secondary transporters use the energy derived from proton or cation electrochemical gradients across the lipid bilayer.

EmrE is a prototype secondary transporter from *Escherichia coli* and is a prototype of the Small Multidrug Resistance (SMR) family (3, 4). SMRs represent the smallest transporters in nature; each polypeptide has only 105 to 120 amino acid residues and four transmembrane helices, and forms homo- or hetero-oligomers (3). EmrE is well documented to function as a homooligomer (3–9) and confers resistance to positively charged hydrophobic antibiotics, such as tetracycline, ethidium, and tetrathenylphosphonium (TPP) (3, 4). EmrE exchanges two or more protons per drug molecule through a “hydrophobic” translocation pathway (10, 11).

The general model for multidrug efflux by EmrE and other secondary transporters is the alternating access mechanism (12, 13). In this model, the EmrE transporter has at least two conformations, inward-facing and outward-facing, with the drug-binding site accessible to the cytoplasm or periplasm, respectively. Interconversion between the two conformations is promoted by drug and/or proton binding. Here, we describe the x-ray crystal structure of one conformation of the EmrE transporter in complex with the drug TPP. The structure was determined to 3.7 Å resolution by anomalous dispersion methods, using the arsine analogue of TPP and selenomethionine (SeMet)–substituted proteins (Fig. 1A) (14).

SeMet-labeled proteins used for this study were produced in a cell-free system, because SeMet-EmrE did not express well in vivo. Briefly, EmrE was expressed by use of the T7 promoter in *E. coli* lysates supplemented with nucleotide triphosphates, T7 polymerase, and appropriate amino acids (14). Experimental maps derived from Se and As data are very well correlated, indicating that in vitro- and in vivo-expressed EmrE proteins adopt a similar structure. Our work shows that cell-free methods are a viable alternative to traditional large-scale protein expression systems.

Consistent with biochemical studies showing that EmrE is primarily a dimer in detergent and binds drugs with a 2:1 protein/drug ratio (9, 15), the asymmetric unit of the EmrE-TPP crystal is composed of two molecules of EmrE and one molecule of TPP (Fig. 1). The minimally functional unit of EmrE is therefore
Editor's Summary

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