

GEOCHEMISTRY

Identifying remnants of early Earth

Isotope analysis reveals portions of Earth that have remained the same since accretion

By Tais W. Dahl

The chemical composition of Earth's mantle can tell us how our planet formed and how subsequent mantle dynamics have since homogenized the mantle through convective processes.

Most terrestrial rocks have a similar tungsten (W) isotope composition (1), but some rocks that have been dated at 2.8 Ga (billion years old) (2), 3.8 Ga (3), and 3.96 Ga (4) have elevated $^{182}\text{W}/^{184}\text{W}$ ratios. This is reported as $\mu^{182}\text{W}$, in parts per million (ppm) deviation from the bulk silicate Earth. Until now, the outliers have included only these ancient rock samples with a small $\mu^{182}\text{W}$ excess (≤ 15 ppm) that can be attributed to the final $\sim 0.5\%$ of Earth's mass that accreted late in its accretion history. On page 809 of this issue, Rizo *et al.* (5) report W isotope data from young mantle-derived rocks with $\mu^{182}\text{W}$ excesses of 10 to 48 ppm. This result is spectacular because the range of $\mu^{182}\text{W}$ values in mantle-derived rocks is larger than can be accommodated by late accretion; the implication is that remnants of Earth's earliest mantle have been preserved over the entirety of Earth's history.

Two decades ago, geochemists started measuring W isotopes in terrestrial and meteoritic samples to estimate the timing of Earth's core formation (6). During core formation, it is presumed that W preferentially partitioned into the metal melt and sank to the core, whereas hafnium (Hf) remained in the silicate mantle. Therefore, the silicate mantle has a higher Hf/W ratio. As ^{182}Hf decayed to ^{182}W with a half-life of 8.9 million years, the silicate mantle developed ^{182}W excesses relative to its source material. Most of

the $\mu^{182}\text{W}$ variability in the solar system is produced by the separation of metal from silicate during the first 60 million years of solar system history. As a point of reference for calibration, mantle material would have gained a $\mu^{182}\text{W}$ excess of >1000 ppm if Earth and its core formed at the very beginning of our solar system. The mantle, however, displays a nearly uniform $\mu^{182}\text{W}$ excess of $+200$ ppm relative to primitive meteorites, which

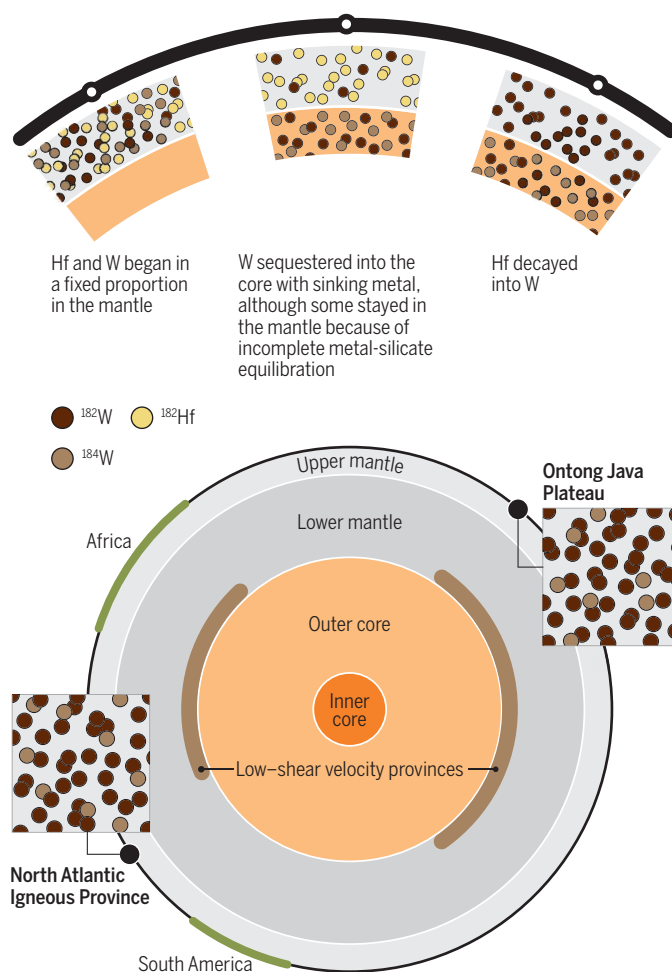
suggests that the last metal-silicate equilibration event occurred ~ 30 million years into the history of our solar system.

The Moon formed after ^{182}Hf went extinct ~ 4.51 billion years ago. This inference is based on the tiny $\mu^{182}\text{W}$ excess in the Moon relative to Earth's mantle, $+20$ ppm (7). The small ^{182}W excess may well have developed by disproportionate late accretion on Earth and the Moon (7), where the addition of nonradiogenic material had a greater effect on Earth.

The new data from flood basalt lavas that erupted into the North Atlantic Igneous Province (Baffin Bay locale) and the Ontong Java Plateau (western Pacific Ocean) show larger $\mu^{182}\text{W}$ variability than between the Moon and Earth's mantle. In fact, the mantle source of the Ontong Java and Baffin Bay lavas prior to late accretion probably had a radiogenic W excess of $+70$ ppm. This exceeds what can be accomplished by late accretion. By implication, these parts of Earth's mantle predate the Moon and did not chemically equilibrate metal and silicate during the giant impact that formed the Moon.

W isotope heterogeneity in the mantle is likely to arise during the late stages of planet accretion. The planet accreted from dozens of collisions between differentiated bodies with metallic cores and silicate mantles, all with potentially unique W isotope compositions (8). The cores contained nonradiogenic W, whereas the radiogenic counterpart was hosted in their mantles. As the planet accreted, Earth's silicate mantle would have lost both radiogenic and nonradiogenic W to its core, assuming that an appreciable portion of each impactor's metal core disintegrated into smaller blobs and mixed down to diffusion-length scales where chemical equilibration occurred.

Several factors may lead to mantle heterogeneity. First, the



Equatorial cross section of Earth. Large low-shear velocity provinces (LLSVPs) occur at the base of the mantle under Africa and the Pacific Ocean. Flood basalts erupted at the North Atlantic Igneous Province and the Ontong Java Plateau show substantial radiogenic W excess relative to rest of the mantle. This compositional heterogeneity may preserve remnants after incomplete metal-silicate equilibration during Earth's core formation in the first 60 million years of solar system history. The chemical heterogeneity may have been preserved in LLSVPs at the base of the mantle for more than 4.5 billion years.

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far-side effect generates heterogeneity on a hemispherical scale, because an impact hits only one side of the planet. Second, portions of the mantle may have been isolated from mixing with the rest of the mantle. Perhaps such a hidden reservoir has existed at the base of the mantle (see the figure). Alternatively, self-gravitating cores may have plunged through the mantle without appreciable emulsification, thus preventing enough metal to mix with the silicate mantle down to small enough length scales for chemical equilibration to occur (9).

What is surprising is that such an initial W isotope heterogeneity could be preserved in the mantle today. The mantle source reservoir for the flood basalts is a matter of contention. One candidate is the large low-shear velocity provinces (LLSVPs) at the base of the mantle (see the figure). These regions consist of dense, hot material (10) and are thought to be stable at their present antipodal position on the core-mantle boundary close to the equator (11). Rizo *et al.* suggest that these regions have existed for essentially all of Earth's history.

Previous analyses of oceanic basalts thought to be derived from deep mantle plumes, including samples from the Ontong Java Plateau, found no ¹⁸²W excesses (± 5 ppm) (2). If we accept both studies at face value, then the chemical heterogeneity apparently exists within a single source domain, excluding W heterogeneity created by the far-side effect.

Future studies must first rule out the possibility of analytical artifacts, because several processes may obscure high-precision isotope analyses of W poor samples (for example, lavas), including isotope fractionation in the laboratory, contamination, and interferences. In the end, identifying primitive signatures in Earth's mantle today elucidates the style of Earth's core formation and requires certain parts of the mantle to stay sufficiently buoyant to escape convective mixing throughout essentially all of Earth's geodynamical history. ■

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10.1126/science.aaf2482

EVOLUTION

Toward a prospective molecular evolution

Fitness landscapes provide a prospective understanding of chance and necessity in evolution

By Xionglei He and Li Liu

The field of molecular evolution is concerned with evolutionary changes in genes and genomes and the underlying driving forces behind those changes. Current studies in molecular evolution are almost entirely retrospective, with a focus on the mutations that were fixed during evolution, and the conclusions are often explanatory, offering no predictive insights. Because only a tiny fraction of all mutations that have ever occurred during evolution have been fixed, the “successes” that we see today provide an incomplete or even biased

“One of the most intriguing aspects of a fitness landscape is...the interactions seen between mutations.”

understanding of the evolutionary process. One way to circumvent this problem is to obtain the whole fitness landscape of a gene to understand, prospectively, chance and necessity in evolution (see the figure). Two studies in this issue, by Li *et al.* on page 837 (1) and Puchta *et al.* on page 840 (2), each take on this challenge by characterizing the *in vivo* fitness landscape of two RNA genes.

The enormous mutational space of a typical gene poses a considerable challenge to the characterization of fitness landscapes. For example, there are a total of 4¹⁰⁰ (or 10⁶⁰) possible variants for an RNA gene of 100 nucleotides, and 20¹⁰⁰ (or 10¹³⁰) for a protein of 100 amino acids. The advent of second-generation DNA sequencing goes some way toward addressing this problem. For example, in 2010 a pioneering study used second-generation DNA sequencing to measure the *in vitro* biochemical activities of millions of variants of a gene (3). Li *et al.*

and Puchta *et al.* both go one step further than this *in vitro* study. Li *et al.* generated a library comprising >65,000 mutant alleles of a 72-nucleotide transfer RNA (tRNA) gene of the yeast *Saccharomyces cerevisiae*. They then competed all the yeast strains—each carrying a different allele of the tRNA gene—in a liquid coculture. The frequency of each allele was determined by sequencing the amplicons of the target tRNA gene pool. The increase or decrease in the frequency of a mutant allele relative to the wild-type allele during the competition represents the relative fitness of the allele. In the second study, Puchta *et al.* adopted largely the same strategy and estimated the relative fitness of ~60,000 mutant alleles of a 333-nucleotide small nucleolar RNA (snoRNA) gene, also in yeast. Although the number of mutants they examined is still a small fraction of all possible variants of the genes, most of the possible genotypes that differ from the wild-type by one or two point mutations were characterized. Thus, a high-quality local fitness landscape of a gene has been constructed.

The capability to map large fitness landscapes opens the door to study gene evolution prospectively. Both studies used the landscape constructed to understand the various conservation levels of different sites in the two RNA genes. The same idea could be applied to the study of among-gene differences in evolutionary rate. An outstanding question here is why expression level acts as the most important determinant of sequence conservation (4). Mapping fitness landscapes of the same gene expressed at different levels, or different genes expressed at the same level, by manipulating promoter activity would help test many competing hypotheses (5).

One of the most intriguing aspects of a fitness landscape is epistasis, or the interactions seen between mutations. Both studies observed widespread epistasis, especially negative epistasis, meaning that the combined deleterious effect of two harmful mutations is greater than that expected from the individual mutations (6). Sign epistasis (7), where a deleterious mutation becomes beneficial in the presence of another mutation, is of special interest because it can generate fitness peaks that trap an adapting popula-

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Science **352** (6287), 768-769. [doi: 10.1126/science.aaf2482]

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