

and there are four nuclear spin modifications with different symmetry. This has allowed them to demonstrate yet another subtlety of the interconversion. Because the parity (the symmetry of the wave functions with respect to an inversion in space) is rigorous in atomic and molecular physics, the parity selection rule, unlike the *ortho/para* selection rule, should not be violated in these experiments. In other words, the nuclear spin interaction considered by Wigner and enumerated by Curl *et al.* may mix different spin species but cannot mix parity. This is clearly demonstrated in figure 2 of Sun *et al.* (2). Figure 2A (2) shows that there is an interconversion between the B_{2u} and B_{3u} species, and figure 2B shows that there is no interconversion between the B_{2u} and A_g species. The symbols g and u represent symmetric and antisymmetric states with respect to the molecule-fixed inversion operation, i.e., interchange of two pairs of H nuclei and inversion of space. However, all rotational functions are g with respect to this operation, and thus it turns out for a planar molecule like ethylene that g and u nuclear spin functions are associated with rotational–nuclear-spin wave functions of + and – parity. Thus, $B_{2u} \leftrightarrow B_{3u}$ conversion in ethylene is parity allowed but $B_{2u} \leftrightarrow A_g$ is parity forbidden, as indeed shown in figure 2 of Sun *et al.* (2).

This leaves an interesting problem to be solved. The authors should be able to determine the magnitude of the interaction term from the observed interconversion rate. In

order to do this, the authors need to locate a pair or pairs of levels with the B_{2u} and B_{3u} symmetry that are accidentally or systematically (9) close through which the conversion proceeds. They also need to estimate collision cross sections that are temperature dependent. Experimentally, it will be interesting to measure the temperature dependence of the conversion rate. Also measuring the conversion rate caused by other gases will be interesting, especially paramagnetic gases such as oxygen. It is well known that *para*-H₂ converts to *ortho*-H₂ much faster in the presence of O₂. The mechanism of such conversion must be different from that considered by Curl *et al.*

Which other molecules will be interesting to study? Benzene, C₆H₆, has spin modifications with six different symmetries: A_{1g} , A_{2g} , E_{2g} , B_{1u} , B_{2u} , and E_{1u} . Here also, the molecule is planar, so one might expect that the parity selection rule will be equivalent to $g \leftrightarrow g$ and $u \leftrightarrow u$. Because rotational levels in this symmetric-top molecule with $K = 6n$ (where $n \neq 0$) systematically consist of very nearly degenerate B_{1u} – B_{2u} nuclear spin pairs, rotational levels with quantum number $K = 6n + 3$ consist of very nearly degenerate A_{1g} – A_{2g} nuclear spin pairs, and the E nuclear spin functions do not cluster, one can further speculate (9) that conversion rates within the nuclear spin A species or within the B species will be much faster than rates between A and E or between B and E species. Ethane, C₂H₆, has spin modifications with seven different symmetries

A_1 , A_4 , E_1 , E_2 , E_3 , E_4 , and G. Because the molecular symmetry group of ethane does not have any element corresponding exactly to inversion in space, the connection between symmetry species and parity is more complicated than for the planar molecules mentioned above. One can thus wonder if permutation-inversion symmetry species together with systematic level clustering will in the end provide a more unified way of discussing allowed nuclear spin conversions than parity together with accidental degeneracies does. In any case, a study of nuclear spin conversion rates in other highly symmetric molecules will almost certainly reveal further subtleties of the mechanism. However, the experiments will become more challenging as one goes to heavier molecules because of the larger rotational partition function.

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GEOCHEMISTRY

A Tale of Early Earth Told in Zircons

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No rock or mineral record has been preserved from Earth's "dark age"—the mysterious time after accretion of the planet about 4560 million years ago. Thanks to a continuous effort to find the oldest pieces of our planet, however, the duration of this unknown era is becoming shorter and shorter. Following the development of modern isotopic dating, the extent of the dark age was established at about 800 to 1000 million years by the discovery of exceptionally old rocks in western Greenland (1). The discovery of still older grains of zircon (zirconium silicate, a common if not very abundant com-

ponent of crustal rocks, and an extraordinarily resilient mineral) in Archean sedimentary rocks in Western Australia reduced the dark age to 400 to 300 million years (2, 3) and recently to less than 200 million years (4), a mere 5% of Earth's life span. That this was an eventful time is clear from studies of the Moon and Mars, where internally driven magmatism and differentiation ceased quickly or slowed down. We know that the processes that shaped further evolution of these bodies—large-scale mantle differentiation and formation of the primary crust—were occurring within the first few hundred million years.

On page 1947 of this issue, Harrison *et al.* (5) report their use of some of the oldest known zircons to explore the prehistory of

the source rocks of these minerals. Their approach relies on the slow radioactive decay of the rare isotope ¹⁷⁶Lu to ¹⁷⁶Hf (half-life 37 billion years). This decay process increases the ratio of ¹⁷⁶Hf to other isotopes of hafnium, usually expressed as ¹⁷⁶Hf/¹⁷⁷Hf. The rate of growth of the ¹⁷⁶Hf/¹⁷⁷Hf ratio is proportional to the Lu/Hf ratio. In geochemical studies, the ¹⁷⁶Hf/¹⁷⁷Hf ratio in a mineral or rock is expressed as a deviation from this ratio in bulk silicate earth (thought to be broadly similar in composition to, and determined from, chondritic meteorites). This deviation is measured in parts per 10,000 and is denoted as $\epsilon_{\text{Hf}}(T)$, where T is time. When primitive mantle differentiates to form continental crust (a cover of less dense aluminum- and silicon-rich rocks) and depleted mantle (the more dense and refractory magnesium- and iron-rich residue left after extraction of crust-forming melts), the depleted mantle acquires a Lu/Hf ratio several times that found in crustal rocks. As a result, the ¹⁷⁶Hf/¹⁷⁷Hf ratio in the mantle grows faster than in the crust and $\epsilon_{\text{Hf}}(T)$ becomes positive, whereas the complemen-

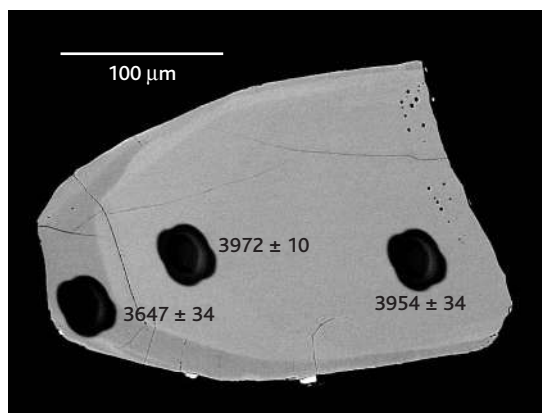
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tary crust develops more and more negative $\epsilon_{\text{Hf}}(T)$. When a melt derived from ancient crust or depleted mantle crystallizes and zircon is formed, the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio in the melt is imprinted in the zircon and remains nearly unchanged over billions of years, owing to the low Lu/Hf ratio and high concentration of Hf in zircon (about 1%). If we measure the present-day $^{176}\text{Hf}/^{177}\text{Hf}$ and Lu/Hf ratios in the zircon crystal and determine the age of the zircon by decay of uranium isotopes to lead, we can trace the growth of the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio backward and determine when primitive mantle separated into crust and depleted mantle. Alternatively, if the time of mantle differentiation is estimated independently, we can calculate the Lu/Hf ratios in the crust and depleted mantle, and try to infer the nature of these early Earth reservoirs by comparing these ratios to the Lu/Hf ratios measured in younger rocks of various compositions.

Most $^{176}\text{Hf}/^{177}\text{Hf}$ values determined by Harrison *et al.* (5) are close to or slightly below the primitive mantle evolution line, as would be expected for crustal rocks extracted from the mantle shortly before formation of the zircons. Some of the oldest zircon grains, however, plot well above or below the primitive mantle evolution line and require extreme fractionation of lutetium and hafnium and very early separation of their source rocks from the primitive mantle, probably around 4500 million years ago—less than 100 million years after the accretion of Earth. This result is interpreted by the authors as evidence for large-scale mantle differentiation and possibly an onset of plate tectonic activity between 4500 and 4400 million years ago. Whether the plate processes operated on a global scale or locally remains to be determined.

The report by Harrison *et al.* opens up many new questions. The first is the possibility that $\epsilon_{\text{Hf}}(T)$ in zircon can be erroneously high or low if the zircon crystal includes domains that grew at different times (see the figure). Coexistence of domains with different ages within one crystal, very common in zircon, is the opposite side of the exceptional resistance of this mineral. If a zircon gets into magma, new layers can grow around the original crystal. The new zircon layer can have a chemical and isotopic composition different from the composition of the original crystal. Because the concentration of uranium and radiogenic lead (the decay product of ura-

nium) can be quite different between the two domains while the concentration of hafnium remains relatively constant, the ages of the two components in a complex zircon crystal do not mix in the same proportion as their hafnium isotopic ratios. The $^{176}\text{Hf}/^{177}\text{Hf}$ ratio in zircon is arrested because of low Lu/Hf, but the $^{176}\text{Hf}/^{177}\text{Hf}$ in the reference reservoir (primitive mantle) evolves more rapidly. Hence, the use of a wrong age produces an erroneous $\epsilon_{\text{Hf}}(T)$ that can mimic mantle differentiation. To avoid this problem, we need to study the



Messenger from an early era. This zircon crystal from Jack Hills, Western Australia (length 0.3 mm) contains a rim that is younger than the central part by 300 million years. The brightness in this image, taken in backscattered electrons, reflects the difference of average atomic mass (heavier is brighter) due to variable concentration of hafnium, uranium, thorium, and rare earth elements—the most common minor components of zircon. The ages (in millions of years) were determined by SHRIMP (sensitive high-resolution ion microprobe) U-Pb analysis, similar to the dating technique of Harrison *et al.* (5). (The black spots are sites of the ion microprobe analyses, where the charge-dissipating gold coating was removed by ion bombardment.)

internal structure and age distribution in ancient zircon in great detail. More reliable hafnium isotope data could be obtained from crystal domains that are shown to be homogeneous. However, analysis of these small crystal domains produces less precise data. Further progress in early Earth studies thus requires more sensitive and precise mass spectrometers for measuring $^{176}\text{Hf}/^{177}\text{Hf}$ ratios.

A fundamental uncertainty is whether the bulk silicate Earth indeed has the same Lu/Hf and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios as the accepted reference that is based on analyses of chondrites. Recent discovery of a difference in the Sm-Nd isotopic system (a geochemical cousin of Lu-Hf) between chondrites and Earth (6) raises the possibility that our planet and undifferentiated asteroids (the source of chondritic meteorites) were assembled from different reservoirs of matter that never completely mixed with each other. Moreover, the Lu/Hf ratios in chon-

drates are variable (7, 8), and this makes choosing the accurate reference value for the bulk Earth even more difficult. The choice of bulk silicate Earth parameters would not change the spread of the earliest hafnium data, but it would change the proportion of those that show enriched crustal versus depleted mantle signatures. It also affects the mass balance of known reservoirs in the present-day Earth. Currently accepted parameters imply that these reservoirs are not in balance, which suggests either that the parameters are wrong or that there is an unknown reservoir that has sequestered lutetium and hafnium. Thus, the key to understanding the evolution of Earth's mantle and continents over time is establishing the precise chemical connection among Earth, meteorites, and the solar system as a whole, represented by the composition of the solar photosphere (9).

A final and perhaps most intriguing question is the mechanism whereby the signatures of extreme differentiation in the mantle-crust system during the first 500 million years were almost completely erased. Although there is some evidence for early differentiation in the oldest rocks, the average $^{176}\text{Hf}/^{177}\text{Hf}$ evolution curve defined by most mantle-derived rocks over the rest of Earth's history diverges from the chondritic curve at about 4 billion years, which is when the rock record begins (10). Something reset the clock on a planetary scale. On the basis of the lunar record, a period of massive meteorite bombardment is thought to have occurred at that time. If so, it must have induced homogenization of mantle and crust on a scale vastly greater than can be explained by recent plate tectonic processes. We are indeed fortunate that the fragmented memory of an earlier time has survived in the form of zircon crystals.

References and Notes

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