

GEOCHEMISTRY

Meteoritic Clues Point Chromium Toward Earth's Core

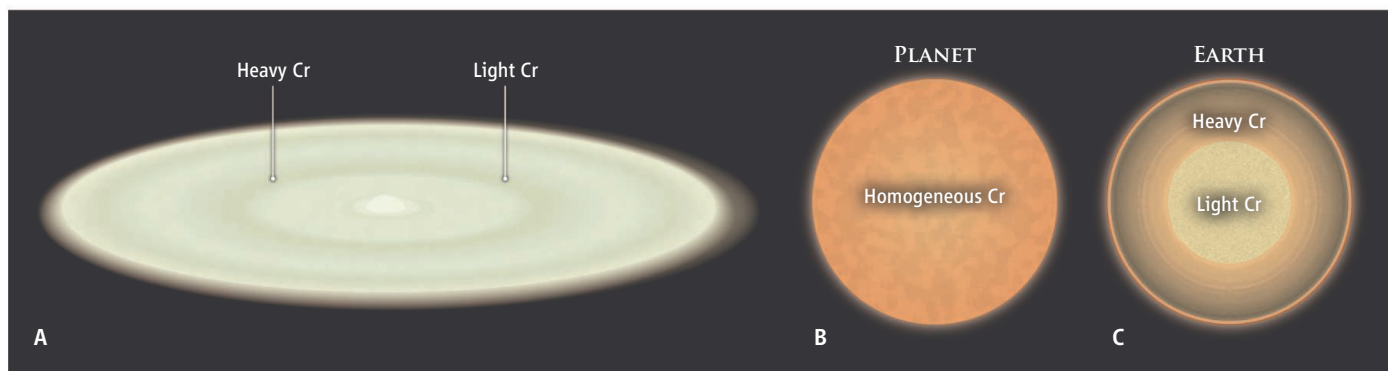
William F. McDonough

Chromium, named for the Greek word for color, is a wonderful element that adds green to emeralds, red to rubies, brilliance to plated metals, and corrosion-proof quality to stainless steels. It is Earth's 10th most abundant element and is distributed almost equally between the metallic core and the rest of the planet. It normally occurs as a trivalent ion (able to form bonds with three other atoms), but there is also an oxidized hexavalent form that is hazardous to life. By studying the distribution of chromium's isotopic forms on Earth and in the solar system, researchers can gain insight into the processes that formed planets and

processing, planetary accretion, and core-mantle separation. Moynier *et al.* reveal that the accessible parts of Earth (the mantle and crust, but not the core) have a chromium isotopic composition that is distinct from that of chondritic meteorites, the primitive, undifferentiated building blocks of the solar system. They assume that Earth's initial planetary composition was similar to these meteorites and conclude that there are now two distinct but complementary compositional domains inside Earth: the accessible portions that we analyze, and the inaccessible core. Moynier *et al.* conclude that this compositional difference is due to a process known as "core

The different chromium isotopic compositions of chondrites and the mantle offer insight into Earth's early history.

explore how material is exchanged between the core and the mantle (5, 6). Core formation chemically fractionated, or redistributed, stable isotopes of silicon and chromium. Tungsten isotopes record the fractionation of hafnium (Hf), which stayed in the silicate Earth, and tungsten, 90% of which was sequestered into the core. The short-lived, now-extinct isotope ^{182}Hf decayed to ^{182}W during the first ~60 million years of Earth history. Due to early core-mantle separation, excess ^{182}W remained in the silicate Earth, leaving it enriched in this isotope compared with primitive meteorites. Collectively, these differences, plus osmium isotopic abun-



produced the differentiation of Earth's core and mantle. On page 1417 of this issue, Moynier *et al.* (1) report that Earth's chromium isotopic composition is distinct from most primitive meteorites, lending support to one explanation for core and mantle formation. They also report that chromium's isotopic composition varies among different groups of meteorites, suggesting that the early solar nebula had at least two components with different isotopic compositions.

The isotopic compositions of materials provide DNA-like fingerprints that researchers can use to identify inorganic objects with shared histories or origins. In chromium, the relative abundance of its four isotopes—50, 52, 53, and 54—provides clues to the element's chemical behavior during nebula

partitioning," rather than an alternative process involving the volatilization of certain chromium isotopes. Core partitioning took place during Earth's early history at high temperatures, when the core separated from the silicate earth, leaving the core with a distinct composition that is enriched with lighter chromium isotopes (see the figure).

The excitement for the earth sciences community is that this finding adds another investigative tool for understanding and documenting past and present planetary processes. For the cosmochemistry and meteoritics communities, the findings further bolster the view that the solar nebula was a heterogeneous mixture of different components.

Over the past decade, studies have found that the isotopic composition of tungsten (W) (2, 3), silicon (4), and now chromium in chondritic meteorites differs from that of Earth's silicate shell (the mantle and the crust). These differences, in turn, provide additional means by which investigators can

Chromium's origins. New evidence suggests that, in the early solar nebula (A), chromium isotopes were divided into two components, one containing light isotopes, the other heavy isotopes. In the early Earth (B), these components formed a homogeneous mixture. During core partitioning (C), the core became enriched with lighter chromium isotopes, and the mantle with heavier isotopes.

dances (6) (which is inferred to vary between the inner and outer core), can be used to test the hypothesis that there is core-mantle exchange across a leaking boundary layer.

For instance, magmas at intraplate centers, such as Hawaii, are believed to originate at the core-mantle boundary. However, studies of osmium (6) and tungsten (5) isotopes from Hawaiian lavas, inferred to carry signatures of such mass exchange, have not resolved the issue (7). This equivocal state exists because researchers have had to make assumptions about the relative abundances of the elements in the core and mantle, and about the differ-

ences in the isotopic composition of the two domains, and because of the precision of the measurements needed to resolve these issues. Now, investigations of core-mantle exchange can be extended using chromium isotopes.

A related question—What is the chromium isotopic composition of the Moon?—can also be explored. Lunar rocks have oxygen and tungsten isotopic compositions that are identical to that of Earth's mantle and, thus, Earth's distinctive chromium isotopic composition might also be found in lunar rocks. If not, would this imply that chromium isotopes were fractionated during lunar core formation or during the giant impact that is believed to have created the Moon?

Another stimulating issue arising from Moynier *et al.* is what chromium isotopes tell us about processes in the solar nebula and chondrite formation, which represents the least understood first step in planet formation (8). It appears that different types of chondrites, and even subgroups within these types, have different isotopic compositions. Major classes of chondrites can

be distinguished by the oxidation state of their metal-loving elements. These may be dominant in the reduced, iron-nickel (Fe-Ni) alloy form (e.g., as in enstatite chondrites); in the oxidized forms, where iron almost always occurs as an oxide (e.g., as in most carbonaceous chondrites); or as a mixture of both (e.g., as in common ordinary chondrites, which represent ~90% of all chondrites). Moynier *et al.* show that the ordinary chondrites generally have heavier chromium isotopic compositions than carbonaceous chondrites. At the same time, they show that those subgroups of carbonaceous chondrites with greater amounts of refractory materials (known as the CO and CV types) also have increasingly heavier chromium isotopic compositions. The issue for cosmochemists and astrophysicists is how this information can be used to improve models of mixing in the solar nebula and chondrite formation.

For more than half a century, it has been observed that meteorites (9) and planets (10) are composed of both a refractory (and per-

haps reduced) component and a volatile-rich, oxidized component. It is hoped that a certain brilliance will come from plating this story with chromium isotopes, which can contribute to unraveling where, in time and space, these components existed and were mixed together.

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Tracking State-to-State Bimolecular Reaction Dynamics in Solution

Stephen Bradforth

If two reactant molecules collide with sufficient energy and the geometry between them is right, then the reactants can pass through a transition state to form new chemical products. A “state-to-state” study maps out how distributing energy (such as in different bond vibrations) in the reactant states affects the likelihood of reaction, as well as the corresponding state population of the products. For gas-phase reactions, the product states, rather than being populated statistically (with population falling off exponentially with increasing energy), can instead show higher population in excited states than the ground state. This so-called state inversion is the basis for the powerful HF chemical laser (1). But does this state-to-state behavior matter at all for bimolecular reactions run in liquids? The constant fluctuations of the solvent should randomize the state of the reac-

tant right up to the transition state, and speed the relaxation of product excited states back to a statistical distribution. On page 1423 of this issue, Greaves *et al.* (2) show that a vibrational state inversion can in fact be achieved in a hydrogen transfer reaction in a common liquid solvent by tuning the time scales of the relaxation processes.

In the 1960s, Polanyi formulated a simple set of rules for what energy states in the reactants would enhance reaction, and in what states the energy released should appear (3). These rules, for example, explained why the reaction powering the HF chemical laser, the transfer of a hydrogen atom between molecular hydrogen and fluorine to produce hydrogen fluoride, exhibited a vibrational state inversion (1). Modern gas-phase reaction dynamics, aided by laser-assisted reactant-state preparation and product-state interrogation, now provides stunning detail on the bimolecular reactions of small molecules, revealing the detailed forces acting at the transition state (4, 5). Studies under vacuum

A bimolecular reaction can produce a large fraction of highly vibrationally excited products despite the collision and confinement effects of the surrounding liquid.

conditions can ensure that the only collision between two molecules is the reactive event itself, and that all of the information encoded in the product state distribution is preserved.

In liquids, it is hard to observe such non-statistical product-state distributions precisely because the constant buffeting molecules suffer is acting to rapidly degrade this fingerprint into a statistical distribution (6). Indeed, energy released into translation and rotation is nearly always (7, 8) relaxed into the solvent on the time scale of the reactive event itself, but vibrations can relax much more slowly. High-frequency vibrations like those involving hydrogen atom stretches in diatomic and triatomic molecules can take hundreds of picoseconds to relax (9, 10), so it should be possible to observe a vibrational distribution for a solution-phase reaction (6). However, there are few examples for a bimolecular reaction where this state distribution has even been measured (11).

The Polanyi rules provide insight into the origin of nonstatistical energy distributions in

Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482, USA. E-mail: stephen.bradforth@usc.edu