and other remote sensing measurements of Mars that cannot be satisfied by the martian meteorites.

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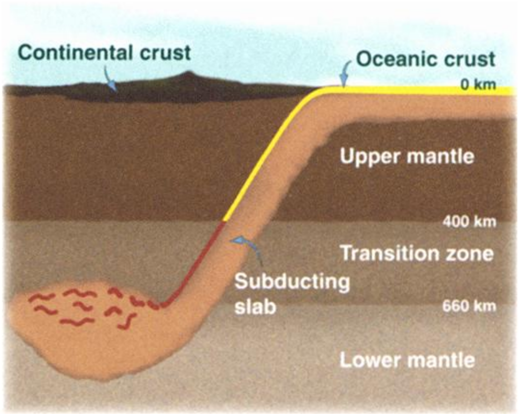
PERSPECTIVES: MANTLE GEOPHYSICS

Clues from a Shocked Meteorite

Masaki Akaogi

Earth's crust contains silicon, aluminum, and alkali metals in higher abundances than in the mantle. In particular, the abundance of sodium and potassium in the crust is one or two orders of magnitude higher than that in the average mantle. It is generally accepted that the crust was formed by transportation of magmas that were produced in the mantle and enriched in the above elements. Feldspars—mineral solid solutions in the system $NaAlSi_3O_8$-$KAlSi_3O_8$-$CaAl_2Si_2O_8$—are major hosts of alkali elements and are among the most abundant constituent minerals of Earth's crust. However, little is known about alkali-host minerals in the deep Earth, and behaviors and transport processes of alkali elements to the crust are not well understood. A hollandite-structured phase in the system $NaAlSi_3O_8$-$KAlSi_3O_8$ has been proposed as a likely alkali-host mineral in the transition zone and the lower mantle (*1*), but this phase has never been found in nature. On page 1633 of this issue, Gillet *et al.* (*2*) report the natural occurrence of $NaAlSi_3O_8$-rich hollandite, not in rocks derived from Earth's mantle but in a meteorite from interplanetary space.

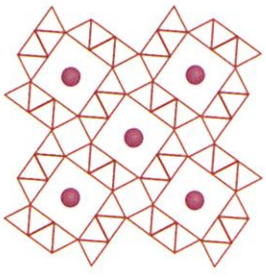
Many meteorites show evidence for high-velocity collisions of parental asteroids. Shock compression at the collision produces very high pressure and temperature, in some cases in excess of 50 GPa and 2000°C, inducing phase transitions and melting of minerals. Dense silicate minerals such as ringwoodite, majorite, ilmenite, and perovskite, which Earth scientists accept as constituent minerals of the transition zone (at depths of 400 to 660 km) and the lower mantle (660 to 2900 km), have been discovered in shocked meteorites (*3*). Hence, shocked meteorites can serve as a window to look down into Earth's deep interior.



Deep down inside Earth. Hollandite can be stable in subducted crustal materials in the transition zone and the upper part of the lower mantle (red).

Gillet *et al.* (*2*) have identified the hollandite phase in the heavily shocked Sixiangkou meteorite by micro-Raman spectroscopy and x-ray microdiffraction. Tomioka *et al.* (*4*) have also reported the occurrence of the same structured mineral in the shocked Tenham meteorite by analytical transmission electron microscopy.

Gillet *et al.* (*2*) tightly constrained the peak pressure and temperature in the shock synthesis processes of the hollandite, based on high-pressure experiments (*1*, *5*). The absence of calcium ferrite–structured $NaAlSiO_4$ and stishovite indicates a peak pressure of about 23 GPa. This pressure corresponds to the interface between the transition zone and the lower mantle. An assemblage of majorite-garnet solid solution and magnesiowüstite observed in the shock veins constrained the temperature to 2000° to 2300°C. This very high synthesis temperature is consistent with the stability field of $NaAlSi_3O_8$-rich hollandite suggested by high-pressure experimental studies (*1*).



Crystal structure of hollandite. Large alkali cations (circles) are accommodated in the large tunnels of the structure.

Hollandite has a unique structure (see the figure to the right), consisting of edge-sharing $(Si,Al)O_6$ octahedra, eight members of which form large tunnels, with Na and K occupying the sites in the tunnels. Compared with feldspars, which have a framework of $(Si,Al)O_4$ tetrahedra, hollandite in the system $NaAlSi_3O_8$-$KAlSi_3O_8$ is about 40 to 50% higher in density. In spite of its dense structure, hollandite can accommodate large mono- and divalent cations, including Na, K, Rb, Sr, and Ba (*6*). It is generally accepted that these elements, except for Na, are "incompatible" elements, which are incorporated preferentially in melt rather than in coexisting minerals, when partial melting occurs in the upper mantle. However, hollandite can be a host mineral of these "incompatible" elements with large cation sizes.

The identification of $NaAlSi_3O_8$-rich hollandite in a natural material has important implications for the behavior and processing of alkali elements in Earth's deep mantle (see the figure above). It is widely accepted that oceanic crust and sediments are subducted into the transition zone and presumably into the lower mantle (*7*). A part of the continental crust can also be subducted into the deep mantle. These crustal materials can be returned to Earth's surface as components of magmas derived from the mantle. Because the subducted crustal materials have high abundances of Na, K, Si, and Al, the hollandite phase in the system $NaAlSi_3O_8$-$KAlSi_3O_8$ is likely to form in the depth range of the transition zone and the upper part of the lower mantle. In low-temperature regions of subducting slabs, $KAlSi_3O_8$-rich hollandite would be stable, whereas $NaAlSi_3O_8$-rich hollandite could reside in high-temperature regions such as ascending plumes. It is recognized that the subduction of oceanic crust and sediments introduces large amounts of water as hydrous minerals into the upper mantle, the transition zone, and presumably the lower

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The author is at the Department of Chemistry, Gakushuin University, Toshima-ku, Tokyo, 171-8588, Japan. E-mail: masaki.akaogi@gakushuin.ac.jp

mantle (*8*). The water decreases the melting temperature, resulting in partial melting. Some high-pressure partitioning experiments suggest that, when partial melting occurs in subducted crustal materials, hollandite can preferentially incorporate several incompatible elements (K, Pb, Sr, light rare earth elements, and so forth) but is not likely to be a host for uranium and heavy rare earth elements, relative to the coexisting melt (*9*). Therefore, the stability of hollandite will strongly influence trace element geochemistry of magmas produced in the deep mantle as well as alkali transport processes in the transition zone and the lower mantle.

Detailed studies of shocked meteorites may provide further evidence for dense minerals stable in the deep mantle. Other alkali-host minerals such as calcium ferrite–type $NaAlSiO_4$ and a related structural phase (*1*, *10*) may be found in shocked meteorites. Together with comprehensive experimental studies on the melting relations and trace element partitioning between the alkali-host minerals, silicate melt, and fluid at the pressure-temperature conditions of the transition zone and the lower mantle, they will shed light on the behavior of alkali elements in the deep mantle and on crust formation processes.

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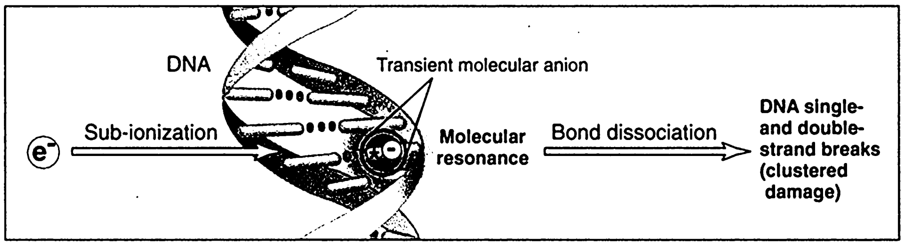
PERSPECTIVES: MOLECULAR BIOLOGY

A Sting in the Tail of Electron Tracks

Barry D. Michael and Peter O'Neill

It almost seems paradoxical that the molecular damage induced by high-energy ionizing radiation—with energies typically in the range of millions of electron volts (eV)—is actually the result of a multitude of low-energy events. Most of these are small transfers of energy (on the order of 10 eV) deposited by low-energy electrons that are set in motion around the tracks of energetic charged particles (*1*). Little is known about the damage induced by low-energy electrons, except in the simplest molecular systems. Understanding how low-energy electrons damage more complex molecules such as DNA should ultimately lead to explanations for many aspects of the biological actions of radiation. A clearer picture of the basic mechanisms (and potentially new chemical pathways) that induce DNA damage should also benefit the development of improved radiotherapy strategies for treating diseases such as cancer.

Recently, a number of studies have started to address this question by, for example, measuring single- and double-strand breaks (SSBs and DSBs) in DNA after exposure to monoenergetic photons (*2*, *3*) or electrons (*4*). Boudaïffa *et al.* (*5*), reporting on page 1658 of this issue, have lowered the energy of electrons incident on DNA to 3 eV (an electron energy far below that used in previous studies). The authors find that low-energy electrons, as they slow down to energies too low to cause ionization, still have a surprising "sting in the tail" of their tracks. Their findings challenge the conventional notion that damage to the genome by ionizing radiation is only induced by electrons with sufficient energy to ionize DNA.



Tracking DNA damage. Low-energy electrons produce complex DNA damage. Electrons that have slowed down to energies too low to induce ionization of DNA undergo resonant attachment to DNA bases (blue) or to the sugar-phosphate backbone. The transient molecular anion formed (*) then reacts further to break one or both strands of the DNA (*5*). One electron can in this way produce a multiple lesion, thus amplifying the clustering of damage induced in DNA by a single radiation track (*1*). Clustered lesions are difficult for the cell to repair and are therefore likely to lead to permanent damage to the genome (*8*).

Damage to the genome of a living cell by sparsely ionizing radiation, such as hard x-rays, is about one-third "direct" (from energy deposited in the DNA and its closely bound water molecules) and two-thirds "indirect" (from free radicals produced by energy deposited in water molecules and other biomolecules located close to the DNA). Studies with scavenger molecules such as dimethylsulfoxide (*6*) indicate that almost all of the indirect damage to DNA is due to attack by the highly reactive hydroxyl radical (•OH). Furthermore, it seems that the reducing counterparts of •OH (principally the hydrated electron, e_{aq}^{-}) are relatively ineffective, especially at inducing DNA strand breaks.

The radiation chemistry of water is reasonably well understood, as is the chain of events leading from the initial production of water radicals to indirect DNA damage (*7*). In particular, it is clear that induction of a DSB by a single track of radiation is the result of a localized attack by two or more •OH radicals. Alternatively, damage may be caused by a hybrid attack where one strand is damaged by an •OH radical and the other strand sustains direct damage within about 10 base pairs of the •OH attack. The closely spaced depositions of energy along the radiation tracks are known to generate such clusters of hybrid damage. Where more than two elementary lesions are induced in close proximity by •OH or by direct effects on the DNA, a complex lesion can develop. This has important consequences for biological effects because such damage presents a greater challenge to the DNA repair machinery of the cell (*8*).

Less is known about the mechanisms of direct damage by low-energy electrons. However, the report by Boudaïffa *et al.* (*5*)

B. D. Michael is in the Cell and Molecular Biophysics Group, Gray Laboratory Cancer Research Trust, Mount Vernon Hospital, Northwood, Middlesex HA6 2JR, UK. P. O'Neill is in the DNA Damage Group, MRC Radiation and Genome Stability Unit, Harwell, Didcot, Oxon OX11 ORD, UK. E-mail: michael@graylab.ac.uk, p.oneill@har.mrc.ac.uk