

Minerals in the Deep Earth: A Message from the Asteroid Belt

Dieter Stöffler

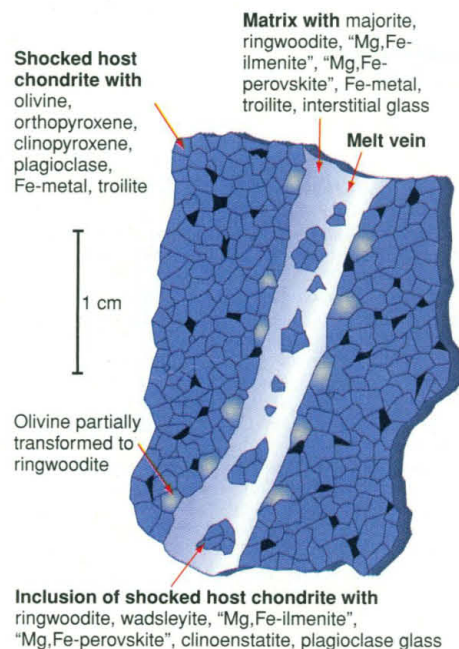
From the time that scientists recognized the existence of Earth's metallic core and silicate mantle, the question of what mineral phases make up the mantle at various depths has been a fundamental issue in Earth and planetary science. Answering this question is of vital importance in understanding the processes of crust formation and in interpreting the physical properties and dynamical behavior of the mantle. Ultimately, we would like to

modifications of olivine and pyroxene, the most common minerals of chondrites and the Earth's mantle, can be seen as a historical revival of the early idea of learning to understand the Earth's mantle from the study of meteorites.

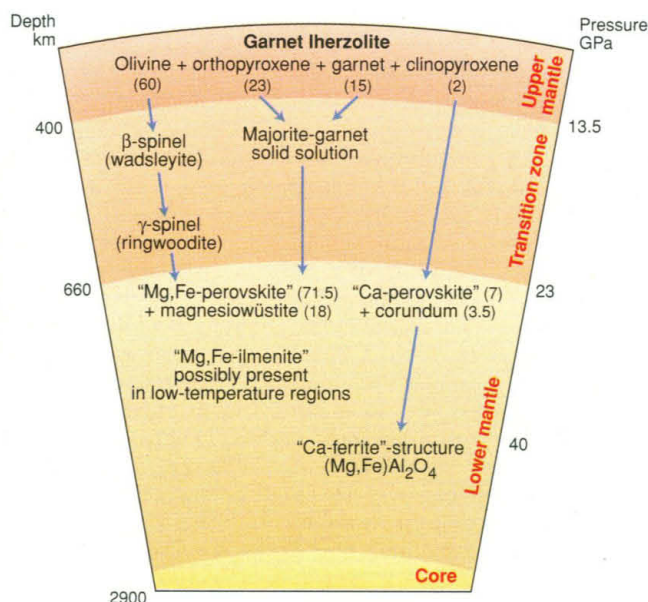
A Japanese (1) and a United States-German (2) group of researchers have detected in the Tenham and Acfer 040 chondrites dense modifications of pyroxene displaying the ilmenite and perovskite crystal structures, coex-

creasing depth (see mantle diagram). Seismologists demonstrated that the velocity of the seismic waves increases discontinuously in the so-called transition zone of the mantle at depths of about 400 and 660 km. Thanks to the monumental effort of high-pressure experimentalists between 1955 to 1975 (4), we learned that the minerals of the upper mantle must undergo phase transitions to denser crystal structures in which the $[\text{SiO}_4]$ tetrahedra are replaced by $[\text{SiO}_6]$ octahedra (3). The predicted crystal structures for olivine $^{[6]}(\text{Mg,Fe})_2\text{SiO}_4$ and pyroxene $^{[6]}(\text{Mg,Fe})\text{SiO}_3$ (coordination numbers are given in square brackets) below the 400-km discontinuity are the spinel $^{[6]}(\text{Mg,Fe})_2\text{SiO}_4$ and garnet $^{[8]}(\text{Mg,Fe})_3\text{Si}^{[4]}(\text{Mg,Fe})\text{Si}_3\text{O}_{12}$ structures, respectively. In spinel, Si is still in fourfold coordination ($^{[4]}\text{Si}$), whereas in garnet, some Si atoms are already in a sixfold coordination ($^{[6]}\text{Si}$) with oxygen. Furthermore, high-pressure petrologists were able to synthesize polymorphs of olivine and pyroxene, which form at even higher pressure than the spinel and garnet structures. They found that the garnet structure transforms to the ilmenite $^{[6]}(\text{Mg,Fe})\text{SiO}_3$ and perovskite $^{[8]}(\text{Mg,Fe})\text{SiO}_3$ structures (5). These transformations likely explain the steep increase in seismic velocities at 660 km.

An exciting discovery happened around 1970, an amazing analogy to the one presented here. Binns *et al.* (6) and Smith and Mason (7) found the predicted high-pressure polymorphs of olivine and pyroxene in the strongly shock-metamorphosed chondrites Tenham and Coorara, respectively, and named the minerals ringwoodite (γ -spinel structure) and majorite (garnet structure), after Ringwood and Major of the



Contrasting the microscopic... Diagram of high-pressure mineral assemblages of the major upper mantle minerals olivine, pyroxene, and garnet in shocked chondrites.



...with the megascopic. Section of Earth's upper mantle, transition zone, and lower mantle showing where different minerals occur at depth. Figures in parentheses are volume fractions (%) of the respective minerals in the mantle (3).

understand their impact on plate tectonics, volcanism, and the global seismic activity of Earth. In the 1930s, Goldschmidt was among the first to establish a compositional link between Earth and primitive meteorites. He initiated the idea of Earth having a chondritic composition, referring to the meteorite class of chondrites, which represent the least processed primitive solar system material. On an advanced level, the recent discoveries of high-pressure

isting with previously discovered ringwoodite and wadsleyite (dense modifications of olivine) and majorite (another high-pressure form of pyroxene). This exciting discovery represents the first natural occurrence of these phases, which are believed to be major constituents of the lower mantle below the 660-km seismic discontinuity (see diagram of mantle).

It is well accepted that Earth's upper mantle consists, as chondrites do, mainly of the minerals olivine, low-Ca orthopyroxene, high-Ca clinopyroxene, and plagioclase (3). In the upper mantle, the latter is replaced by $(\text{Mg,Fe})\text{Al}_2\text{O}_4$ -spinel and garnet with in-

Australian National University. Somewhat later, the modified spinel structure of olivine (β -spinel) was also found in the Tenham chondrite (8) and named wadsleyite, after Wadsley, who worked with Ringwood. The newly discovered $(\text{Mg,Fe})\text{SiO}_3$ ilmenite and perovskite phases, likely to represent major components of Earth's lower mantle and still to be named, share a common origin with ringwoodite, majorite, and wadsleyite: They occur in melt veins within shocked chondrites (see diagram of shocked chondrite). These veins were apparently produced by shock-induced melting as a result of hypervelocity collisions of the parent

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asteroid. This interpretation is confirmed by characteristic shock effects in olivine and plagioclase within the unmelted host chondrites that indicate peak shock pressures in excess of 50 to 60 GPa (9). The findings of (1) and (2) have two key implications: (i) The observed high-pressure-phase assemblage is a quenched disequilibrium assemblage formed during shock pressure release at variably high shock-induced temperatures, and (ii) the high-pressure polymorphs crystallized in two different textural settings in the meteorite (see chondrite diagram) by two kinetically different processes (1, 2): At the contact of the melt veins and in chondrite inclusions within the melt, primary grains transform in a "quasi-solid-state process" to ringwoodite, wadsleyite, $(\text{Mg,Fe})\text{SiO}_3$ perovskite, $(\text{Mg,Fe})\text{SiO}_3$ ilmenite, and clinoenstatite. Within the vein's matrix $(\text{Mg,Fe})\text{SiO}_3$ perovskite, $(\text{Mg,Fe})\text{SiO}_3$ ilmenite + ringwoodite, and majorite + magnesiowüstite (2, 10) crystallize in this order from a melt above an estimated pressure of 23 to 26 GPa at temperatures well above some 900°C. These observations leave open questions. Why don't we see the predicted breakdown reactions of olivine (spinel) and orthopyroxene: perovskite + magnesiowüstite and spinel + stishovite, respectively? Is there any chance to find a $(\text{Mg,Fe})\text{Al}_2\text{O}_4$ mineral with Ca-ferrite structure? Supporting theoretical studies and more elaborate shock-wave experiments are probably needed to solve the puzzle.

What is important about this discovery and what do we learn about the constitution of Earth's and planetary mantles and regarding the fundamentals of impact metamorphism of rocks? First, almost all of the high-pressure phases predicted to constitute the transition zone and lower mantle do exist in nature and can be formed by shock processes, ironically, in space, at the very surface of asteroids shattered by interplanetary collisions. Second, the shock-induced high-pressure phase assemblages in chondrites tell us about the kinetics of the crystallization of such phases, the partitioning of minor and trace elements, and the extent of solid solutions of the Mg and Fe silicate end members. In general, we learn from the observed disequilibrium assemblages something about the expected equilibrium conditions in the deep mantle, following an old principle of how to unravel the equilibrium conditions of rock metamorphism from metastable phases. Third, the high-pressure mineralogy of chondrites teaches a fundamental lesson about the pressure-temperature-time paths characteristic of impact metamorphism on planetary surfaces, leading to a better understanding of the collision history of asteroids.

Although the shocked meteorites carry a message that is not yet fully understood, the work by the Japanese and United States-German research groups will have a fundamental impact on the understanding of

Earth's and planetary silicate mantles. In addition, this work represents another triumph of high-resolution analytical transmission electron microscopy. It will stimulate a more comprehensive study of all types of highly shocked meteorites, which very probably experienced quite different pressure-temperature-time histories and as a result may display variable high-pressure phase assemblages. More exciting information about Earth's deep interior may still be found in the asteroid belt.

References

1. N. Tomioka and K. Fujino, *Science* **277**, 1084 (1997).

POLYMER SCIENCE

Fashioning Flow by Self-Assembly

Tom McLeish

The cytoskeleton, molten polyethylene, an egg white, knee-joint tissue, shampoo.... A strange juxtaposition of soft materials, but with a common thread: All require precisely tuned flow properties that are achieved by means of molecular engineering, whether human or natural. The strange properties of "viscoelastic" materials display solidlike and liquidlike behavior, depending on the time scale of the applied deformation. This balance is hard to achieve but is as important for polymer processing as it is for the structural stability and function of living cells.

Careful control of the macromolecular structures within these complex fluids is known to be the key. Moreover, in the biological sphere in particular, the polymers frequently self-assemble. Yet, this rapidly-growing area of study within the interdisciplinary science of soft condensed matter is hungry for simple model molecules that are sufficiently rich in their behavior. A report on page 1601 of this issue of *Science* from a group of polymer chemists at the Eindhoven University of Technology describes a promising new candidate (1).

When in concentrated solution or melt form, ordinary long-chain molecules of high molecular weight exhibit the twin characteristics of elasticity and long relaxation times, or "memory," for their internal stresses. Both properties have been the bane of the polymer-processing industry for many years. Since the 1970s and the work of de Gennes,

2. T. G. Sharp, C. M. Lingemann, C. Dupas, D. Stöffler, *ibid.*, p. 352.
3. G. C. Brown and A. E. Mussett, *The Inaccessible Earth* (Chapman & Hall, London, 1993).
4. F. Birch, *J. R. Astron. Soc.* **4**, 295 (1961); E. A. Ringwood, *Composition and Petrology of the Earth's Mantle* (McGraw-Hill, New York, 1975).
5. L.-G. Liu, *Geophys. Res. Lett.* **1**, 277 (1974); *Earth Planet. Sci. Lett.* **31**, 200 (1976).
6. R. A. Binns, R. J. Davis, S. J. B. Reed, *Nature* **221**, 943 (1969).
7. J. V. Smith and B. Mason, *Science* **168**, 832 (1970).
8. A. Putnis and G. D. Price, *Nature* **280**, 217 (1979).
9. D. Stöffler, K. Keil, E. R. D. Scott, *Geochim. Cosmochim. Acta* **55**, 3845 (1991).
10. M. Chen, T. G. Sharp, A. El Goresy, B. Wopenka, X. Xie, *Science* **271**, 1570 (1996).

Doi, and Edwards, the molecular basis for standard polymer viscoelasticity has been understood as arising from the topological interactions (or "entanglements") between the chains. The polymer solution acts as a fixed network under rapid deformation until the chains collectively escape from their mutual entanglements. For linear polymers, the dominant mechanism is random curvilinear diffusion along their own contours, around which they are trapped within a tube-like region. Termed "reptation," this snake-like motion gives rise to a dominant relaxation time that increases rapidly with molecular weight (2). Careful dynamical ("rheological") measurements on specially synthesized monodisperse polymer melts

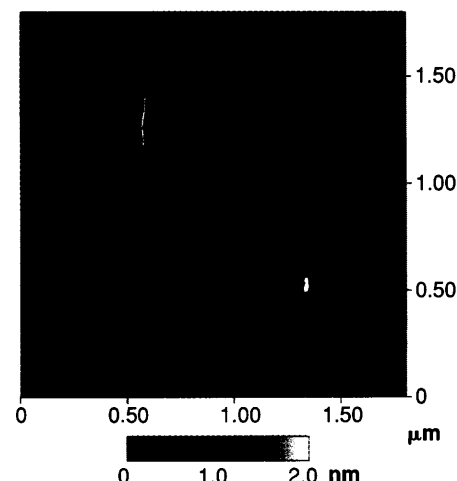


Image of self-assembled polymer with twisted ribbon structure taken with atomic force microscope. Color bar indicates height above substrate.

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