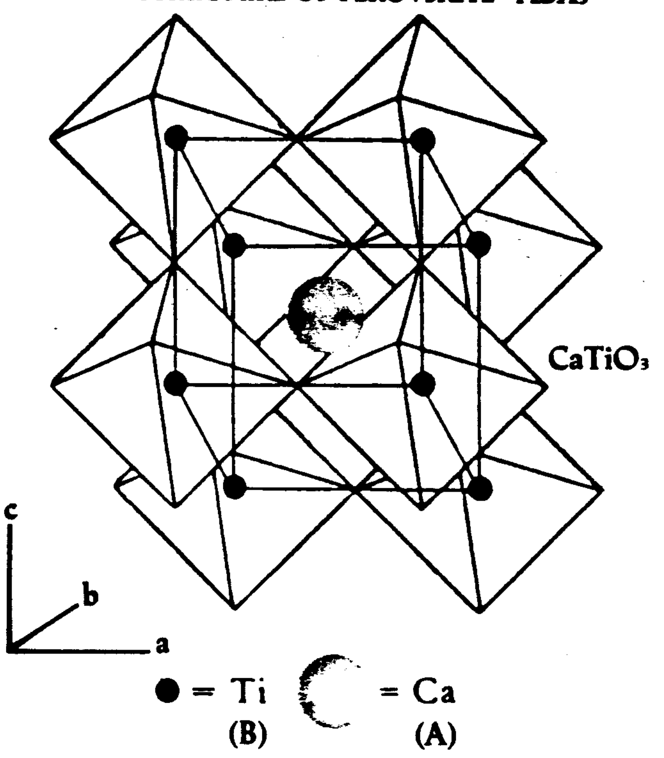
#125 Earth in Space 1, #3 1988

# Understanding Perovskites of Benefit to Science and Industry—An Interdisciplinary Approach

**Robert M. Hazen**
*Geophysical Laboratory,*
*Carnegie Institution of Washington, Washington, D.C.*

***Perovskites are gaining increased attention from the scientific and business communities: silicate perovskites are believed to make up almost half of the volume of the solid Earth, while commercial perovskites—which are used as electrical insulators, semiconductors and superconductors—form the basis of a $20 billion per year industry.***

**IDEAL STRUCTURE OF PEROVSKITE $ABX_3$**




**B Ions surrounded by regular octahedra of oxygens which share corners to form three-dimensional framework.**

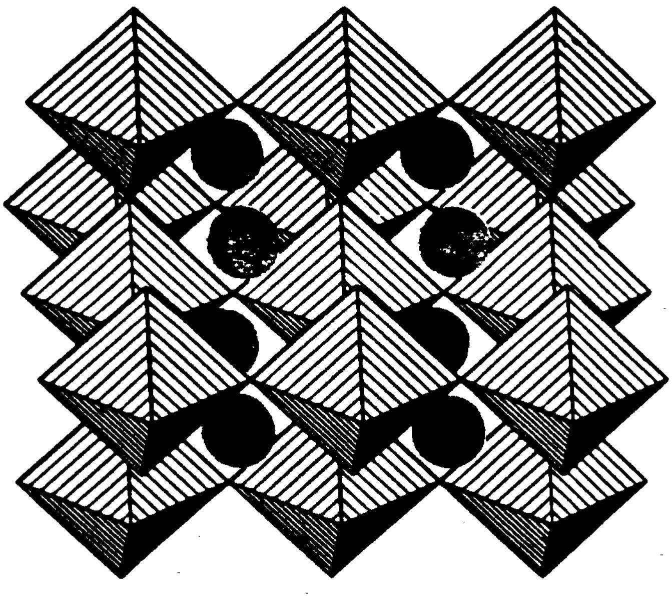
**A & B are cations, i.e. ions with positive charge**
**X is anion, i.e. with a negative charge**

Perovskites, a class of compounds with the ideal formula $ABX_3$, occur in one of the most adaptable crystal structures known to man. The ideal form, represented by the mineral perovskite ($CaTiO_3$, which gives the group its name), is among the simplest crystal structures (Figure 1). This high-symmetry structure may be altered in any number of ways, however, by slight distortion of the atomic framework, by missing atoms, by layering, and by other variations that lead to atomic arrangements of extraordinary complexity. These modifications cause many of the unique properties of perovskites. For example, perovskites are the only crystal structures that can perform as electrical insulators, semiconductors, superionic conductors, metal-like conductors, and superconductors.

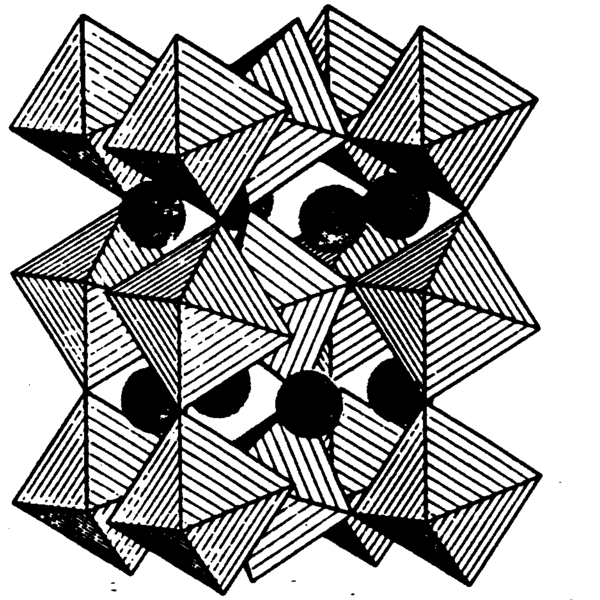
## Importance of Magnesium Silicate Perovskite

From October 30 to November 2, 1987, an international group of 75 physicists, chemists, geophysicists and materials scientists met in Bisbee, Arizona, for an AGU Chapman Conference on perovskites. The purpose of the meeting was to focus on the diversity and complexity of perovskites as viewed by scientists from different disciplines. (Chapman Conferences are named for Sydney Chapman, whose career is described elsewhere in this issue.)

The first session of the meeting dealt with magnesium silicate perovskite (ideally, $MgSiO_3$; see Figure 2), a high-pressure phase of special concern to



1. **Simple cubic perovskite structure, with an ideal chemical formula $ABO_3$, has a corner-linked array of octahedral atom clusters. Cages formed by the octahedra hold large metal atoms.**



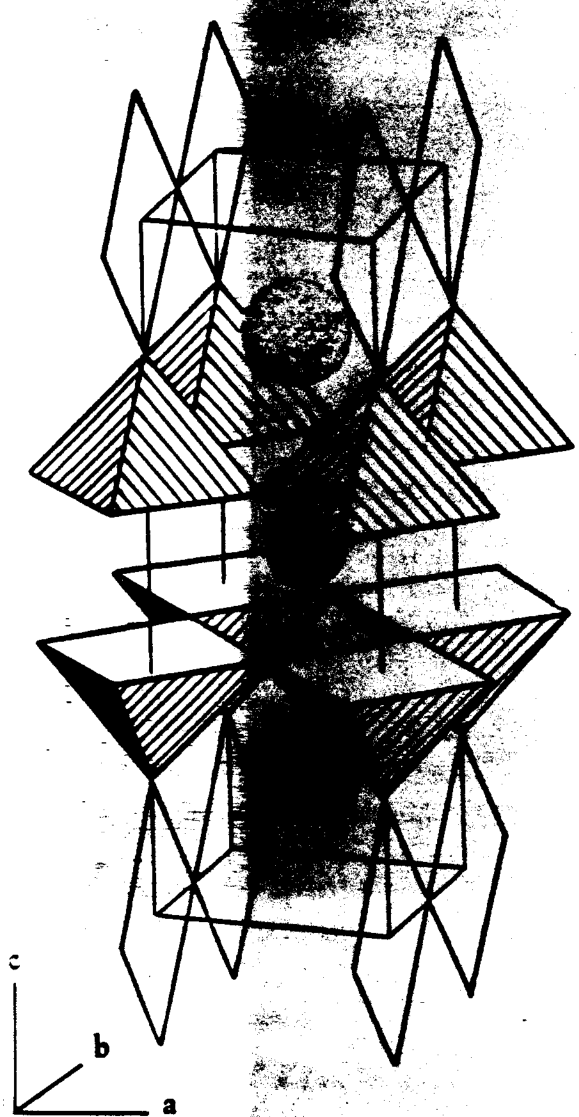
2. **Ferromagnesian silicate perovskite, (Mg,Fe)-$SiO_3$, is believed to be abundant in Earth's lower mantle. The structure is related to the simple cubic perovskite by tilting of the octahedra.**

the mineral physics community. Silicate perovskites are believed to constitute almost half the volume of the solid Earth. A number of detailed experimental studies of $MgSiO_3$ perovskite have been made possible through E. Ito's (Okayama University, Okayama, Japan) synthesis of single crystals with diameters greater than 0.1 mm. However, the common assumption that $MgSiO_3$ perovskite is stoichiometric at high pressure and temperature, especially in iron- and calcium-bearing varieties, has yet to be demonstrated and may well be wrong. Perovskites are commonly deficient in cations, and these defects will drastically alter key physical properties such as creep, electrical conductivity, and trace element partitioning.

## Perovskites as Technological Materials

The second session focused on perovskites as technological materials. As such they are the basis of a $20 billion per year market. Three types of perovskites used as technological materials are barium titanate (cation-doped $BaTiO_3$), the most widely used dielectric; PZTs (solid solutions of $PbTiO_3$ and $PbZrO_3$), piezoelectric ceramics; and PTC (positive temperature coefficient of resistance) materials that are used in voltage surge protectors. The next generation of commercially produced perovskites, the high-temperature oxide superconductors, all have structures related to perovskites (Figure 3). It was evident from the discussions that high-pressure silicate perovskites must be viewed in the context of other exotic $ABX_3$ compounds, rather than as just another insulating silicate mineral.

A later session was devoted to theoretical approaches to understanding perovskites. Ekhard Salje (Cambridge University, Cambridge, U.K.) discussed mechanisms and kinetics of perovskite phase transitions, noting that four different mechanisms—octahedral tilting, B cation "off-centering," covalent deformation, and A cation "off-centering"—contribute to soft mode transitions. Complex perovskite transformations may involve the interaction of two or more of these mechanisms. It was pointed out that the symmetry of metastable magnesium silicate perovskite at room conditions need not be the same as that of the phase deep within the Earth. Salje's review was followed by contrasting computer simulations of the structure and properties of $MgSiO_3$. One simulation was able to reproduce the observed structure, equation of state properties, and vibration frequencies remarkably well. It was evident from these theoretical




3. **High-temperature superconducting perovskite $YBa_2Cu_3O_7$** has a tripled *c* crystallographic axis as a consequence of barium (large circles) and yttrium (small circles), which are ordered in a sequence Ba-Y-Ba, Ba-Y-Ba. Two of every nine perovskite oxygens are absent, giving the superconductor a uniquely ordered arrangement of oxygen atoms.

presentations that computer simulations can aid in the interpretation of existing experimental data as well as provide useful insights in the absence of experimental data.

Defects and nonstoichiometry, recurrent themes of the conference, were the focus of another session. A review of some of the bewildering variety of perovskite-related defect structures was presented as well as a thermodynamic model for point defects in

city of perovskite was fea-
report on discrepancies in
ts and experimental values
ore synthetic crystal speci-
acterization, and indepen-
al mineral data.

hasized perovskite plastic-
microstructure. Nothing is
n behavior of $MgSiO_3$ at
s certain is that the plastici-
extension the convection
nantle, is dependent on the
ects.

rence on perovskites sent a
se in attendance. Materials
n a broad, interdisciplinary
not fundamentally different
nor can Earth scientists af-
h of other materials scien-
magnesian silicate perovs-
ost abundant mineral—we
om both experiment and
silicate and analog systems
ne structure and properties

*r the Superconductor*, Robert M.
New York, N. Y., 1988.

that results from long ap-

erial in which displacement
er conduction currents, i.e.

hase that is stable with re-
ces but that is capable of
f energy if sufficiently dis-

physically distinct portion

ertain crystals, the develop-
ial in certain crystallograph-
anical strain is applied, or,
chanical strain, hence vibra-
tential is applied.

erence to a compound or a
e exact proportions of its
its chemical formula; it is
stoichiometric phase does
rom its ideal composition.