Thermodynamic properties of high-pressure high-temperature minerals derived from phonon spectra; successes and limitations

F. Guyot — Laboratoire Minéralogie-Cristallographie and Institut de Physique du Globe, Paris, France

P. Gillet — Laboratoire Sciences de la Terre, Ecole Normale Supérieure de Lyon, France

The calculation of thermodynamic data for minerals from lattice dynamics provides a major connection between solid state physics and geochemistry. Y. Bottinga had a major influence in this field and, specifically, was a pioneer of calculations of isotopic equilibria involving solid phases, using their vibrational characteristics. The advances in our knowledge of phonon spectra of minerals during the recent years make increasing precisions in such calculations possible. The purpose of this presentation is to discuss the successes, but also the limitations of this approach.

A major application of phonon spectra in geochemistry is to allow calculation of thermodynamic properties and isotopic characteristics of minerals at deep Earth high-pressure and temperature conditions. This will be discussed in detail for silicate perovskite, following the study by Gillet *et al* (1998). Consequences for the Mg/Si ratio in the lower mantle and in the bulk Earth will be investigated. Another major application is the calculation of thermodynamic properties of metastable or unstable minerals. For example, high-temperature thermodynamic properties of carbonates (Matas *et al.*, 1998) are otherwise difficult to retrieve because of the decarbonation of these phases. Consequences of such phonon modelling for the geochemical internal cycle of carbon will be discussed. For each calculation presented, the following points will be examined:

What is the role of incomplete coverage of the phonon spectrum by experimental methods?

What is the role of dispersion over the Brillouin zone?

What is the role of anharmonicity, with special emphasis to its effect on high-temperature isotopic fractionnations?

How can possible electronic and configurational effects be estimated?

References

Matas, J. Gillet, Ph., Ricard, Y. and Martinez, I. (1998) *Thermodynamic properties of carbonates at high-pressures: implications for carbonate stability in the Earth mantle.* Submitted

Gillet, Ph., Daniel, I., Guyot, F. Matas, J. and Chervin, J.C. (1998) *A thermodynamic model for $MgSiO_3$-perovskite derived from pressure, temperature and volume dependence of the Raman mode frequencies.* Submitted.