Volatiles in the Earth's mantle: insights from mineral and melt physics

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Volatiles like H_2O, CO_2 and rare gases are outgassed from the Earth's mantle by volcanism. The way they are stored in the upper and lower mantle is still uncertain. Moreover, their behaviour (compatible *vs* incompatible) during melting at various pressures is poorly known. Experiments at high pressures and temperatures as well as thermodynamic models provide insights on these important issues. We present recent results on CO_2 and rare gases to illustrate how the precise knowledge of thermodynamic properties can be used to tackle the behaviour of volatiles in the deep Earth mantle.

The stability of magnesite

High-pressure experiments have shown that in the CO_2-peridotite system at pressures in excess of 3 GPa (i.e. depth greater than 100 km), CO_2 is no longer a free phase and is stored in magnesite ($MgCO_3$) (Canil *et al.*, 1990). It has then been observed that in the presence of silicates, magnesite could be the host for carbon in the Earth's upper and lower mantle (Katsura *et al.*, 1990; Biellmann *et al.*, 1993; Martinez *et al.*, 1998) at least down to 1000 km. If so, magnesite, and more generally carbonates, may buffer the oxygen fugacity in the Earth's mantle (Blundy *et al.*, 1991).

The stability field of magnesite under pressure and temperature conditions of the Earth's mantle is studied using recent experimental data. Accurate compressibility measurements up to 90 GPa and room temperature (Fiquet *et al.*, 1998, submitted, Am. Mineral.) and spectroscopic data are used to calculate the specific heat, entropy and equation of state of magnesite up to 135 GPa and 3500 K (Matas *et al.*, 1998, in prep.). A good agreement is observed with the existing experimental data. The model is then used to calculate the decarbonation curve $MgCO_3$-MgO-CO_2 which provides an upper limit for the stability of magnesite in the Earth's mantle even in the presence of silicates. The computed curve is sensitive to the values of bulk modulus and its pressure derivative as well as on the thermal expansion. A distinct possibility exists that magnesite breaks down below 2000 km. If so, CO_2 cannot be stored in magnesite at the bottom of the lower mantle if carbonate-rich lithospheric plates are driven down to the core-mantle boundary. The consequences of these results on the CO_2 storage and cycle are discussed.

The solubility of noble gases in melts

The solubility of noble gases in silicate melts and minerals at high pressure is of fundamental importance for understanding the early history of the Earth and its present day degassing. They serve as tracers for deciphering mantle structure and constrain the number and size of geochemical reservoirs. It has been proposed that the budget of ^{40}Ar, produced by the radioactive decay of ^{40}K, provides the strongest argument for chemical layering within the mantle although the geochemical models used to arrive at this conclusion are currently under re-examination. A major source of uncertainty is the lack of data on Ar and other rare gases incompatibility during melting. It is assumed, based on low-pressure data, that noble gases are always highly incompatible independent of pressure. Solubility data of Ar in olivine melt at very high pressure which indicate that the degree of incompatibility is strongly dependent on pressure, especially in the 4–5 GPa range (Chamorro *et al.*, 1998).

It is assumed that noble gases are always strongly incompatible during partial melting, i.e. that they are preferentially fractionated into the melt. This assumption is supported by low pressure (<0.2 GPa) experimental data indicating that the olivine-melt partition coefficient ($K_d = [Ar]_{crystal}/[Ar]_{melt}$) is ~$10^{-2}$. In previous geochemical modelling, it is implicitly assumed that this value is pressure independent. However, our data indicate an abrupt decrease in Ar solubility in the melt, by at least one order of magnitude, in the 4-5 GPa range. Unless there is a corresponding change in the crystal solubility at this pressure, which is unlikely, the behaviour of Ar will change from strongly incompatible toward moderately incompatible, or even compatible if the melt solubility becomes lower than that of the crystal. Simple arguments, based on melt structure and compressibility, suggest that similar effects are expected at lower pressures for heavy noble gases like Kr or Xe, and higher pressure for He. The geochemical implications of these results will be briefly outlined.

References

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