The stability of nitrides in meteorites and in the Earth’s mantle: a thermodynamic and experimental study

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Meteorites contain the only naturally occurring nitrides: for example, osbornite (TiN), sinoite (Si2N2O) and nierite (Si3N4) have been identified in several enstatite chondrites. Recently, however, Javoy (1995, 1997) has suggested that nitrides (predominantly TiN in solid solution within clinopyroxenes or spinels) are the major host phases of nitrogen in the upper mantle of the Earth. This hypothesis, which could imply important consequences for the nitrogen cycle in the Earth, needs to be tested further. The stability of nitrides in chondrites, i.e. at low pressures, has been discussed by several authors (e.g. Hemdon and Suess, 1976, Fegley, 1983). In this study, we have investigated the stability of nitrides at pressure and temperature conditions pertinent to the Earth’s mantle, using both experimental and thermodynamic methods.

High pressure-high temperature experiments have been carried out in laser-heated diamond-anvil cell, using either YAG-laser and no pressure medium (fO2 close to initial sample oxygen fugacity, i.e. FMQ) or CO2 laser with pressure medium (no fO2 control, but better P and T determination). A mixture of a silicate powder with the pyrolite composition + nitride (here Si3N4) was compressed and heated at lower mantle conditions. The recovered samples were prepared for Transmission Electron Microscopy (TEM) in order to study stability and possible solid solutions of nitrides into main mantle silicates. Preliminary observations suggest that nitrides ions are the stable form of nitrogen at mantle conditions.

Using updated thermodynamic data, in particular for estimation of oxygen fugacities in the mantle (Balhaus, 1995), the calculated relationships between nitride activities and nitrogen fugacities are calculated at various temperatures, total pressures and oxygen fugacities, relevant for enstatite chondrites or the Earth’s mantle. Moreover, using vibrational spectroscopic data available for nitrogen and nitrides, extremely strong isotopic fractionation factors are predicted between the two types of species, even at high temperatures (Fig. 1). The main comments

Fig. 1.
about these results are:

(1) for a given T and $f_{N_2}$, pressure favours the
formation of nitride,

(2) at any P, T, $f_{O_2}$ conditions, osbornite is the most
easily formed nitride, when compared to nierite or
sinoite. This suggests that nitrogen is preferentially
associated to Ti-bearing phases in the upper mantle,
chiefly clinopyroxenes.

(3) nitrides ions are the stable form of nitrogen at
mantle conditions.

If the total budget of mantle nitrogen is accounted
for by nitride in minerals, an $f_{N_2}$-T relationship can be
estimated for the mantle. These results are discussed
in terms of global volatile cycles.

References