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

I. Martinez
M. Javoy

IPGP, Lab Géochimie des Isotopes Stables, 4 place Jussieu, 75251 Paris cedex 05, France

Meteorites contain the only naturally occuring nitrides: for example, osbornite (TiN), sinoite (Si_2N_2O) and nierite (Si_3N_4) 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. Herndon 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 (f_{O_2} close to initial sample oxygen fugacity, i.e. FMQ) or CO_2 laser with pressure medium (no f_{O_2} control, but better P and T determination). A mixture of a silicate powder with the pyrolite composition + nitride (here Si_3N_4) 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 fractionnation factors are predicted between the two types of species, even at high temperatures (Fig. 1). The main comments

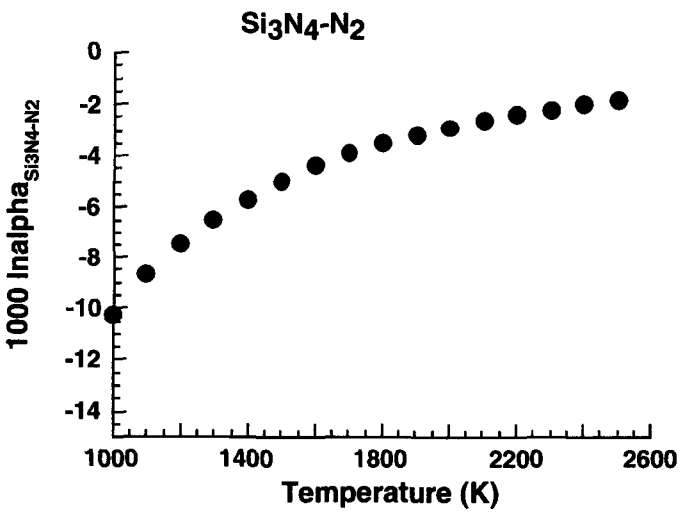

FIG. 1.

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.

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