Nitrides and carbonitrides from the lowermost mantle and their importance in the search for Earth’s “lost” nitrogen

FELIX KAMINSKY1,* AND RICHARD WIRTH2

1KM Diamond Exploration Ltd., 2446 Shadbolt Lane, West Vancouver, British Columbia V7S 3J1, Canada
2Helmholtz Centre Potsdam, GFZ German Research Center for Geosciences, 14473 Potsdam, Germany

ABSTRACT

The first finds of iron nitrides and carbonitride as inclusions in lower-mantle diamond from Rio Soriso, Brazil, are herein reported. These grains were identified and studied with the use of transmission electron microscopy (TEM), electron diffraction analysis (EDX), and electron energy loss spectra (EELS). Among nitrides, trigonal FeN and orthorhombic Fe3N are present. Carbonitride is trigonal Fe9(N0.8C0.2)4. These mineral phases associate with iron carbide, Fe7(C,N)3 and Fe9(N,C)4, with M/(C,N) from 1.65 to 3.98. We conclude that the studied iron nitrides and carbonitrides were formed in the lowermost mantle as the result of the infiltration of liquid metal, containing light elements from the outer core into the D″ layer, with the formation of the association: native Fe0 + iron nitrides, carbides, and transitional compounds + silicon carbide. They indicated that major reservoirs of nitrogen should be expected in the core and in the lowermost mantle, providing some solution to the problem of nitrogen balance in the Earth.

Keywords: Nitride, carbide, nitrogen, lower mantle

INTRODUCTION

Earlier, we reported upon finds of a series of iron carbides with admixtures of up to 7.3–9.1 atom% N [N/(N+C) = 0.19–0.27], included in lower-mantle diamonds, in association with native iron and graphite. It was established that the iron carbides formed within the Earth’s core at a pressure interval of 50–130 GPa; these phases associate with iron carbide, Fe-C3, silicon carbide, SiC, Cr-Mn-Fe and Mn-Fe oxides; the latter may be termed Mn-rich xieite. Our identified finds demonstrate a wide field of natural compositions from pure carbide to pure nitride, with multiple stoichiometries from M7(C,N)3 to M23(C,N)6 and with M/(C,N) from 1.65 to 3.98. We conclude that the studied iron nitrides and carbonitrides were formed in the lowermost mantle as the result of the infiltration of liquid metal, containing light elements from the outer core into the D″ layer, with the formation of the association: native Fe0 + iron nitrides, carbides, and transitional compounds + silicon carbide. They indicated that major reservoirs of nitrogen should be expected in the core and in the lowermost mantle, providing some solution to the problem of nitrogen balance in the Earth.

hand, Li et al. (2013) concluded that the mantle may still contain an amount of nitrogen one to two orders of magnitude larger than the present atmospheric reservoir. Nitrogen is suggested to have siderophile behavior in the core’s metal alloy and extremely high solubility, with partitioning of nitrogen Kmetal/Silicate around 10000 (Miyazaki et al. 2004). Such high value implies a nitrogen mass, in the core, hundreds of times greater than that in the atmosphere; an estimate for the total proportion of nitrogen in the core by Miyazaki et al. (2004) is \(1 \times 10^{24}\) g. This suggestion is supported by high concentrations of nitrogen in iron meteorites (Sugiura 1998) and provides a basis to consider the Earth’s core as a major reservoir to nitrogen (Roskosz et al. 2013), containing perhaps 97% of its total planetary inventory (McDonough 2014). The most recent calculations conclude that the fraction of nitrogen within the Earth’s core may be between 10 and 90%, depending upon the oxygen fugacity values in force during metal-silicate equilibration, and whether the core is a significant, but not dominant reservoir of terrestrial nitrogen (Dalou et al. 2016). The exact quantities of nitrogen in the core and the mantle remain unclear.

Here we report the first finds of iron nitrides, FeN, Fe2N, and carbonitride, Fe9(N,C)4, as inclusions in lower-mantle diamond from Rio Soriso, Brazil. We suggest that iron nitrides and carbonitrides are mineral phases, characteristic to the core/mantle boundary. These phases associate with iron carbide, Fe-C3, and silicon carbide, SiC. We conclude that: (1) the presence of these minerals at the core/mantle boundary is the result of the infiltration of liquid metal, containing light elements, from the outer core into the D″ layer, with the formation of the association: native Fe0 + iron nitrides, carbides, and transitional compounds + silicon carbide; and (2) major reservoirs for Earth’s nitrogen should be expected in the core and in the lowermost mantle.