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Highlights and Breakthroughs

Looking for'missing' nitrogen in the deep Earth

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Nitrogen is the main elemental constituent of Earth's atmosphere, but the deep Earth cycle of nitrogen is enigmatic because the speciation of nitrogen in the mantle has not been well constrained. Xenoliths from Earth's upper mantle contain small amounts of nitrogen: from a few ppm in the depleted sub-ridge mantle to nearly 100 ppm in mantle-enriched domains formed by the recycling of organic materials transported to the deep mantle by subduction. It has been also suggested that the redox conditions in the mantle wedge resulting from subduction favor the development of the nitrogen-enriched atmosphere of the Earth (Mikhail and Sverjensky 2014).

The comparison of the composition of bulk Earth and carbonaceous chondrites shows that the nitrogen in Earth is depleted by an order of magnitude relative to hydrogen, carbon and most noble gases (Marty 2012). That depletion can be due to un-accounted nitrogen that is stored, in the Earth's deep interior. The 'missing' nitrogen would likely have been sequestrated into the core or retained in the mantle during core-mantle differentiation. A host for nitrogen could be also deep mantle crystalline phases, which can capture nitrogen to variable degrees, depending upon oxygen fugacity and pressure. Thus, there are several different deep mantle reservoirs that may hide significant amounts of nitrogen, in yet unknown forms.

Unsurprisingly then, evidence for nitrogen reservoirs in the deep mantle are currently scarce. Much of our knowledge of Earth's deep interior comes from theoretical models, which are in turn based on experimental petrology and seismology data, rather than direct observation of deep mantle phase compositions. But we believe that some diamonds do indeed sample the deep mantle; inclusions in diamonds often appear to represent unique natural samples containing inclusions of mantle materials entrapped during diamond growth and preserved during long periods of geological evolution. The deep levels of the Earth's interior, e.g., sub-lithospheric depths below 410 km, would thus appear to now be accessible in the form of 'superdeep' diamonds, which can contain mineral assemblages that originated in the transition-zone or in the lower mantle (e.g., Harte et al., 1999). Most 'superdeep' diamonds are nitrogen-free or nitrogen-poor, but some contain several hundreds ppm of nitrogen and more. Nitrogen bearing micro- and nano-sized inclusions have also been identified in 'superdeep' diamonds (Rudloff-Grund et al., 2016). Metal-silicate partition experiments suggest that at sublithospheric mantle depths nitrogen would be concentrated in metal phases (e.g., Miyazaki et al., 2004), or be closely associated with Fe-carbides, where N readily replaces C at high pressure (Litasov et al., 2016). The isostructural behavior of Fe-nitrides and Fe-carbides has been confirmed at pressures corresponding to the deep mantle and the core (Minobe et al., 2015; Litasov et al., 2017). These observations are widely discussed to identify a potential influence of core-mantle differentiation on the evolution of terrestrial nitrogen.

In the highlighted paper, Kaminsky and Wirth (2017) present new data on unique inclusions of iron nitrides (Fe_2N and Fe_3N) and carbonitride ($Fe_9(N,C)_4$) in association with iron carbide (Fe_7C_3), silicon carbide (SiC) and exotic Cr-Mn-Fe oxides in a 'superdeep' diamond from Rio Soriso, Brazil. The authors link the formation of those inclusions to infiltration of a liquid metal containing light elements from the outer core into the D" layer at the core/mantle boundary. Based on the composition of the inclusions and on the experimental studies carried out under mantle conditions, the authors conclude that major nitrogen reservoirs occur in the core and in the lowermost mantle. However, extrapolation of these samples to the core or core-mantle boundary is not necessary. The samples can represent reduced domains (e.g., Smith et al., 2016), which can locally be preserved throughout the mantle marking primordial redox heterogeneity, inefficient (and now inhomogeneous) core-mantle separation, significant amounts of disproportionated Fe, or even reduced portions of subducted slabs enriched in organic carbon (Sokol et al., 2017). Nevertheless, the new discovery of carbide and nitride phases in superdeep diamonds creates new horizons and opens great perspectives in looking for 'missing' nitrogen in the deep Earth's mantle.

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