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Subduction in early Proterozoic mantle: Implications from nitrogen in carbonatites

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Nitrogen in the mantle exists in various speciation depending on oxidation conditions. Based on thermodynamic calculations, it predominantly occurs as N₂ under relatively oxidized conditions and as NH₄⁺ when conditions are reducing (Mikhail and Sverjensky, 2014). The speciation has an effect on its compatibility behaviour, being more soluble in melts when in reduced form, while the reverse is true for fluids (Mysen, 2019). Carbonatites are very important to constrain the nitrogen composition of the mantle with important implications for the subduction history of the Earth. Carbonatites entrain components from different reservoirs including the deep Earth near the core-mantle boundary and, temporally encompass a wide range in age (Dauphas and Marty., 1999; Basu and Murty, 2015). Studies from some young carbonatites in India from Sung Valley (107 Ma) and Ambadongar (65 Ma) indicate that the nitrogen is present as more than one component in the source, unhomogenised and hence identifiable, that can be related to their occurrence in more than one chemical form (Basu and Murty, 2015).

The emergence of efficient and long-lived plate tectonics is thought to be as early as Late Archean, based on nitrogen isotopic composition of placer diamonds from Witwatersand from the Kapvaal craton (Smart et al., 2016). While this may represent a global occurrence, we have undertaken a more robust study with carbonatites ranging in age from 2500 to 770 Myrs, with the goal of identification of the initiation of subduction in a global scale and investigation of any change in the nitrogen stored in the mantle with time. The carbonatites studied are from Khambamettu (2.5 Ga), Hogenakal (2.4 Ga), and Sevattur (770 Ma), located in the southern part of India. Calcites and apatites separated from the host rocks were analysed by vacuum crushing. The apatites were also analysed by stepwise pyrolysis to release and decouple different components at different temperatures. In the carbonates, the nitrogen contents vary from 140 to 1507 ppb with accompanying $\delta^{15}\text{N}$ ranging from 4.7 ± 0.4 to 11.7 ± 1.3 ‰. The nitrogen in the apatites from Hogenakal and Khambamettu show depleted signatures with $\delta^{15}\text{N}$ as low as ~ -22 ‰, accompanied by low nitrogen content of ~ 60 to 140 ppb. The apatite from the younger Sevattur complex is comparable to the carbonates in terms of both concentration and isotopic composition. This can be related to increase in nitrogen input via subduction with time during Earth's history since the Proterozoic, transported to the deep mantle, consequently overprinting any primordial signatures inherited from precursor building material such as the chondrites.

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