In situ SIMS analyses of nitrogen in high pressure rocks reveal variable nitrogen behaviour during fluid-rock interaction

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Subduction is the primary mechanism through which nitrogen (N) and other volatile elements are recycled from the atmosphere to the deep Earth. Quantifying this aspect of the geological N cycle requires an understanding of how N behaves during subduction zone metamorphism. Here we present *in situ* measurements of N in silicate minerals by secondary ion mass spectrometry, focusing on eclogite and blueschist-facies rocks representing subducted oceanic crust (Harris *et al.*, 2022). We investigate the partitioning of N between metamorphic minerals and its behaviour during fluid-rock interaction. Bulk rock N concentrations calculated from mineral N concentrations and mineral modal abundances are consistent with N concentrations measured by bulk combustion, which confirms that most N is hosted within silicate minerals and not along grain boundaries or in fluid inclusions. Our data confirm that white mica (phengite, paragonite) is the primary host for N, containing up to 320 µg/g, whereas other minerals including clinopyroxene, amphibole and epidote contain <5 µg/g N. Chlorite is typically N-poor but can also contain significant amounts of N (up to 83 µg/g) and may play a previously unrecognised role in subduction zone N cycling. We investigated the fluid-mineral partitioning behaviour of N by combining analyses of N with other trace and major elements. Open system trace element modelling was used to model the evolution of N, B and Li contents during fluid-rock interaction in phengite from a garnet-phengite quartzite. Fluid-rock interaction at eclogite-facies conditions resulted in 25-50% loss of N from the rock. By comparison to existing partitioning data for B and Li, the phengite-fluid partition coefficient for N was estimated to be 0.1-1.5. In a separate case study on a retrogressed eclogite, the growth of paragonite during blueschist-facies fluid-rock interaction was shown to sequester N from existing phengite, limiting bulk N loss to the fluid. In addition, several samples show evidence of N addition during subduction, likely from sediment-derived fluids. Thus, mafic crust can act as a sink for N if white mica is stable, and the stability of white mica during fluid-rock interaction is critical in controlling the behaviour of N. The balance between N retention in the downgoing slab and N loss to the mantle wedge is controlled by a combination of metamorphic reactions and fluid-rock interaction. Our work provides the first natural constraints on the fluid-mineral partitioning behaviour of N at subduction zone conditions and emphasises the complexity of N mobility within subduction zones, with redistribution between different phases and lithologies being a key factor.

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