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Decoupled geochemical behavior between ammonium and other fluid-mobile elements from seafloor alteration to blueschist-facies metamorphism

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Blueschist-facies meta-basalts generally show enriched ammonium and other fluid-mobile elements (FME), such as K, Rb, Ba, Sr, Pb. These enrichments have been attributed to seafloor hydrothermal alteration in the protoliths and/or subduction-zone metasomatic addition. Traditionally, the behavior of ammonium is considered to be in pace with other FMEs during alteration and metasomatic processes. Here, we report two suites of blueschist-facies meta-mafic rocks from the Luobei region of the Heilongjiang Complex in NE China that record contrasting behavior between ammonium and other FMEs. The first suite was derived from an N-MORB protolith and exhibit significant ammonium enrichment (N = 56.2–112.4 ppm with an average of 85.8 ppm; n = 3). Nitrogen contents correlate positively with K, Ba, and Pb contents, indicating that most of the N was added by subduction-zone metasomatism, with minor by seafloor alteration. This behavior is consistent with those reported for blueschist-facies meta-basalts from the Raspas Complex (southwest Ecuador), the Yilan–Mudanjiang segments of the Heilongjiang Complex, and the Central Qiangtang Metamorphic Belt in Tibet. In contrast, the second suite, derived from an E-MORB protolith, shows strong depletions in K, Ba, and Pb relative to its protolith while retaining N contents (11.6–44.8 ppm with an average of 26.6 ppm; n = 15) ~four-times higher than that of the seafloor altered basalts (average N content = 7 ppm). This systematic decoupling between N and other FMEs could be attributed to a two-stage alteration history: (i) seafloor hydrothermal alteration (possibly under high-temperature or freshwater condition) that stripped FMEs from the E-MORB protoliths while modestly increase N by stabilizing NH_4^+ in the crystal structures of alteration phases (e.g., clay minerals and chlorite) prior to subduction; and (ii) subsequent N enrichment within the subduction channel via interaction with metamorphic fluids derived from the metasedimentary component in the mélange complex. These results demonstrate that N can behave independently to classic FMEs during seafloor alteration and subduction metamorphism and should thus be treated cautiously when integrated with the other FMEs.