Mineral record of abiotic nitrogen reduction

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Abiotic nitrogen reduction (ANR) in hydrothermal systems has been long considered as the most likely mechanism to transform N_2, the dominant N species on the pre-life Earth's surface, into NH_4^+, an essential compound for abiotic synthesis of large organic molecules facilitating the emergence of life in the early oceans [1]. Mineral-induced ANR process has been demonstrated by laboratory experiments [2-4], but not yet been verified in natural hydrothermal systems.

To trace the footprint of ANR, we examined NH_4^+ contents (expressed as N contents below) and N isotope compositions of coexisting muscovite and biotite minerals in 15 granite samples from a fossil hydrothermal system in Eastern China. The samples were formed in a rifting setting of middle Neoproterozoic, where granite H and O isotopes were modified by continental glacial meltwater at high temperature [5]. Our results indicate that muscovite in the samples always have typical granitic signature of low N contents (30-110 ppm) and high $\delta^{15}N$ values (2.5-12.6‰). However, except 2 samples displaying equilibrium NH_4^+ partitiong and N isotope fractionation between muscovite and biotite, the biotite in all other samples show significant N enrichment (N contents from 110-2400 ppm) coupled with lowered $\delta^{15}N$ values (2.4‰ to -6.8‰). This feature can be only explained by a kinetic isotopic effect [6] associated with N reduction by Fe^{2+} in biotite during fluid-rock interaction. Accordingly, these rocks provide a first geological record for ANR process in natural hydrothermal system.

Reference

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