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Anomalous nitrogen isotopes in ultrahigh-pressure metamorphic rocks from the Sulu orogenic belt: Effect of abiotic nitrogen reduction during fluid–rock interaction

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ABSTRACT

Modern nitrogen (N) fixation is primarily mediated by biological processes. However, in the early Earth where biological activity was absent or limited, abiotic N reduction in hydrothermal systems is thought to be a key process to transform atmospheric N_2 and NO_x to ammonium, an essential nutrient to support the emergence of life and also an N form that can be incorporated into rocks. Surprisingly, evidence for abiotic N reduction in the rock record has not been clearly identified. In this study, we reported anomalously low N isotope compositions ($\delta^{15}N$ values as low as $-15.8‰$) of mica samples in ultrahigh-pressure metamorphic rocks from the Donghai area in the Sulu orogenic belt, eastern China. Compared with mica samples with typical crustal $\delta^{15}N$ values (3–9‰) in similar metamorphic rocks from the western Dabie orogen, the ^{15}N-depleted mica samples from the Sulu orogen are characterized by significant N enrichment (10 times higher) and extreme ^{18}O depletion ($\delta^{18}O$ values as low as $-9‰$). These features can be best explained by assimilation of N from a source characterized by extremely low $\delta^{15}N$ values (less than $\sim -16‰$). The extremely low $\delta^{15}N$ value would be produced by abiotic N reduction during reaction of a meteoric-hydrothermal fluid with crustal rocks before subduction. This observation provides a clue to the occurrence of abiotic N reduction in continental supracrustal rocks and infer that abiotic N reduction process could be a fundamental process driving the geological N cycling in early Earth.

1. Introduction

Nitrogen (N) exists as different species in Earth's reservoirs: mainly as N_2 and in minor amounts as NO_x and NH_3 in the present-day atmosphere; mainly as NO_3^- and NH_4^+ in the hydrosphere (e.g., Sigman et al., 2009); bound with reduced C in the biosphere (e.g., Ader et al., 2006); as NH_4^+ (replacing K^+) in mineral structure in the crust and nitride, N_2, and/or NH_3 in the mantle (Honma and Itihara, 1981; Roskosz et al., 2006; Watenphul et al., 2009; Li et al., 2013; Li and Keppler, 2014).

The N cycling between different reservoirs requires a change in N species. For example, N transfer from the surface reservoirs (i.e., the atmosphere and hydrosphere) to the lithosphere involves transformation of N_2 and NO_x to ammonium. This has been primarily mediated by biological processes since at least the Phanerozoic and likely earlier. Phytoplankton and cyanobacteria can assimilate NO_3^- and N_2, respectively, to produce reduced N forms (in C–N bonds) in their biomass. The latter can be further decomposed to NH_4^+ which is subsequently incorporated into clay minerals. Geologically controlled transformation of N_2 and NO_x to ammonium by abiotic N reduction (ANR) has been considered to be negligible in global N cycle (see review by Cartigny and Marty, 2013).

However, laboratory experiments have indicated that, at hydrothermal conditions (e.g., $T > 120\,°C$, $P > 50$ bars in presence of reductant and catalyst, such as Fe–Ni, pyrite), NO_x and N_2 can be efficiently reduced into ammonium by fluid–rock interaction (Brandes et al., 1998; Schoonen and Xu, 2001; Smirnov et al., 2008). Given that NH_3 is unstable in the Archean reduced atmosphere due to rapid decomposition by UV light (Kasting, 1982), ANR has consequently been considered as the most feasible mechanism to convert N_2 or NO_x (e.g., from lightning) to ammonium in the prebiotic Earth (Navarro-Gonzalez et al., 2001). Because

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ammonium is one of the essential nutrients for amino acids (the essential blocks for life), ANR has important applications for the origin of life (although other process is also possible, see Kuga et al., 2014), but remains unobserved in the field. The main reason for the lack of field ANR records is likely attributed to the overprinting by secondary alteration. Numerous field-based studies have indicated that ammonium can be remobilized by fluid circulation (e.g., from sediments with N of organic origin to igneous rocks; Bebout et al., 1999; Busigny et al., 2005b; Li et al., 2007; Svensen et al., 2008) or be decomposed/oxidized and subsequently released as NH_3/N_2 during metamorphism (Bebout and Fogel, 1992; Mingram and Bräuer, 2001).

One possible ANR case was recorded in the lower section of Jurassic oceanic crust from the western Pacific (Li et al., 2007). The basaltic rocks from the Ocean Drilling Program (ODP) Sites 810 and 1149 in the Pigafetta Basin contain N mixed between the mantle with $\delta^{15}N$ [where $\delta^{15}N = (^{15}N/^{14}N)_{Sample}/(^{15}N/^{14}N)_{Air} - 1$] value of $-5‰$ and an end-member with $\delta^{15}N$ value less than $-12‰$. This extremely low $\delta^{15}N$ value may be attributed to kinetic N isotope fractionation associated with alteration-related ANR, which preferentially utilizes ^{14}N for ammonium production (Li et al., 2007). However, due to difficulties in identifying both N speciation and the minerals hosting N in the basalts, the involved phases (e.g., ammonium or some other N species, such as nitrosyl; Roskosz et al., 2006) as well as the possibility of involving equilibrium isotope fractionation processes remain uncertain.

In this study, we investigated the N concentrations and isotope compositions of micas (including phengite, muscovite and biotite) in ultrahigh-pressure (UHP) metamorphic rocks from Donghai area in the Sulu orogen. These UHP rocks experienced intensive hydrothermal alteration by meteoric water-dominated fluid during the intrusion of their protoliths in the Neoproterozoic (740–780 Ma; Rumble et al., 2002; Zheng et al., 2004; Tang et al., 2008a) and were metamorphosed much later in the Triassic (~210–240 Ma; e.g., Li et al., 1993). As a comparison, we also investigated mica samples (phengite and muscovite) in metamorphic rocks from the western Dabie orogen, which experienced similar metamorphic history but different protolith alteration history (i.e., no alteration or only slight alteration by low-T hydrothermal fluid on the surface). Nitrogen in micas dominantly occurs as ammonium substituting K in the lattice (Honma and Itihara, 1981; Boyd, 1997), and thus provides better constraints on the understanding of N isotopic signature.

2. Geological settings, samples and analytical methods

The Dabie–Sulu orogenic belt in eastern China (Fig. 1) was formed by northward subduction of the South China Block beneath the North China Block in the Triassic (Li et al., 1993; Zheng et al., 2003). Petrological studies indicate that the continental crust was subducted to mantle depths of at least 120 km (Xu et al., 1992), maybe even >200 km (Ye et al., 2000). Geographically, the UHP unit lies in the middle of the nearly EW extension belt, with low-T/high-P blueschist and eclogite units in the south and high-T/low-P migmatite complex in the north (Fig. 1).

Oxygen isotope studies have shown strong ^{18}O depletion with $\delta^{18}O$ values [where $\delta^{18}O = (^{18}O/^{16}O)_{Sample}/(^{18}O/^{16}O)_{VSMOW} - 1$] as low as $-15‰$ (Zheng et al., 2007) widespread in the Dabie–Sulu orogenic belt (Zheng et al., 2003; Tang et al., 2008b). These values are interpreted as a result of isotope exchange between rocks and meteoric-hydrothermal fluid at high T (see review by Zheng et al., 2008). Geochronological studies on ^{18}O-depleted zircons from UHP eclogites and orthogneisses gave two groups of U–Pb ages at Neoproterozoic (740–780 Ma) and Triassic (210–240 Ma), which represent the ages of protolith emplacement and subduction-zone metamorphism (Rumble et al., 2002; Zheng et al., 2004; Tang et al., 2008a, 2008b), respectively. High-T hydrothermal alteration resulting in the ^{18}O depletion occurred during the protolith emplacement of the UHP meta-igneous rocks in the Neoproterozoic in response to the breakup of the Rodinia supercontinent (Zheng et al., 2003, 2008).

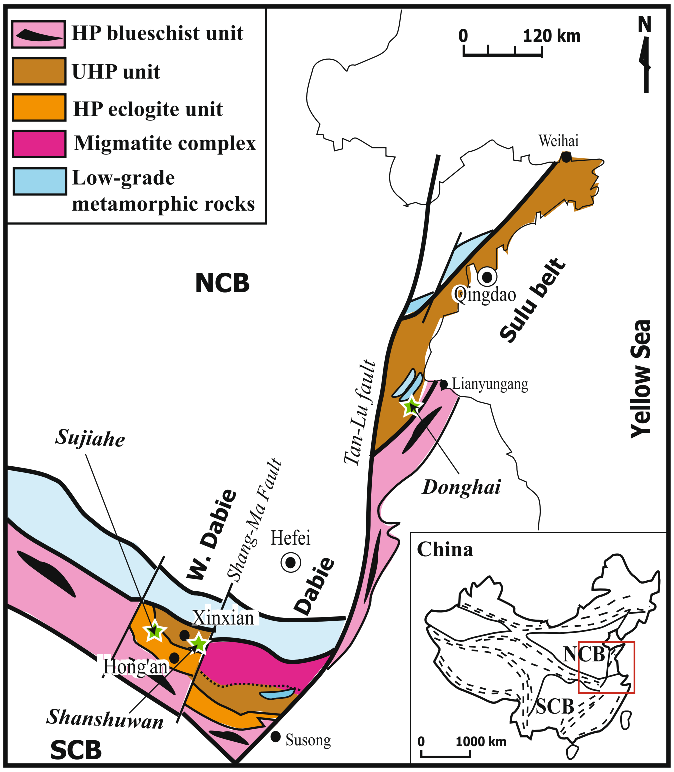

Fig. 1. Schematic map showing the geology of the Dabie–Sulu orogenic belt. Sample sites in the western Dabie (Sujiahe in the Huwan HP zone and Shanshuwan in the Xinxian UHP zone) and Sulu (Donghai in the UHP unit) are donated by stars. NCB = North China Block; SCB = South China Block.

The Dabie orogen was divided into several zones by later faulting. The western Dabie zone was truncated from the central Dabie zone by the Shang–Ma fault (Fig. 1). The samples studied here include 2 eclogite samples from Shanshuwan in the Xinxian UHP zone and 4 eclogite and 1 mica schist samples from Sujiahe in the Huwan HP zone. The UHP eclogites at Shanshuwan occur as lenses enclosed in biotite gneisses, which are all surrounded by granitic gneisses (Li et al., 2001). The protolith ages of these eclogites are ~790 Ma (Fu et al., 2013), which is consistent with the protolith ages of most other HP and UHP rocks in the Dabie–Sulu orogenic belt. Oxygen isotope analyses on these two samples gave whole-rock $\delta^{18}O$ of 5–6‰ (Li et al., 2001; Fu et al., 2003), within the $\delta^{18}O$ range of mid-ocean ridge basalts (Eiler, 2001), suggesting little modification by external fluids. Samples from Sujiahe were all collected in the Huwan shear zone (Fig. 1), where eclogites generally interlayer with mica schists. Based on field observation and geochronological evidence, the protoliths of the Sujiahe HP eclogites are most likely Paleotethyan oceanic crust (Fu et al., 2002; Cheng et al., 2009; Wu et al., 2009) although a Neoproterozoic continental crust is also proposed (Liu et al., 2004; Peters et al., 2013). The 4 eclogite samples from Sujiahe contain high-salinity aqueous fluid inclusions and exhibit whole-rock $\delta^{18}O$ of 4.3–11.2‰ (Fu et al., 2002), similar to those of modern oceanic basalts that have been hydrothermally altered by seawater at low to medium T (<250 °C; Alt, 2003).

The Sulu orogen is considered as an eastern extension of the Dabie orogen, but has been displaced northward for 550 km by the Tan–Lu fault (Okay et al., 1989; Fig. 1). Owing to the discovery