Nitrogen and argon isotopes in the Archaean continental crust: investigating the evolution of the early earth

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Tracing the origin and fate of major volatiles, such as nitrogen, it is important to understand the evolution of the early earth. However, the geochemical behaviour of N is still poorly constrained and the resulting N evolution model of the earth is rather complicated. The general view supposes a mantle source with N being depleted in heavy isotopes (δ^{15}N −25‰) and its degassed product (atmospheric-crustal N) and the residual mantle both enriched in heavy isotopes (δ^{15}N from 0‰ to +12?tf="Pi2">%). To reconciliate this paradoxical view, two diverging models of the earth evolution have been proposed: (1) an original N source from enstatite chondrite (δ^{15}N −25‰) mixed with a tardive veneer (δ^{15}N +42‰) recycled in the mantle by subduction (Javoy, 1997); or (2) the fractionation, due to atmospheric escape, of an enstatite chondrite original source (Marty and Humbert, 1997).

These hypotheses need to be verified by measuring the N isotopic composition in the early earth, particularly in the Archaean crust. Until now, sparse data were available (e.g. Sano and Pillinger, 1990). The aim of this ongoing study is to obtain precise isotopic N data from the Archaean crust. We selected (1) 3.5–2.4 Ga cherts from Pilbara Craton and Hamersley Basin, Western Australia, rocks that have been never metamorphosed above the pumpellyte-prehnite facies (~250°C); and (2) 3.8 Ga cherts and BIF (Banded Iron Formation) from Isua, West Greenland, metamorphosed to amphibolite facies (~600°C). The choice of measuring N isotopes in the Isua samples was mainly dictated by the need to investigate: (1) the efficiency of N retention in subduction-related recycling; and (2) whether N primordial components have been preserved or not from high grade metamorphism processes.

Nitrogen was extracted using a stepwise combustion technique, whose isotopic ratio was measured by a static type mass spectrometer, together with argon isotopes and carbon amount. Calibration of N relative to argon isotopes has been proven to be effective in deconvoluting N sources in rocks (Yamamoto *et al.*, 1998).

First results showed two volatile fractions in the Archaean sediments, released at 500–900°C and at 1000–1200°C, respectively. The N amount was low (0.05–1.7 ppm) and it was accompanied by low ^{36}Ar contents ($0.2–2 \times 10^{-14}$ mole/g), but high C contents, from 11 up to 3100 ppm. The δ^{15}N values ranged from -5‰ to +19‰. The ^{40}Ar/^{36}Ar ratios ranged from 300 to 19,000. Electron microprobe analysis and literature data gave K contents of 20–2000 ppm, low, but theoretically sufficient to produce the high ^{40}Ar/^{36}Ar ratios. This point is to be confirmed by ICP-MS analysis of K to decipher if the

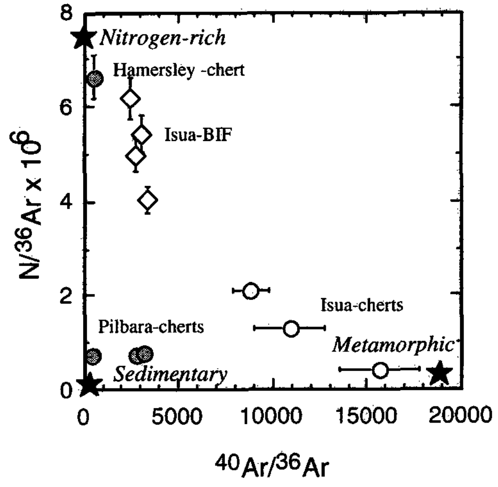

FIG. 1. ^{40}Ar/^{36}Ar *vs.* N/^{36}Ar ratios (1000–1200°C steps) measured in Archaean samples. The stars show possible volatile components.

samples had been in a closed system, and thus N primordial components have been preserved.

The C/N *vs.* $^{40}Ar/^{36}Ar$, $N/^{36}Ar$ *vs.* $^{40}Ar/^{36}Ar$ and N *vs* $\delta^{15}N$ relationships allowed to identify the following components: (1) a *nitrogen-rich* component (N ~1.7 ppm; $\delta^{15}N$ ~+10‰, $N/^{36}Ar = 8 \times 10^6$, C/N ~1,000), observed at the low and high temperature steps of Isua BIF and in a chert associated with BIF of Hamersley Basin (Fig. 1); (2) a *metamorphic* component characterized by devolatilization of N and ^{36}Ar, compared to C (C/N ~10,000; $^{40}Ar/^{36}Ar$ ~19,000; $\delta^{15}N$ ~ +20‰, N ~0.05 ppm) in Isua samples; (3) a *carbon-rich*, component (C/N ~40,000; $N/^{36}Ar$ ~3×10^5; $^{40}Ar/^{36}Ar < 4,000$; $\delta^{15}N$ of ~10‰), observed in Isua metacherts. It could be contained in carbonates (~2 wt.%) or in graphite occurring in these samples. (4) a *sedimentary-like* component in Pilbara cherts, characterized by variable N contents (0.1–0.5 ppm), $\delta^{15}N$ from –5‰ to +10‰, low C/N ratios of ~1000 and intermediate $^{40}Ar/^{36}Ar$ ratios of 300–3000.

Analyses of new BIF samples from Isua and Hamersley Basin will be decisive in deciphering if the *nitrogen-rich* component of Isua BIF is a reduced species of N, such as ammonia, which may be bound with Archaean oxygen mainly stored in BIF deposits, or possibly an early sedimentary or atmospheric N component, enriched in heavy N isotopes.

References

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