A ^{15}N-enriched Archean atmosphere

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Introduction

The origin and evoltion of nitrogen in Earth's atmosphere is controversial. Earlier results on Archean cherts and BIF show a range of $\delta^{15}N$ from –6 to 30‰. Given temporal and spatial association of chert-BIF with volcanic sequences erupted from mantle plumes, we selected blacks shales distal from chert-BIF to obtain a marine biogenic signature, together with hydrothermal micas from gold provinces, to constrain the secular varistion of $\delta^{15}N$ through time.

Results

Kerogen in metashales from the 2.7 Ga Sandur belt, E. Dharwar craton, is characterized by $\delta^{15}N$ 13.1 ± 1.3‰, and C/N 303 ± 93. Kerogen from 1.7 Ga carbonaceous shales of the Cuddapah basin average 5.0 ± 1.2‰, close to the mode at 3 to 4‰ for kerogen and bulk rock of Phanerozoic sediments. Hydrothermal micas from late-metamorphic quartz-vein systems of the 2.6 Ga Kolar gold province, E. Dharwar craton, that proxy for average crust, are enriched at 14 to 21‰, which are also consistent with other late Archean gold provinces, confirming that the N–budget of the hydrothermal fluids is dominated by sedimentary rocks.

Discussion and Implication

Enriched values in Precambrian rocks cannot be caused either by N-isotopic shifts due to metamorphism or Rayleigh fractionation, or by long-term preferential diffusional loss of ^{14}N. It is possible that the ^{15}N-enriched values stem from a different N-cycle in the Archean, with large biologically mediated fractionations, yet the magnitude of the fractionations between atmospheric N_2 and organic nitrogen observed exceeds any presently known. We attribute the ^{15}N-enriched reservoir to a secondary atmosphere derived from CI-chondrite-like material and comets with $\delta^{15}N$ of +30 to +42‰. Shifts of $\delta^{15}N$ to its present atmospheric value of 0‰ can be accounted for by a combination of early growth of the continents with sequestration of atmospheric N_2 into crustal rocks, and degassing of mantle N ~ -5‰.

References

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Experimental study of sulfur isotope fractionation associated with pyrite oxidation by H_2O_2

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Radiolysis of water can accelerate water/rock interaction through production of radicals (e.g., H˙, HO$_2$˙, OH˙) and reactive molecules (e.g., H_2, H_2O_2, O_2). Radiolytic oxidation can be observed in modern groundwater associated with uranium ore bodies and can be inferred for ancient groundwater. Prior to development of an O_2-rich atmosphere on Earth, radiolytically generated oxidants could have reacted with pyrite and provided local sources of partially to fully oxidized sulfur species suitable for microbial metabolism.

We evaluated sulfur isotope effects associated with reactions between pyrite and radiolytic oxidants using a series of sealed-quartz-tube experiments run with 60 mg of acid-cleaned pyrite, 10 ml of deoxygenated water, and concentrations of H_2O_2 at micromolar levels. Experiments ranged in temperatures from 4 to 150ºC and had durations from 1 to 10 days.

In initial experiments, primary oxidation products were dissolved sulfate, elemental sulfur, iron sulfate minerals, and iron oxyhydroxide minerals. X-ray diffraction patterns and images from scanning electron microscopy reveal anhedral to subhedral hydrated iron sulfates in globular clusters of about 10-30 μm in diameter forming on pyrite surfaces. $\delta^{34}S$ remained unchanged for pyrite but showed distinct enrichment of ^{34}S in produced sulphate and elemental sulphur. $\Delta_{sulfate-pyrite}$ was 0.5-1 permil and $\Delta_{elemental\ sulphur-pyrite}$ was 1-2 permil. Our results indicate that pyrite oxidation by H_2O_2 induces greater fractionation that has been recognized in previous studies. Although Δ values for sulphates and elemental sulphur are not large, compensating depletion of ^{34}S in undetected products could be substantial if the proportional yields are small. Preliminary isotope results from high-temperature experiments indicate that the ^{34}S-depleted fraction might be held in iron sulfate and/or iron oxyhydroxides.