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Life detection in Archean rocks: are stable isotopes reliable?

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Among signatures of ancient biological activity, stable isotopes of C, S, Fe and N hold an important place. Indeed, metabolic processes tend to produce different, and sometimes diagnostic, enrichment or depletion in certain isotopes. Large environmental and biological changes at the surface of the Earth, as those provoked or provoking the oxygenation of the primitive atmosphere are clearly imprinted in the C, S, N and Fe geological record. Yet, the reliability of stable isotopes as biological and environmental proxies has been recently questioned. Short-chain hydrocarbons synthesized via Fischer-Tropsch-type reactions in hydrothermal environments are depleted in ¹³C in a way typically ascribed to metabolic processes such as photosynthesis and methanogenesis (small $\delta^{13}\text{C}_{\text{PDB}} = [(^{13}\text{C}/^{12}\text{C})_{\text{sample}}/(^{13}\text{C}/^{12}\text{C})_{\text{std}} - 1] \times 1000 = -30$ to -60 permil). This suggests that carbon isotopic composition might not be an effective discriminant between biologic and non-biologic sources. Sulfur isotopes, and particularly the ³³S/³⁴S ratios show variations in the geological record usually interpreted as reflecting changes in the redox state of the atmosphere and in the biologically related sulfur cycle. Yet, thermochemical reactions might produce similar isotopic fractionations. Nitrogen has been longtime ignored as biosignature because being extremely fragile compared to the more stable graphitic forms of C. Indeed, it can be easily fractionated by metamorphic or hydrothermal-driven reactions. However, N has an advantage over other isotopic systems such as those of C and S. The dominant source of N at the surface of the Earth, that is, the atmospheric triple-bonded N₂, is so stable that only a very limited number of metabolic processes can bridge the abiotic and biotic world. Finally Fe (small $\delta^{56}\text{Fe} = (^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}}/(^{56}\text{Fe}/^{54}\text{Fe})_{\text{std}} - 1 \times 1000$) has very little isotopic fractionation (± 1 permil) and numerous studies shown that the biological-induced fractionation is not completely understood or yet measured. Here we present new data on N isotopes and their behavior in cherts and banded iron formations of South Africa (3.45 Ga Hooggenoeg Fm., Barberton Greenstone Belt) and India (2.9-2.7 Ga Bababudan Group, Dharwar Craton). Combination of two or more isotope markers (N, C and Fe) with largely different geochemical natures may help us to discriminate between possible fractionation pathways, biotic or abiotic, and/or rule out part of the anticipated post-depositional fractionation events. This is the case of the India Banded Iron Formations, where N isotopes have been coupled with Fe and C isotopes. Observed Fe, C and N isotopic co-variations in cherty and iron-rich layers have been related to the appearance of denitrification and dissimilatory iron reduction in the water column at the onset of the Great Oxygenation Event. Organic nitrogen was trapped as ammonium (NH₄⁺) in hydromuscovite and feldspars preserved in cherty formations of the Hooggenoeg Fm. at the Komati River, South Africa. Here nitrogen isotopes have been coupled with argon isotopes (⁴⁰Ar/³⁶Ar). Indeed, an indirect relation relates NH₄⁺ which replace K⁺ ions in the structure of K-bearing silicates and radiogenic ⁴⁰Ar*, which is produced by electron capture of K⁺. These formations show small $\delta^{15}\text{N}$ values of $+7.1 \pm 0.5$ to $+12.6 \pm 0.4$ permil, higher than those usually found in Early Archean ammonium (-5 to $+2$ permil). K-Ar dating of mica and feldspars give younger Proterozoic ages of 2137 ± 15 Ma and 1191 ± 27 Ma, respectively. This suggests that the mineral phase preserving ammonium is not a closed system and post-depositional metamorphic events likely reset the K-Ar clock. The same phenomenon possibly caused 1) partial devolatilization of the pristine organic N with preferential loss of ¹⁴N and increase of the small $\delta^{15}\text{N}$ values; or 2) isotopic exchange with metasomatic fluids which usually contain ¹⁵N-enriched nitrogen.

Keywords: life, Archean, stable isotope