

Ion microprobe carbon isotope analysis of Archean microfossils?

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Metapelites of the Archean Wutai Group (>2.5 Ga) of North China have been found to contain abundant graphite discs. These discs are confirmed to be composed of carbon by elemental mapping through electron and Raman microprobe analyses. Application of the graphite Raman geothermometer suggests these discs experienced metamorphic temperatures of ca. 500°C, consistent with the amphibolite grade of the host rock. We investigated these circular discs by ion microprobe techniques to determine whether they are metamorphic or biological in origin. It has been suggested that these simple discs, which are 20-220 µm in diameter, were originally spherical vesicles of acritarchs (potentially eukaryotic photoautotrophs) with a thick resistant organic wall, and that these were deflated and compressed during compaction and diagenesis. Some of the discs show evidence of folding, breakage, and medial split, all of which are seen in younger acritarchs with coherent and robust walls. If correct, the discovery of these acritarchs would extend the range of eukaryotic fossils back into the Archean, consistent with recent biomarker data. Ion microprobe analyses of five different discs were conducted with the Cameca 6f ion microprobe at high mass resolution at the Carnegie Institution of Washington. The magnitude of instrumental mass fractionation (IMF) inherent to surface ionization mass spectrometry was quantified by the repeated (n = 7) analysis of the standard Mao diamond ($\delta^{13}\text{C} = -6.5\%$, IMF = $53.1 \pm 0.4\%$). The primary Cs⁺ beam intensity was 0.5 nA and was focused down to a 20-25 µm spot, which allowed for multiple analyses of the same individual. In most cases the variability of $\delta^{13}\text{C}$ values between spots on the same individual was small (< 2%), but the range of values between different individuals spanned from -7.3 to -35.8%. The overall average of all analyses is close to the -21.3‰ value determined by standard techniques for bulk kerogen. The wide variability between individuals may be tentatively interpreted as biological in origin, insofar as metamorphic graphite measured by the same ion microprobe technique shows much smaller magnitude of variation in primary grains lacking secondary overgrowths.

Molybdenum isotope prospects

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The oxygenation of the oceans has varied through time but the timing and extent of these variations are not well understood, nor do we have a good understanding of the connections between changes in atmospheric and ocean oxygenation. The development and refinement of ocean paleoredox proxies is therefore a high priority.

The molybdenum (Mo) stable isotope system is emerging as a valuable tool for investigating ocean paleoredox. To first order, Mo enters the oceans via rivers and is removed in oxic environments by adsorption to Mn oxides and in sulfidic settings via scavenging of Mo oxythiomolybdates. The isotopic contrast between these sinks is ~ 2 ‰. Hence, the steady-state Mo isotope composition of the oceans should reflect the balance between Mo removal to Mn-oxides vs. removal in sulfidic settings. Fractionation occurs during removal to Mn-oxides. Today, this process generates a steady-state isotopic offset between average crustal Mo (~0‰) and seawater (~ 1.6‰). This offset would have been smaller - i.e., seawater isotopically lighter - during extended periods of expanded ocean anoxia because a smaller fraction of isotopically light Mo would have been buried in association with Mn-oxide sediments. This system is particularly valuable because it may constrain regional or global ocean redox, rather than only local redox, as a result of the long ocean residence time of this element.

Mo isotope systematics are already being used to obtain qualitative and semi-quantitative information about ancient ocean redox (e.g., Arnold et al, 2004). Quantitative applications require better understanding of a number of parameters, including: The importance of suboxic (O₂ < 5 µM) settings for Mo removal and isotope fractionation; the magnitude of isotope fractionation during adsorption to Mn oxides and the sensitivity of this fractionation to temperature and other variables; and Mo isotope variability due to weathering and riverine transport. The current status of research in these areas will be reviewed.

Reference

Arnold G.L., Anbar A.D., Barling J. and Lyons T.W., (2004), *Science* **304**, 87-90.