



Highlights of Analytical Chemistry in Switzerland

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Mass Extinction and Mass Spectrometry: Pursuing the Fate of the Earliest Multicellulars

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Since the middle of the last century, stable isotope analyses have been successfully applied to earth science problems. Up to ten years ago only the lighter elements (mainly H, O, C, N, and S) were analysed, as isotope fractionations of heavier elements were analytically not resolvable. The invention of multicollector plasma source mass spectrometers (MC-ICP-MS) largely overcame these problems. In 1998, the Institute of Geological Sciences in Bern acquired a NuInstruments™ MC-ICP-MS. One of the developments of our group has been the protocol for measuring the Mo isotope fractionation to study the evolution of free oxygen through Earth history. The principle is that Mo is very soluble as oxyanion (molybdate), but immobile in reducing environments. The variations of the $^{98}\text{Mo}/^{95}\text{Mo}$ ratio in present-day oceans are as large as 3 permil, which is well-resolved given our analytical uncertainty of 0.1 permil.



Ediacaran fauna, painting by Mary Parrish (Courtesy of Smithsonian Institution, Washington, DC)

About 600 million years (Ma) ago, at the end of the Precambrian era, the dominant life forms were a group of the earliest multicellular, soft-bodied animals, the so-called *Ediacara* fauna. About 540 Ma ago, at the Precambrian/Cambrian boundary, this biota was wiped out. This mass extinction provided room for new lifeforms, notably species with skeletons.

Late Precambrian oceans were stratified, with a deep layer where the decomposition of settling organic matter led to H_2S production by sulfate reducing bacteria. Dissolved molybdate (deriving from weathering of continents) accumulated in the upper layer. According to our hypothesis, a major change in ocean circulation produced an upwelling of the deeper waters and thus the mixing of H_2S -rich deep waters with Mo-rich upper waters. **H_2S is the only scavenging agent that could have been present in large enough amounts to produce the quasi complete Mo removal from ocean water, and this dramatic removal is necessary to explain the observed fast fluctuation of the Mo isotope signal, which is archived in coeval black shales. This sudden burst of toxic H_2S erased the shelf-dwelling *Ediacara* fauna.** Subsequent oxidation of H_2S by atmospheric oxygen allowed the shallower oceans to become habitable again.

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M. Wille, T. F. Nägler, B. Lehmann, S. Schröder, J. D. Kramers, *Nature* **2008**, 453, 767.



Earliest Cambrian black shales (Yangtze Platform, China), rocks which carry the Mo isotope signal following the extinction event

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