

## 6.5.13

### Progress in multiple sulfur isotope analysis by ion microprobe

S.J. MOJZSIS

Dept. of Geological Sciences, University of Colorado,  
Boulder, CO 80309, USA (mojzsis@colorado.edu)

High-resolution ion microprobe multicollector data have been measured for mass-independently fractionated (MIF) sulfur isotopic signals, expressed as  $\Delta^{33}\text{S}$  or the deviation from a mass-dependent fractionation line for the 3-isotope system ( $^{34}\text{S}/^{32}\text{S}$  vs.  $^{33}\text{S}/^{32}\text{S}$ ). Samples were derived from a variety of Phanerozoic, Proterozoic and Archean sediments [1]. The  $\Delta^{33}\text{S}$  values are identifiable at the scale of the ion microprobe beam ( $<25\ \mu\text{m}$ ) in individual sulfide grains and are resolvable from  $\delta^{34}\text{S}/\delta^{33}\text{S}$  ratios on the (terrestrial) mass-fractionation line at a level better than  $\sim 0.2\%$ . Indeed,  $\Delta^{33}\text{S}$  is so commonplace in ancient rocks it no longer makes sense to use the term “anomalous”. MIF in  $\delta^{34}\text{S}/\delta^{33}\text{S}$  observed in pre-2.47 Ga cherts, banded iron-formations, quartzite (metachert) and ferruginous metapelites provides compelling evidence that much of the sulfur in these rocks originated in the atmosphere, probably as aerosols [2,3]. A likely route was via  $\text{SO}_2$  and/or  $\text{H}_2\text{S}$  volcanic degassing, photochemical transformation in an anoxic atmosphere that imparted MIF to these gaseous species, ocean sediment deposition and conversion to sulfide or sulfate. A growing body of data is consistent with the operative photochemistry for MIF sulfur isotope reactions occurring under high-UV conditions deep in the pre-2.4 Ga atmosphere [4] and  $p\text{O}_2(\text{atm}) \ll 10^{-5}$  PAL [3].

The multicollector technique has a high sampling rate ( $\sim 7.5$  min./analysis) with little sample preparation and provides improved spatial resolution for specific high temporal-resolution sample sets such as sediments spanning the critical 2.4–1.9 Ga “Great Oxidation Event” at the Archean-Proterozoic transition [5]. Many of the marine shales and carbonates from that time contain abundant sulfides; the spatial selectivity of the ion probe technique facilitates measurement of  $\Delta^{33}\text{S}$  at the scale of individual sulfide grains allowing determinations from sediment cores, sulfidic microbands and possibly microfossils where they are preserved and interpretable. Thus the method is useful for describing the rate function and timescale of oxygen increase in the early Proterozoic (expected to have been inversely related to  $\Delta^{33}\text{S}$  over time), in exploring the mode of sulfur metabolisms of early life as well as providing a powerful tool for identification of sedimentary protoliths even in terranes that have experienced high grade metamorphism and deformation.

#### References

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## 6.5.14

### Dating the rise of atmospheric oxygen

A. BEKKER<sup>1</sup>, H. D. HOLLAND<sup>2</sup>, P.-L. WANG<sup>1</sup>,  
D. RUMBLE III<sup>1</sup>, H. J. STEIN<sup>3</sup>, J. L. HANNAH<sup>3</sup>,  
L. L. COETZEE<sup>4</sup> AND N. J. BEUKES<sup>4</sup>

<sup>1</sup>Geophysical Laboratory, Carnegie Institution of Washington,  
5251 Broad Branch Road, NW, Washington DC 20015,  
USA (a.bekker@gl.ciw.edu; p.wang@gl.ciw.edu;  
d.rumble@gl.ciw.edu)

<sup>2</sup>Department of Earth and Planetary Sciences, 20 Oxford  
Street, Harvard University, Cambridge, MA 02138, USA  
(holland@eps.harvard.edu)

<sup>3</sup>AIRIE Program, Department of Geosciences, Colorado State  
University, Fort Collins, CO 80523, USA  
(hstein@cnr.colostate.edu; jhannah@cnr.colostate.edu)

<sup>4</sup>Department of Geology, Rand Afrikaans University,  
Auckland Park 2006, Johannesburg, South Africa  
(njb@na.rau.ac.za)

Several lines of geological and geochemical evidence indicate that the level of atmospheric oxygen was extremely low prior to 2.45 Ga, and that it had reached considerable levels by 2.22 Ga. Here we present evidence that the rise of atmospheric oxygen occurred between 2.45 and 2.32 Ga. Syngenetic pyrite is present in organic-rich shales of the 2.32 Ga Rooihogte and Timeball Hill formations, South Africa. The range of the isotopic composition of sulfur in this pyrite is quite large and shows no evidence of mass independent fractionation. Both observations indicate that atmospheric oxygen was present at levels  $>10^{-5}$  PAL during the deposition of these units. The presence of rounded pebbles of sideritic iron-formation at the base of the Rooihogte Formation and an extensive and thick ironstone consisting of hematitic pisolites and oolites in the upper Timeball Hill formation indicate that atmospheric oxygen rose significantly, perhaps for the first time, during the deposition of the Rooihogte and Timeball Hill formations. These units were deposited between what are probably the second and third of the three Paleoproterozoic glacial events and are broadly time equivalent with carbonates of the Upper Duitschland Formation, South Africa that record positive carbon isotope excursion in seawater composition up to  $+10.1\%$  (Bekker *et al.*, 2001). The data are consistent with the stepwise oxidation of the atmosphere between 2.45 and 2.22 Ga when transition from anoxic methane-rich atmosphere to oxygenated  $\text{CO}_2$ -rich atmosphere led to climatic perturbations reflected by global glaciations. Glaciations were initiated by lowered atmospheric methane levels due to the rise of atmospheric oxygen and lasted until  $\text{CO}_2$  from mantle degassing reached levels sufficient to counteract low luminosity at that time. The rise of atmospheric oxygen corresponds with the latest stages in assembly of the Late Archean supercontinent Kenorland and the first emergence of large continental masses.