



## Insights from isotope stratigraphy

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A symposium on Precambrian isotope stratigraphy was held within the frame of the 33rd IGC held at Oslo, Norway, August 2008. This symposium spawned the idea for a special issue on this theme and ultimately to the ten papers assembled here. This special issue provides the results of some of the latest cutting edge research on traditional (C, Sr, S) isotope chemostratigraphy and introduce some newer isotope systems (REE, Ca) and Hg chemostratigraphy as a potential tracer for glacial events and estimate of the buildup of volcanic gases (including CO<sub>2</sub>) during glaciations. Moreover, it provides a distribution of studies that are broad in both space and time, highlighting chemical events from the Palaeoproterozoic (Africa, South America, Europe and India), Mesoproterozoic (South America), and Cryogenian-Ediacaran (North America, South America and India). Special attention is given to Neoproterozoic chemostratigraphy and problems with reliability of the use of carbon isotopes for Neoproterozoic stratigraphic correlation. A special focus is given to the atmospheric, climatic, and biogeochemical changes in both ends of the Proterozoic Eon.

The use of chemostratigraphy as a tool in the correlation of global events in the Precambrian followed the pioneer research by William T. Holser on ancient ocean water chemistry (Kaufman et al., 2007). Several researchers focused on carbon isotope variations across thick successions to investigate long-term fluctuations in the chemistry of the seawater (Veizer et al., 1980; Magaritz et al., 1986 and references therein). However, despite widespread

effects of late diagenesis on the isotope record, important isotope events could be demonstrated on a global scale (Magaritz et al., 1986; Holser, 1997, among many others) as it became evident that contemporaneous, apparently well-preserved, geographically distant marine strata registered similar isotopic compositions. Thereafter, chemostratigraphy has served as one of the principal means of intra- and extra-basinal stratigraphic correlation to assemble Precambrian stratigraphic record from fragments preserved in scattered successions. It is as an important tool in providing a time line compensating for poor biostratigraphic resolution of Precambrian fossils (Veizer et al., 1980; Magaritz et al., 1986; Knoll et al., 1986; Knoll and Walter, 1992; Kaufman et al., 1997; Corsetti and Kaufman, 2003; Halverson et al., 2005). Correlations established through chemostratigraphy can be used to comment on biogeochemical and climate changes through time.

The determination of the base of the Ediacaran Period was largely based on chemostratigraphy of cap carbonates that overlie glacial diamictites (Knoll et al., 2006) and have been accumulated during post-glacial transgression, recording the most profound carbon, sulfur, and strontium isotope variations in Earth history, and being the central focus for the 'snowball Earth' hypothesis (Kirshvink, 1992; Hoffman et al., 1998; Bekker et al., 2005). The lack of radiometric constraints on the absolute age of most of these extreme isotope excursions has led to debates on their temporal equivalence (Kaufman et al., 1997; Kennedy et al., 1998). The number of studies relying on isotope stratigraphy has grown substantially over the past 25 years and it is worth noting that in the case of carbon isotope stratigraphy, this method can be applied,

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with care, to metamorphic rocks up to the amphibolite facies (Melezhik et al., 2005b; Nascimento et al., 2007) and may retain depositional  $\delta^{13}\text{C}$  values in even diagenetically altered carbonates.

In order to apply the carbon isotope record for chemostratigraphic correlation of sedimentary sequences, it is important to have good knowledge of the secular variations of marine carbon isotope ratios. An attempt to compile carbon isotope data to obtain a secular variation curve of  $\delta^{13}\text{C}$  (Karhu and Holland, 1996; Hoffman et al., 1998; Kah et al., 1999; Melezhik et al., 1999, 2007; Lindsay and Brasier, 2002; Bekker et al., 2006; Halverson et al., 2005, among others) has revealed remarkable  $\delta^{13}\text{C}$  anomalies. In the Paleoproterozoic, the Lomagundi-Jatuli carbon positive anomaly, between 2.3 and 2.1 Ga, shows magnitude and duration unique in Earth history (see review by Melezhik et al., 1999, 2007; Karhu et al., 2008). In the Neoproterozoic, unprecedented carbon isotope fluctuations in the Cryogenian and Ediacaran, including the Shuram-Wonoka anomaly reach values of  $<-10\%$  through thick successions of sedimentary rocks deposited during tens of millions of years in Oman, Australia, Brazil, southern China, Namibia, Norway and Siberia (Brasier et al., 2000; Walter et al., 2000; Halverson et al., 2005; Melezhik et al., 2005b; Fike et al., 2006; Le Guerroué et al., 2006a,b,c; Figueiredo, 2006; McFadden et al., 2008; Melezhik et al., 2005a,b; Alvarenga et al., 2009; Le Guerroué and Cozzi, 2010; Boggiani et al., this special issue). Besides, in the Cambrian, the Steptoean positive C-isotope excursion = SPICE (Saltzman et al., 2000, 1998) and Sunwaptan negative C-isotope excursion = SNICE (Sial et al., 2008) are important tools in refining Upper Cambrian stratigraphy. Carbon isotope stratigraphy has also demonstrated that  $\delta^{13}\text{C}$  minima follow the main extinction events (Magaritz, 1989).

It is known that carbon isotopes speak with a robust voice (Knauth and Kennedy, 2009) and have tales to tell about Earth's history, although post-depositional alteration of the carbonate rocks being studied may radically alter the story (Arthur, 2009). However, the indiscriminate use of carbon isotope stratigraphy to correlate Neoproterozoic carbonates has been cautioned by Frimmel (2008, 2009, this special issue) who has studied the REE + Y distribution in a variety of Neoproterozoic (Cryogenian and Ediacaran) carbonates from different settings in the Saldania, Gariiep, Damara and West Congo belts in southwestern and central Africa. These studies have revealed systematic differences in REE + Y patterns, explained by varying palaeoenvironmental factors and have led Frimmel to consider that a short residence time of REE and a comparatively short residence time of carbon and a strong influence of river-born particles on the REE + Y patterns pose some doubt on the usefulness of these carbonates for stratigraphic correlation of Neoproterozoic sediment successions based on carbon isotopes. One can argue that REEs and DIC behave differently in seawater and are affected in a complete different way by diagenesis, but even so Frimmel's observations seem to deserve further investigation.

Many studies have reported carbon isotope variations in Neoproterozoic carbonate rocks and linked them to perturbations of the global carbon cycle. Knauth and Kennedy (2009) have examined the data by concentrating on substantial oxygen isotope measurements obtained as part of the carbon isotope analysis but often overlooked. They came to the conclusion that the combined oxygen and carbon isotope systematics are identical to those Phanerozoic examples that lithified in coastal pore fluids receiving a groundwater influx of photosynthetic carbon from terrestrial phytomass. Instead of being perturbations to the carbon cycle, decrease in  $^{13}\text{C}/^{12}\text{C}$  in Neoproterozoic carbonates, would be more easily interpreted by analogy to the Phanerozoic examples. This may imply an extensive greening in the late Precambrian times, as a transition from the Precambrian microbial world to the Cambrian metazoan world, according to Knauth and Kennedy (op. cit.).

Such a provocative work, of course, needs further considerations because although it has many implications, no direct evidence for existence of a widespread flora in the Neoproterozoic has been shown in Knauth and Kennedy's paper as pointed out by Arthur (2009). In any event, their work cautions Neoproterozoic isotope stratigraphers on the necessity of careful examination of the diagenetic history of rocks in light of the principles applied to carbonate rocks from the Phanerozoic.

Sulphur isotopes are largely used in Neoproterozoic and Phanerozoic isotope stratigraphy, especially after Claypool et al. (1980) have built a secular variation curve of the  $\delta^{34}\text{S}$  values of evaporates (1.0 Ga to present). A critical evaluation of the isotopic composition of sedimentary sulphur through time and the rather limited potential of sulphur isotopic investigations of sedimentary sulphides from time boundaries have been reviewed by Strauss (1997).

Sedimentary sulphur isotope data are subdivided into those recording seawater sulphate ( $\delta^{34}\text{S}_{\text{sulph}}$ ) and epi- or authigenic pyrite ( $\delta^{34}\text{S}_{\text{pyr}}$ ) (Halverson et al., 2010). Sulphur isotope data on sulphate is recovered from evaporites, barite, phosphorites, and carbonates (as carbonate-associated sulphate, or CAS). Pyrite data record the fractionation that occurs during bacterial sulphate reduction (BSR), plus additional fractionation effects of reactions during oxidative recycling of sulphides (Canfield and Teske, 1996). A detailed discussion on sulphur isotopes and their use on Neoproterozoic stratigraphy is found in Halverson et al. (2010, this special issue).

Recent technological advances in analyses of some non-traditional stable isotopes (Johnson et al., 2004) with MC-ICP-MS (mainly Li, Mg, Ca, Mo, Cr, Fe, Cu, Zn, Se) have open new avenues, some still to be explored in terms of isotope stratigraphy. Among these elements, particularly Ca, Mo and Fe, have received more attention aiming at Precambrian isotope stratigraphy (Kasemann et al., 2005; Arnold et al., 2004; Siebert et al., 2003; Johnson and Beard, 2006; Staubwasser et al., 2006, among others) and Cr isotopes may become an important tool in this regard (Frei et al., 2009).

The stratigraphy of the post-Sturtian and post-Marinoan cap carbonate sequences is very different, the former beginning at the maximum flooding surface (and thus lacking the transgressive cap dolostone). Global Ca isotope signal displayed by post-Marinoan carbonate successions suggests the use of Ca isotope stratigraphy as an additional tool to correlate post-glacial Neoproterozoic carbonate successions (Kasemann et al., 2005; Higgins and Schrag, 2003; Silva Tamayo et al., 2007, 2010, this special issue). Although it is not well-understood how Ca isotopes work in modern carbonate rocks, or the extension on how diagenesis affects them, these authors have claimed that the Neoproterozoic Ca isotopic record, still far from complete, is perhaps an archive of changes in the oceanic Ca isotopic composition. Calcium isotopes suggest rapid glacier melting and important increase in the Ca input to the ocean immediately after deglaciation, followed by progressive increase in carbonate precipitation and burial compensating for the large initial Ca input. Post-Sturtian global  $\delta^{44/40}\text{Ca}$  patterns are, perhaps, different from post-Marinoan ones, implying a difference in Ca mass balance evolution among the two deglaciation events due to contrasting glacier melting regimes (Silva Tamayo et al., this special issue). The different Ca isotopic evolutions makes Ca isotope stratigraphy a promise, perhaps, to discriminate and correlate Neoproterozoic post-glacial carbonate successions. Boron and calcium isotopes have been used to estimate paleoenvironmental conditions in the aftermath of a major Neoproterozoic glaciation in Namibia (Kasemann et al., 2005). Negative  $\delta^{11}\text{B}$  excursions were observed in post-glacial carbonates and interpreted as an indication of temporary decrease in seawater pH.

A potentially more suitable approach in the discrimination of post-Sturtian from post-Marianoan cap carbonates, perhaps, is the use of triple oxygen isotope evidence as suggested by Bao et al. (2008, 2009). They demonstrated that triple oxygen isotope composition of sulphate from ancient evaporates and barite shows variable negative oxygen-17 isotope anomalies over the past 750 million years. An important difference in  $^{17}\text{O}$  isotope anomalies of barite at the top of dolostones from Marinoan cap carbonates (negative spike  $\sim -0.70\%$ ) suggest that by the time this mineral was precipitated,  $P_{\text{CO}_2}$  was at the highest level in the past 750 million years ( $\text{CO}_2$  levels reached 0.01–0.08 bar during and just after  $\sim 635$  Ma glacial event (Bao et al., 2008, 2009).

It is known that the Neoproterozoic is transitional between an earlier Proterozoic world with widespread deep-water anoxia and a Phanerozoic world with large oxygen-utilizing animals. Details of the Neoproterozoic marine oxygenation remains unclear as the relationship between short, ice age-associated intervals of iron deposition and the broader evolution of Neoproterozoic atmospheric and oceanic chemistry. Also poorly understood is the connection between the Mesoproterozoic sulfidic marine conditions, the Neoproterozoic ocean chemistry, and the predominantly oxic conditions of the Phanerozoic Eon (Canfield et al., 2008). These authors made efforts to clarify the story of Neoproterozoic oxygenation, perhaps the behavior of Fe, Cr or Mo isotopes (Frei et al., 2009; Scott et al., 2008) may prove to be of some help in providing further answers to some of the above questions.

Chromium is highly sensitive to the redox state of the surface environment, oxidative weathering processes producing the oxidized hexavalent Cr. Oxidation of the reduced Cr on land is accompanied by isotopic fractionation (Frei et al., 2009 and references therein). The isotopic systematics of the chromium cycle including incorporation into BIF has been discussed into details by Lyons and Reinhard (2009). Stable Cr isotopes from BIFs can track the presence of hexavalent Cr in Precambrian oceans providing a picture of the oxygenation history of the Earth's atmosphere-hydrosphere system as demonstrated by Frei et al. (2009).

The utility of nitrogen isotopes for stratigraphic correlation or study of the evolution of the atmosphere chemistry remains ambiguous, although some results have suggested they are a promising tool (Beaumont and Robert, 1999; Papineau et al., 2005; Algeo et al., 2008; Cremonese et al., 2009). Nitrogen isotope values for bulk samples from sections in South China that straddle the Ediacaran-Cambrian boundary show highly systematic variability (positive values in upper Ediacaran strata and strong negative shift in Cambrian strata, especially in black-shales) and testify to changes in the biogeochemical cycle of the ancient ocean (Cremonese et al., 2009). The use of  $\delta^{15}\text{N}$  profiles is perhaps a promising chemostratigraphic correlation tool, especially where biostratigraphy is of limited usefulness.

Denitrification, the process by which nitrate and nitrite are reduced to nitrogen gas, is an important part of the global nitrogen cycle in modern oceans (Algeo et al., 2008) and its variations in rates over Quaternary glacial–interglacial timescales may have affected global climate. It is unclear whether denitrification rates varied during pre-Quaternary glacial cycles. Algeo et al. (2008) discussed ratios of  $C_{\text{org}}/\text{N}$  and nitrogen isotope data from Upper Carboniferous black shales and found evidence of variations in the intensity of denitrification associated with glacially driven sea-level changes. According to these authors, sedimentary  $\delta^{15}\text{N}$  increases during the interval of rapid sea-level rise in each cycle, indicative of intensified denitrification, before returning to background levels as sea-level stabilized during the interglacial phase. Therefore, ice ages have produced similar oceanographic conditions and nitrogen cycle dynamics over the past 300 million years. Whether Cryogenian–Ediacaran ice ages

had similar behavior in relation to the nitrogen cycle, however, is something that remains to be investigated.

Fluctuations of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are independent of fluctuations of  $\delta^{13}\text{C}$  and the simultaneous utilization of these two systems has been proven to be ideal in fine stratigraphy studies. Combined, these systems are an even more powerful tool in the resolution of geological problems. The secular  $^{87}\text{Sr}/^{86}\text{Sr}$  variation curve is better known in the Phanerozoic showing a cycling of about 500–550 Ma from the Upper Cambrian (0.709; see Montañez et al., 2000) gradually decreasing with nadir 0.7068 at 250 Ma and reassuming values of 0.709 again in the present-day ocean (Macdougall, 1991). Despite the effort to compiling Sr-isotope data to determine the secular  $^{87}\text{Sr}/^{86}\text{Sr}$  variation curve for the entire Proterozoic or just for the Neoproterozoic (e.g. Jacobsen and Kaufman, 1999; Halverson et al., 2007), the use of strontium isotopes in chemostratigraphy is limited by the paucity of limestone in many of the successions, and by the likelihood of alteration in sample with low strontium contents through the ingrowth of  $^{87}\text{Sr}$  from the decay of  $^{87}\text{Rb}$  in co-existing clay minerals (Kaufman et al., 2009). Geochemical screens ( $^{87}\text{Rb}/^{86}\text{Sr}$ , Mn/Sr, and  $\delta^{18}\text{O}$ ) have been developed to evaluate the degree of alteration of strontium isotopes (Veizer et al., 1983; Kaufman et al., 1992, 1993; Jacobsen and Kaufman, 1999) and have been widely adopted. Unfortunately, because of differences in the tectonic and diagenetic history of individual basins, the empirical limits delimiting altered and unaltered samples has varied – leading to some confusion in the literature. For this reason, it is advisable to consider the analyses of only high Sr abundance limestone, especially those with aragonite pseudomorph crystal fans (e.g. in cap carbonates) which have passed through the most stringent of the geochemical screens.

Neodymium isotopes have been little used as stratigraphic tool although a “global average”  $\epsilon\text{Nd}$  curve for the oceans since 800 Ma has been constructed (Keto and Jacobsen, 1988; Macdougall, 1991). This curve, likewise the Sr-isotope secular curve, indicates  $\epsilon\text{Nd}$  values at the end of the Precambrian oceans not substantially different from those at present oceans. Average  $\epsilon\text{Nd}$  values decrease remarkably in the time interval from 700 to 550 Ma ( $-5$  to  $-15$ ). Even with the measurement precision with modern instrumentation, the scatter in measured values is substantial and this has limited the use of  $\epsilon\text{Nd}$  in chemostratigraphic studies.

The reader is referred to the review on Neoproterozoic chemostratigraphy by Halverson et al. (this special issue) where some problems discussed en passant here are expanded and discussed in detail there.

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