



Anomalous heavy S isotope abundances in Ediacaran carbonates of the North Paraguay Belt, Brazil

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INTRODUCTION

The biogeochemical cycle of sulfur is intimately linked through a variety of processes that redistribute its isotopes between a wide range of surface reservoirs (including dissolved SO_4^{2-} and HS^- , as well as mineral sulfates and sulfides). For ancient environmental studies, the abundance and isotopic compositions of mineral sulfates, present as evaporates or as carbonate associated sulfate (CAS; i.e. structurally bound sulfate in carbonates), and sulfides (CRS), present as pyrite are typically analyzed. The largest fractionation is associated with biological sulfate reduction (BSR) where sulfate is used to respire organic matter resulting in the formation of ^{32}S enriched HS^- and ^{12}C enriched alkalinity and CO_2 . While most of the sulfide is reoxidized back to sulfate (Jorgensen, 1982; Canfield et al., 1991) some is sequestered into sediments by reaction with iron to form pyrite (Lin & Morse, 1991) or as organically bound S (OBS; i.e. in polar compounds; Sinninghe Damste & de Leeuw, 1990). Sulfur is also removed from the oceans through evaporation, which results in the precipitation of sulfate minerals in shallow environments with little isotopic fractionation. The sources of oceanic sulfur include riverine inputs (a mixture of weathered sulfides and sulfates exposed on land) and volcanic gases, both sources being depleted in ^{34}S relative to seawater sulfate (Newton & Bottrell, 2007).

Recent sulfur isotope studies of Ediacaran carbonates worldwide have shown that the magnitude of fractionation between oxidized (sulfate) and reduced (sulfide) reservoirs appears to be increasing towards the Precambrian-Cambrian boundary, especially after the so-called Shuram event. This biogeochemical anomaly is recorded in successions worldwide as a profound negative carbon isotope excursion (down to -10‰ or greater), but is not presently associated with an ice age. It may be related to the oxidation of a large dissolved organic carbon pool in Ediacaran seawater that was depleted as surface environments became oxidized (McFadden et al., 2008). This sulfur and carbon isotope study focuses on Ediacaran aged carbonates between the Marinoan ice age (ca. 635 Ma) and the Shuram event.

GEOLOGICAL SETTING

The Paraguay Belt is located on the southeastern border of the Amazon Craton. It is composed of marine sedimentary rocks deposited on a passive Neoproterozoic continental margin and deformed during the Brazilian-Pan African Orogeny. The base of Paraguay Belt is represented by the Cuiabá Group, which comprises, from bottom to top, organic-rich shale, dolomite, diamictite, rudstone, and mixed sandstone and shale, interpreted as glaciomarine in origin (Alvarenga and Trompette, 1992). Laterally, this group grades into the Puga Formation, which is a diamictite interpreted as glacial in origin. This unit has been correlated to the Marinoan Ice Age, based on the carbon and strontium isotope stratigraphy of post-glacial carbonates (Nogueira et al., 2003).

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The Puga diamictite is immediately overlain by carbonates of the Araras Group, which has been divided into four formations, in ascending order: Mirassol d'Oeste, Guia, Serra do Quilombo and Nobres (Nogueira & Riccomini, 2006). The Mirassol d'Oeste Fm. is composed of pink cap dolostone (ca. 30 m) characterized by tubestone stromatolites, aragonite and barite crystal fans, and mega ripples. The Guia Formation comprises laminated limestone, marl and carbonate breccia (ca. 250 m) deposited in a slope environment. The Serra do Quilombo Formation is not recognized in our study area, where the Guia Formation is overlain by dolostone of the Nobres Formation (< 800 m), which was deposited in a subtidal to peritidal marine environment (Almeida, 1964).

The Araras Group is overlain by the Serra Azul Formation, which contains, from base to top, diamictite (ca. 70 m), brown laminated siltstone and claystone (ca. 70 m) with intercalations of fine laminated sandstone towards the top of the section (Alvarenga et al., 2007, Figueiredo et al., 2008). Above the siltstone member in one location there is a limestone bed (10 m). The Serra Azul Formation is overlain by rudstone, sandstone and arkose of Raizama Formation.

PROCEDURES

Sulfur was extracted from carbonate rocks of this study as carbonate associated sulfate (CAS) and chromium reducible sulfide (CRS). For CAS, about 200 g of pulverized rock was leached with 2 L of NaCl solution (10%) for 24 h, filtered in 0.45 µm filter, to remove solids, and 30 ml of BaCl (8%) was added to the leach solution to precipitate BaSO₄. This process was repeated up to five times until no further precipitate was observed in the leachate. These BaSO₄ precipitates are associated with non-structurally bound sulfate or oxidized sulfides and are therefore likely to be diagenetic in origin. After leaching, the solid residue was acidified by dripping HCl (27%) onto the sample placed in a filter funnel above a beaker, to avoid prolonged contact of the acid with pyrite, separate the non-carbonate fraction and collect the resulting solution. This solution was first passed through a 0.45 µm filter and then 30 ml of BaCl (8%) was added and allowed to react for at least 24 hours. The BaSO₄ precipitates, considered to be the CAS fraction, were collected by passing the solution through a 0.45 µm filter, rinsed and dried.

For the CRS extractions 5 g of powdered sample (carbonate or pelite) was acidified with 3M HCl in a vacuum filter flask to minimize the time sulfides were exposed to acid while remove carbonates. The residues were rinsed with ultrapure Milli-Q water, dried, and then reacted with 25 ml of 1M CrCl₂ solution. HS⁻ released in the reaction was transferred in a stream of N₂ to a 0.3M AgNO₃ trapping solution where it was quantitatively converted to insoluble Ag₂S. The precipitates were aged for two days, filtered, rinsed with ammonia hydroxide solution and Milli-Q water, and dried.

BaSO₄ and Ag₂S extracts (~150 µg) were weighed into tin cups with an excess of V₂O₅ for combustion to SO₂ in a Eurovector elemental analyzer coupled to a GV Isoprime mass spectrometer. Isotopic compositions were reported with the standard δ notation, and uncertainties based on multiple standard materials (NBS 127) run during each analytical session were better than 0.3‰ (1σ).

RESULTS AND DISCUSSIONS

To evaluate the magnitude of diagenetic effects on the sulfur isotope compositions of our Ediacaran aged carbonates from the Guia and Nobres formations we analyzed BaSO₄

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precipitates from both the leachates and CAS extracts from each sample. Results showed that leachates, which are considered to be post-depositional or analytical artefacts and not representative of depositional conditions, were consistently depleted in ^{34}S relative to the CAS fraction in the slope and subtidal environments of the Guia and Nobres formations, but in the peritidal and supratidal environments of the Nobres Formation the leachates and CAS fraction were similar.

Sulfur isotopic composition of both the CAS and CRS precipitates from these post-Marinoan successions were unexpectedly enriched in ^{34}S . These observations may reflect an overall increase of ^{34}S in the Ediacaran ocean as a result of widespread anoxia and dominance of sulfate reducing bacteria in the sediments and water column where organic matter and sulfate were available to fuel the microbial ecosystem. The profound enrichments and relatively small differences in CAS and CRS compositions suggest that sulfate abundance in the early Ediacaran ocean was limited. Other factors that may explain the anomalous sulfur isotopic enrichments include a negligible flux of weathered sulfur from terrestrial environments (possibly associated with an arid climate) and/or low submarine volcanic activity.

Time series results from limestones in deep environments of the Guia Formation above the deeper equivalent-Marinoan cap carbonate yielded $\delta^{34}\text{S}_{(\text{CAS})}$ values ranging between 41 to 55‰ with a notable upsection trend to increasing heavy values. On the other hand, $\delta^{34}\text{S}_{(\text{CRS})}$ values throughout the Guia Formation (including the cap carbonate) ranged from 11 to 44‰ with an average around 20‰. There are no clear trends to the CRS data, but in concert the CAS and CRS suggest an increase in sulfur isotope fractionation towards the top of the section. Notably the $\delta^{34}\text{S}_{(\text{CAS})}$ of Guia Formation limestones are significantly heavier than those reported in the equivalent post-Marinoan Doushantuo Formation in South China (McFadden et al., 2008).

Dolomites from the peritidal and tidal flat environments of the overlying Nobres Formation revealed $\delta^{34}\text{S}_{(\text{CAS})}$ values ranging from 22 to 62‰. There is no apparent stratigraphic trend in the available data, although samples near the middle of the formation are enriched in ^{34}S relative to those nearer the base. Leachates from these samples have similar $\delta^{34}\text{S}$ values to those of CAS. This may be due to the admixture of authigenic mineral sulfate with carbonate in these evaporitic environments. Sulfides from Nobres Formation samples also yielded highly positive $\delta^{34}\text{S}_{(\text{CRS})}$ values, ranging from 17 to 43‰, with predominance of those > 40‰. This more continuous dataset does suggest an upsection trend to heavier $\delta^{34}\text{S}_{(\text{CRS})}$ values. Again, these $\delta^{34}\text{S}_{(\text{CAS})}$ and $\delta^{34}\text{S}_{(\text{CRS})}$ values are heavier than the correlated section of the lower to middle Doushantuo Formation (McFadden et al., 2008).

Assuming these two sections from the Paraguay Belt are direct equivalents of the lower to middle Doushantuo Formation, the disparities in CAS values could be explained in three conceivable ways. First, if Paraguay Basin is restricted, the sulfur isotopic data may not be representative of the global ocean. Second, if there were a strongly stratified water column (Li et al., 2010) the difference between the Brazilian and Chinese sections may be simply related to depth relative to a euxinic wedge within the water column. Third, the variations between equivalent lower Ediacaran Period strata might reflect non-quantitative removal of diagenetic sulfate during the leaching process in the in South China study (McFadden et al., 2008).

To date, limestone samples of the overlying Serra Azul Formation have yielded no CAS precipitates, although these sample do preserve $\delta^{34}\text{S}_{(\text{CRS})}$ values ranging from 13 to 28‰



($\delta^{13}\text{C}$ values range from -3 to -8‰). Assuming seawater sulfate has remained similarly enriched in ^{34}S at this time, the lower $\delta^{34}\text{S}_{\text{(CRS)}}$ values suggest a larger magnitude of sulfur isotope fractionation associated with bacterial sulfate reduction perhaps related to the growth of the sulfate reservoir associated with the oxygenation of surface environments. The Serra Azul sulfur isotope results do not match with those from the uppermost Doushantuo Formation, which is characterized by increasingly negative $\delta^{34}\text{S}$ compositions of both CAS and CRS fractions and the profound negative $\delta^{13}\text{C}$ anomaly known as the Shuram event. It appears that either the Serra Azul carbonates were deposited in a deeper ocean setting below the chemocline as proposed by Li et al. (2010), or the Serra Azul Formation carbon isotope anomaly is equivalent to a similar magnitude event (EN2) recorded in the middle Doushantuo Formation (McFadden et al., 2008). In this case the sulfur isotope results are a better match between the two basins.

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