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A high continental weathering flux into Paleoarchean seawater revealed by strontium isotope analysis of 3.26 Ga barite

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ABSTRACT

Controls on Archean seawater chemistry remain controversial. Many studies have suggested that it was largely controlled by oceanic hydrothermal fluid circulation. Recent work, however, from clastic sequences, Hf–O isotope data from detrital zircons, and models for the Rb/Sr evolution of the continental crust suggest that intense continental weathering and low-temperature surface alteration were more important than previously thought during the early Archean. This is consistent with biogeochemical studies that suggest the Archean had a diverse microbial ecology, which would, in part, need to be sustained by nutrients (e.g., phosphorus) that were derived from continental weathering. To further quantify continental weathering during the early Archean, we analyzed 3.26 Ga barite from the Fig Tree Group, South Africa for strontium, oxygen, and sulfur isotope compositions. We propose that the seawater component of the barite is characterized by $^{87}Sr/^{86}Sr$ ratios >0.701, which is significantly more radiogenic than contemporaneous mantle ($\sim$0.7007–0.7008). The radiogenic nature of seawater at this time suggests that the continental weathering flux at 3.26 Ga had a large impact on ocean chemistry 400 million years earlier than previously suggested.

1. Introduction

Understanding the temporal changes in the volume and composition of continental crust over Earth history bears on models for crust–mantle evolution, as well as changes in the surface environments of the Earth, including the biosphere. For example, CO_2 in the modern atmosphere is consumed during chemical weathering (Beaulieu et al., 2012). Carbon dioxide was a very large component of the Hadean–Archean atmosphere (Kasting, 2014); therefore, continental weathering likely had a significant impact on the climate during this time. In addition, studies of biogeochemical cycles recorded in early Archean sedimentary rocks suggest an early diverse microbial ecology that may have required extensive continentally-derived nutrients such as phosphorus early in Earth history (Blake et al., 2010); such a proposal would require the presence of emergent, evolved crust. In contrast, it has been argued that continental weathering during the early Archean was insignificant, where the majority of continental crust was submerged and relatively mafic in composition, which in turn would suggest that seawater chemistry was largely controlled by oceanic hydrothermal fluid circulation (Shields and Veizer, 2002; Shields, 2007; Flament et al., 2013). This view, however, must be re-evaluated based on recent studies that address continental evolution and alteration in the early Earth. Lithium isotope data from the Jack Hills zircons suggest that continental-like crust was weathering as early as 4300 Ma (Ushikubo et al., 2008). Hafnium and O isotope studies of detrital zircons document a strong increase in recycling of evolved continental crust at $\sim$3.2 Ga, commensurate with a decrease in ε_{Hf} and increase in $\delta^{18}O$ values, suggesting that low-temperature alteration of evolved continental crust was more widespread throughout the Archean than previously thought (Dhuime et al., 2012). Such a proposal is consistent with models that suggest extensive weathering conditions existed throughout the Archean (Hessler and Lowe, 2006 and references therein). This recent work, therefore, requires a re-evaluation of the traditional view that emergent continental crust was minor in the early Archean.

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A common approach for assessing the continental flux to seawater has been the use of $^{87}Sr/^{86}Sr$ ratios on marine carbonate (e.g., Shields and Veizer, 2002), which depends on the balance between the two primary sources of Sr to seawater: (1) oceanic hydrothermal fluids and (2) continental weathering. Although Sr isotope seawater curves have been defined by very large databases for the Phanerozoic, the seawater Sr isotope curve for early- to mid-Archean rocks has been problematic because pristine marine carbonate is rare. As shown by Shields and Veizer (2002) and Prokoph et al. (2008), very few samples define the Archean portion of the seawater curve, except between 2800–2700 Ma. Although the density of data for carbonates of this age is high, the range in $^{87}Sr/^{86}Sr$ ratios is very large (0.70114–>0.708). Restriction to the least radiogenic compositions ($^{87}Sr/^{86}Sr \sim 0.7011$) is one approach to placing estimates on seawater compositions, based on the assumption that the presence of detrital components or later alteration will increase $^{87}Sr/^{86}Sr$ ratios (Shields and Veizer, 2002). The least radiogenic Sr isotope compositions for carbonates of 2800–2700 Ma age, however, all have relatively low $\delta^{18}O$ (VSMOW) values that range from 9.9–17.6 (Prokoph et al., 2008), suggesting that hydrothermal fluids may have altered these samples; this, in fact, suggests that the common approach of using the least radiogenic carbonate to infer seawater, as is generally done for the Phanerozoic, may be flawed, and under-estimate the $^{87}Sr/^{86}Sr$ ratios of Archean seawater.

With little pristine carbonate to define it, there is much uncertainty in the Sr isotope composition of Paleoarchean seawater. Given recent modeling of large databases for igneous rocks which suggests that the Rb/Sr ratios of the continental crust began a continued rise from ~3.2 Ga to the end of the Precambrian (Dhuime et al., 2015), it is important to re-evaluate the Sr isotope seawater curve for this time interval. If Rb/Sr ratios of the continental crust started to rise at ~3.2 Ga, and this crust was emergent, an inevitable outcome would be an increase in the $^{87}Sr/^{86}Sr$ ratio of the continents. Here we re-visit the early Archean seawater Sr isotope curve, using barite, a relatively insoluble mineral that is resistant to isotopic exchange by later alteration as compared to carbonates (see review of Bao, 2015). Although not common in the Archean geologic record, marine barite has the potential to capture the $^{87}Sr/^{86}Sr$ ratio of seawater (Griffith and Paytan, 2012 and references therein), and offers an alternative to marine carbonates as a record for seawater chemistry. Our target is marine stratiform barite deposits of the 3.2 Ga Fig Tree Group, South Africa, and we combine Sr, O, and S isotopes to distinguish between ambient seawater and hydrothermal Sr sources, with the goal of providing, for the first time, a robust datum on the seawater Sr isotope curve in the Paleoarchean.

2. Geologic background

The Barberton greenstone belt (BGB) is comprised, from oldest to youngest, of three main lithostratigraphic units: the Onverwacht Group (primarily volcanic), the volcaniclastic and siliciclastic Fig Tree Group, and the siliciclastic Moodies Group (Lowe, 2013; Fig. 1). In the Barite Valley area in the central greenstone belt, dacitic tuffs from the Mapepe Formation, principal unit of the Fig Tree Group in the middle and southern parts of the greenstone belt, have yielded U–Pb zircon ages between about 3260 Ma near the base of the unit to about 3225 Ma from near the top (Kröner et al., 1991).

The Fig Tree Group represents a variety of depositional environments that range from shallow to deep subaqueous, alluvial and fan-delta. Barite layers are widely developed in the lower part of the Fig Tree Group, where they form discontinuous lenses primarily in the Barite Valley and Conglomerate Quarry areas (Heinrichs and Reimer, 1977; Fig. 1). These barite layers are contained within the shallow-water parts of the Fig Tree Group sequence. Barite occurs in two morphologies: granular and bladed, which are always found in close association (Fig. 2). The granular type is associated with detrital grains of pyrite, Cr-spinel, quartz, zircon, and muscovite, and has been interpreted as a locally reworked primary precipitate (Heinrichs and Reimer, 1977). The granular barite does not likely represent erosion, transport, and deposition from older barite deposits of the Onverwacht Group (Reimer, 1980) because if erosion had stripped the 4–5 km of intervening strata the deposited sediments would be much thicker and more varied in composition, and the barite would be a negligible component. The bladed type can be observed to drag chert bedding upward or bedding can sag around a blade, and both textures suggest that the barite is syn-diagenetic and grew early in the sedimentary sequence (Heinrichs and Reimer, 1977). We interpret the bladed morphology to reflect a separate, primary phase. No evidence exists that the barite blades formed as a replacement after gypsum or that it was re-crystallized by low-grade metamorphism (Bao et al., 2007).

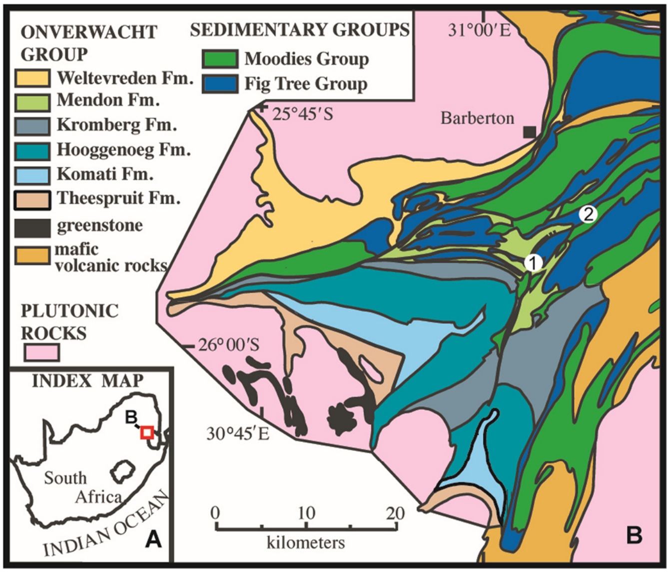

Fig. 1. (A) Map showing the location of the southwestern half of the Barberton greenstone belt. (B) Geologic map of the southwestern half of the Barberton greenstone belt. Number 1 on the map shows the location of the Barite Valley section and number 2 shows the location of the Conglomerate Quarry section. Detailed sample location information can be found in Supplementary Table S1. Map is modified from Lowe (2013).

3. Methods

3.1. Sampling

Samples are from two different stratigraphic positions within the Fig Tree Group (Fig. 3). The stratigraphically lowest samples are typically within 1–5 m of the contact with the cherts at the top of the Mendon Formation in the Onverwacht Group (Fig. 3). These cherts, 40–100 m thick, overlie a thick sequence of Onverwacht komatiites. Samples from here include both the bladed and granular morphology. A second suite of samples was analyzed from the middle Mapepe Formation, where barite is interbedded with dacitic and siliciclastic sediments (Fig. 3). Barites sampled from the middle Mapepe Formation all have a bladed morphology.

The barite samples were cut and polished into flat slabs, from which specific areas could be sampled with a high spatial resolution, including granular-rich and blade-rich morphologies (Fig. 2). Detailed sampling was done using a New Wave Micromill in raster mode, with special care taken to avoid any areas that appeared