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Multiple sulfur isotope geochemistry of Dharwar Supergroup, Southern India: Late Archean record of changing atmospheric chemistry

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ABSTRACT

Earth's tectonic and climatic systems may have changed fundamentally before the Great Oxidation Event (GOE) at about 2.3 Ga. Sulfur Mass Independent Fractionation (S-MIF) has demonstrated that Earth's atmosphere was virtually oxygen-free before the GOE. During 3.0 to 2.4 Ga, the change in $\Delta^{33}S$ and $\Delta^{36}S$ signals may reflect the perturbation of atmospheric chemistry, though the mechanisms of the change are uncertain. Here, we reported multiple sulfur isotopic studies of Archean volcano-sedimentary sequences of the Dharwar Supergroup, distributed in the Chitradurga Schist Belt (CSB), Southern India. New field mapping and zircon U–Pb dating allows us to reconstruct detailed lithostratigraphy of the Dharwar Supergroup. The lower unit consists of post-3.0 Ga conglomerate, stromatolitic carbonate, siliciclastics with diamictite, chert/BIF and pillowed basalt in ascending order, all of which are older than the 2676 Ma dacite dyke that had intruded into the lower unit. The upper unit unconformably overlies the pillow basalts at the top of the lower unit, and consists of conglomerate/sandstone with ~2600 Ma detrital zircons, komatiitic basalt, BIF and siliciclastic sequence with mafic volcanics. Sulfur isotope analysis of extracted sulfides shows MIF signals ($\Delta^{33}S > +1‰$) with clear $\Delta^{33}S$–$\Delta^{36}S$ correlations. The lower group of the Dharwar Supergroup shows a $\Delta^{36}S/\Delta^{33}S$ slope of −1.48, the middle group shows −1.16 and −1.07, and the upper group shows −0.94. Reassessment of all the Archean S-MIF records from sedimentary rocks indicates that the $\Delta^{36}S/\Delta^{33}S$ slope systematically changed during the Archean period. The observed trend in the Indian section is similar to those of its Pilbara–Kaapvaal equivalents, thus it could reflect a global atmospheric signature. Moreover, the isotopic trend seems to correlate with mid-Archean glaciation. Thus, the $\Delta^{36}S/\Delta^{33}S$ slope could be a useful tracer for atmospheric chemistry and its link with climate change before the GOE.

1. Introduction

The late Archean is an important period regarding the Earth's environmental changes. Before the GOE, the atmosphere was probably reducing with trace amounts of molecular oxygen based on the presence of sulfur mass independent fractionation (S-MIF) in pre-2.3 Ga rocks (Farquhar et al., 2000). Sulfur has four stable isotopes (^{32}S, ^{33}S, ^{34}S and ^{36}S). Isotope fractionations by biological or inorganic processes show mass-dependent fractionation ($\delta^{33}S \approx 0.5 \times \delta^{34}S$; $\delta^{36}S \approx 1.9 \times \delta^{36}S$; Hulston and Thode, 1965). S-MIF is known to be produced by SO_2 photolysis in a low oxygen atmosphere based on previous photochemical experiments (Farquhar et al., 2001; Ono et al., 2013; Endo et al., 2015). Based on atmospheric model calculations, it has been hypothesized that the SO_2 photolysis in an anoxic atmosphere would have resulted in two isotopically distinct sulfur aerosols (i.e. sulfate with negative $\Delta^{33}S$ and elemental sulfur with positive $\Delta^{33}S$) that were transferred to and preserved in sediments when the atmosphere was anoxic ($O_2 < 1$ ppm; Pavlov and Kasting, 2002; Ono et al., 2003).

The Archean $\Delta^{33}S$ record exhibits clear changes in the magnitude of MIF over time: minimum $\Delta^{33}S$ at around 2.9 Ga, subsequent large $\Delta^{33}S$ variations culminating at 2.5 Ga, followed by

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its sudden drop in the Paleoproterozoic. The change in $\Delta^{33}S$ signature may possibly reflect a fluctuation in oxygen levels (Ono et al., 2006a), the presence of large volcanic eruptions (Ohmoto et al., 2006), speciation of volcanic gasses (SO_2/H_2S ratio; Halevy et al., 2010) and/or other changes in atmospheric chemistry (Farquhar et al., 2007; Domagal-Goldman et al., 2008; Thomazo et al., 2009; Zerkle et al., 2012; Claire et al., 2014). In addition, the atmospheric $\Delta^{33}S$ value can be diluted by mixing it with mass-dependent sulfur compounds (Ono et al., 2003; Penniston-Dorland et al., 2008; Guy et al., 2012). So far, it has been difficult to decouple the $\Delta^{33}S$ variations caused by atmospheric processes from other reactions in subsequent processes (biology, photolysis, mixing, open system, etc.) before sedimentation (Halevy, 2013).

The $\Delta^{36}S/\Delta^{33}S$ ratio may be able to give us additional information about past atmospheric chemistry because mass dependent processes cannot change the $\Delta^{36}S/\Delta^{33}S$ ratio significantly. Farquhar et al. (2007) used $\Delta^{36}S/\Delta^{33}S$ to distinguish MIF and MDF processes. Mass dependent processes can also produce small non-zero $\Delta^{36}S$ and $\Delta^{33}S$ values, but show a characteristic $\Delta^{36}S/\Delta^{33}S$ ratio theoretically predicted at about −7 (Ono et al., 2006b). On the other hand, mass independent processes that occurred during the Archean show a different $\Delta^{36}S/\Delta^{33}S$ ratio from −1 to −1.5. The mechanism to change the $\Delta^{36}S/\Delta^{33}S$ ratio is still uncertain, though it could potentially reflect the change in atmospheric chemistry before the GOE event (Farquhar et al., 2007).

Geographically, most of the Archean MIF records measured so far are mainly derived from Pilbara Craton, Western Australia and Kaapvaal Craton, South Africa. However, several paleomagnetic and lithostratigraphic studies suggested that Pilbara and Kaapvaal Craton might have been part of the same continent during the late Archean (e.g., Cheney, 1996). Therefore, it is possible that the $\Delta^{36}S/\Delta^{33}S$ ratio may only reflect local changes and not necessarily global events. In order to distinguish the local and global signatures, it is necessary to study other late Archean sections around the world.

Apart from the two cratons, 3.2 to 2.5 Ga volcano-sedimentary sequences are well exposed in continuous stratigraphic successions in the Chitradurga Schist Belt (CSB) in Western Dharwar Craton, Southern India (Fig. 1; e.g. Swaminath and Ramakrishnan, 1981). Our previous lithostratigraphic and geochronological investigations (Hokada et al., 2013) suggest that the depositional setting of the Dharwar Supergroup is different from that of its Pilbara–Kaapvaal equivalent during the late Archean (Fig. 2). For example, the manganiferous nature of the Chitradurga BIF is not observed in its Pilbara–Kaapvaal counterparts. The lithostratigraphic difference and metamorphic history suggest that the Dharwar Craton was geographically separate from the Pilbara–Kaapvaal Craton (Hokada et al., 2013). Moreover, Bleeker (2003) suggested that Dharwar Craton was part of the Slave Craton, which was different from Kaapvaal Craton at ∼2.6 Ga.

In this paper, we report detailed lithostratigraphy of the Dharwar Supergroup that appeared in the CSB together with multiple sulfur isotope geochemistry of the strata. We have conducted a detailed field mapping in the schist belt during several field seasons that have been carried out since 2010. Based on our sedimentological observations, we discuss the link between depositional settings and the multiple sulfur isotope record, and then test the global nature of the S-MIF signals by comparing the data from Pilbara and Kaapvaal Cratons.

2. Geological setting

The Dharwar Craton of southern India consists of Archean gneiss of tonalitic–trondhjemitic–granodioritic (TTG) composition, volcano-sedimentary sequences and calc-alkaline to high-potassic granitoids (Chadwick et al., 2000; Jayananda et al., 2006). The Dharwar Craton has been divided into two blocks: Western Dharwar and Eastern Dharwar Cratons. The Western Dharwar Craton is dominated by an older basement (Peninsular Gneiss interlayered with >3.0 Ga Sargur Group), which is unconformably overlain by Dharwar Supergroup (2.9–2.6 Ga). High-potassic granitic plutons (2.61 Ga) are minor parts of Western Dharwar Craton. The Peninsular Gneiss occurs mainly in the southern part of this region. In contrast, the Eastern Dharwar Craton comprises a younger TTG basement (2.7 Ga) with small remnants of >3.0 Ga TTG, thin elongated 2.7 Ga greenstone belts and abundant 2.55–2.52 Ga calc-alkaline to high-potassic intrusions (Jayananda et al., 2006).

The Chitradurga Schist Belt (CSB) is located at the eastern margin of the Western Dharwar Craton where the two cratons are separated by the steep mylonitic zone, Chitradurga Sh ear Zone (CSZ; Fig. 1). The CSB is the type locality of the Chitradurga Group that comprises the upper part of the Dharwar Supergroup. Well preserved late Archean sedimentary sequences and structures are exposed in this schist belt.

2.1. Chitradurga Schist Belt (CSB)

The CSB extends to a length of over 400 km with an average width of 15 km and attains a maximum width of 40 km in the central region (Fig. 1). There are several important steeply-dipping faults cut across the entire CSB (Fig. 1). The CSB consists of two generations of greenstone sequences: >3.0 Ga older greenstone sequences known as the Sargur Group and 2.9–2.5 Ga younger volcano-sedimentary sequences known as the Dharwar Supergroup. Both of the greenstone-sedimentary sequences are surrounded by >3.0 Ga TTG gneiss (Chadwick et al., 2000; Jayananda et al., 2006). Generally, the Dharwar Supergroup is divided into two groups: Bababudan Group and Chitradurga Group. The Chitradurga Group is divided into three formations: Vanivilas Formation, Ingaldhal Formation, and Hiriyur Formation, in ascending order (Swaminath and Ramakrishnan, 1981). Based on our field mapping of over 5 yr, including detailed logging, sampling and petrological study, the Dharwar Supergroup is subdivided into a lower unit (Bababudan Group, Vanivilas Formation and Ingaldhal Formation) and an upper unit (Hiriyur Formation), which are separated by a major unconformity (Hokada et al., 2013).

The Sargur Group, which is the oldest group in the Dharwar Craton, comprises komatiite, tholeiitic amphibolites, BIF, garnet-biotite schist with kyanite, sillimanite and staurolite, calc-silicate and fuchsite quartzite with barite (Swaminath and Ramakrishnan, 1981). The Sargur Group is only exposed along the western and eastern margins in the CSB. The metamorphic conditions of the Sargur Group are estimated to be low-T/high-P based on the appearance of kyanite and lack of biotite in quartzite (Hokada et al., 2013). A Sm–Nd age of 3352 ± 110 Ma from komatiite was reported by Jayananda et al. (2008), which is considered to be the formation age of the Sargur Group. Furthermore, monazite U–Th–Pb dates of kyanite–muscovite quartzite samples yield a comparable age of 3200–3000 Ma (Hokada et al., 2013).

The Bababudan Group is the lowest part of the Dharwar Supergroup. The basal conglomerate of the Bababudan Group, named Neralekatte conglomerate, overlies the Peninsular Gneiss with a profound unconformity. The conglomerate is overlain by alternated amygdular metabasalt and cross-bedded quartzite, pelite and BIF (Swaminath and Ramakrishnan, 1981). In the CSB, the Bababudan Group is exposed in a narrow zone near southeast Talya, on the eastern flank of the Sirankatte dome and the southern part of the CSB. Carbonate and dolomitic BIF layers are exposed on the eastern side of Sirankatte dome, and well-preserved stromatolites were observed on the southern flank of the CSB (Fig. 1). The occurrence of the stromatolite and cross-bedded sandstones suggest that the