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Atmospheric sulfur rearrangement 2.7 billion years ago: Evidence for oxygenic photosynthesis

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ABSTRACT

Mass-independently fractionated sulfur isotopes (MIF-S) provide strong evidence for an anoxic atmosphere during the Archean. Moreover, the temporal evolution of MIF-S shows increasing magnitudes between 2.7 and 2.5 Ga until the start of the Great Oxidation Event (G.O.E.) at around 2.4 Ga. The conclusion of a completely anoxic atmosphere up to the G.O.E. is in contrast to recent studies on redox-sensitive elements, which suggest slightly oxidizing conditions during continental weathering already several hundred million years prior to the G.O.E. In order to investigate this apparent inconsistency, we present multiple sulfur isotopes for 2.71 Ga pyritic black shales derived from the Kidd Creek area, Ontario, Canada. These samples display high positive $\Delta^{33}S$ values up to 3.8‰ and the typical late Archean slope in $\Delta^{36}S/\Delta^{33}S$ of -0.9. In contrast, the time period before (3.2–2.73 Ga) is characterized by greatly attenuated MIF-S magnitudes and a slope in $\Delta^{36}S/\Delta^{33}S$ of -1.5. We attribute the increase in $\Delta^{33}S$ magnitude as well as the contemporaneous change in the slope of $\Delta^{36}S/\Delta^{33}S$ to changes in the relative reaction rate of different MIF-S source reactions and changes in atmospheric sulfur exit channels. Both of these are dependent on atmospheric CH_4:CO_2 and O_2 mixing ratios. We propose a distinct change in atmospheric composition at 2.7 Ga resulting from increased fluxes of oxygen and methane as the best explanation for the observed Neoarchean MIF-S record. Our data and modeling results suggest that oxygenic photosynthesis was a major contributor to primary productivity 2.7 billion years ago.

1. Introduction

Earth's atmosphere is thought to have witnessed a first significant rise in atmospheric oxygen abundance some 2.4 billion years ago (Ga), commonly referred to as the Great Oxidation Event (Holland, 2006). The temporal record of mass-independently fractionated sulfur isotopes (MIF-S, expressed as $\Delta^{33}S$) in sedimentary rocks of Archean and early Proterozoic age bracket this event between 2.45 and 2.32 Ga (Bekker et al., 2004; Guo et al., 2009). The Archean $\Delta^{33}S$ record, however, displays significant variations in magnitude and sign (Farquhar et al., 2010), which might provide additional information in respect to atmospheric evolution. Different processes were suggested as a cause for the observed MIF-S signals (Farquhar et al., 2001; Francisco et al., 2005; Lyons, 2009; Watanabe et al., 2009), but most widely accepted is the dissociation of SO_2 via short ultraviolet radiation (i.e. $SO_2 + h\nu \rightarrow SO + O$; Farquhar et al., 2001; Ono et al., 2003). This volcanogenic sulfur dioxide is believed to carry no MIF-S signature ($\Delta^{33}S = 0 \pm 0.2$‰; Farquhar et al., 2010). In contrast, the final products of photochemistry under reducing conditions are S_8 (elemental sulfur from $SO + h\nu \rightarrow S + O$ is most stable in this polymerized, cyclic form) with positive $\Delta^{33}S$ values and the residual SO_2 and/or sulfuric acid (H_2SO_4) with negative $\Delta^{33}S$ values (Farquhar et al., 2001; Ono et al., 2003), both of which are delivered to the ocean and subsequently to the sediments. Although the details of how SO_2 photolysis creates specific signs and magnitudes in $\Delta^{33}S$ are still debated (Lyons, 2009; Ueno et al., 2009), modeling results indicate that an atmospheric oxygen concentration lower than 10^{-5} of the Present Atmospheric Level (PAL) is a precondition for the preservation of the distinctly different $\Delta^{33}S$ values in marine sediments (Pavlov and Kasting,

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2002). Consequently, the disappearance of MIF-S signals from the sedimentary rock record at 2.32 Ga was interpreted to reflect the first accumulation of free atmospheric oxygen to greater than 10^{-5} PAL in the Earth's history (Bekker et al., 2004; Guo et al., 2009; Farquhar et al., 2010). Ever since, this presence of large non-zero $\Delta^{33}S$ values in sedimentary rocks was considered as solid quantitative evidence for an anoxic atmosphere in Earth's early history and supporting the notion of a Great Oxidation Event at 2.4 Ga (Holland, 2006). Further on, it was suggested that changes in the magnitude of $\Delta^{33}S$ and the relationship of $\Delta^{36}S$ and $\Delta^{33}S$ would not only constrain the absence of atmospheric oxygen, but also the composition of Earth's reducing atmosphere, specifically with regard to CH_4, CO_2, SO_2, and H_2S (Ono et al., 2003; Zahnle et al., 2006; Ueno et al., 2009; Halevy et al., 2010; Zerkle et al., 2012). The relative abundance of these gases affect the UV transparency and can alter the atmospheric redox state, with implications on MIF-S source reactions as well as on the relative importance of different sulfur species that carry the MIF-S signal from the atmosphere to the sediment (sulfur exit channel fraction) (Zerkle et al., 2012).

Recently several authors proposed the appearance of a "whiff of oxygen" ~100 million years prior to the G.O.E., based on the abundance and isotopic composition of selected redox-sensitive elements (Anbar et al., 2007; Wille et al., 2007; Johnson et al., 2008; Frei et al., 2009; Thomazo et al., 2011). These authors concluded that the atmospheric oxygen concentration was high enough to allow oxidative weathering of these elements (i.e. Mo, Cr, Fe) on the continents one hundred million years before the G.O.E, although there is no consensus on the required minimum concentration of atmospheric O_2. However, the very same sediments from this time period display the highest MIF-S signals in Earth's history (Kaufman et al., 2007; Farquhar et al., 2010), an observation that appears to be inconsistent with ideas of an earlier rise in atmospheric oxygen.

We will utilize newly obtained multiple sulfur isotope data from 2.71 billion years old sedimentary rocks from the Kidd Creek area, Canada, and improved atmospheric modeling to partially resolve this apparent inconsistency and to reconcile MIF-S interpretations and an early increase in atmospheric oxygen abundance. Together with previous suggestions for an early "whiff of oxygen" at 2.5 Ga (Anbar et al., 2007; Kaufman et al., 2007), multiple step-increases in the redox-state of Earth's atmosphere appear more likely than the currently accepted view of a single Great Oxidation Event.

2. Geological setting

The Kidd Creek massive sulfide deposit is part of the Abitibi Subprovince located between Hudson Bay and the Great Lakes in Ontario, Canada (Fig. 1). The Abitibi Subprovince represents one of the largest Archean greenstone belts on the Superior craton. More precisely the Kidd Creek deposit belongs to the Kidd-Munro volcanic assemblage, which is a 200 km long belt of felsic metavolcanic to ultramafic rocks (Hannington et al., 1999a). The assemblage is generally bimodal and consists of predominantly mafic volcanic complexes with only spatial replacements of rhyolite. Felsic volcanism was episodic over the complete depositional time period (2.717–2.711 Ga; Bleeker et al., 1999). The sedimentary rocks (i.e. graphitic argillite layers) analyzed here are of marginal abundance ($<5\%$; Bleeker, 1999). Their deposition occurred in a slowly rifting back arc basin (<1 cm/yr) probably initiated by a mantle plume underneath the rifting center (Bleeker et al., 1999). The long-lived rifting and associated intense hydrothermal activity enabled the sub-aquatic deposition of massive sulfide lenses in graben or half-graben structures (Bleeker, 1999).

The metamorphic grade of the Kidd Creek massive sulfide deposit is sub-greenschist to lower greenschist. Primary depositional features are often well preserved due to this low grade metamorphism and minimal deformation processes (Hannington et al., 1999a). By contrast hydrothermal alteration is assumed to be significant at the Kidd Creek deposit (Slack and Coad, 1989), although temperatures of hydrothermal fluids were relatively low up to 250 °C (Hannington et al., 1999b). Grade and character of this alteration are poorly constrained.

3. Material and methods

The samples for this study are black shales derived from sedimentary argillite layers in between felsic and/or mafic volcanic extrusions. In particular, the samples are from three different argillite horizons (Northern Prosser, Rusty Hill and Chance) that are petrologically comparable. Sample localities are geographically

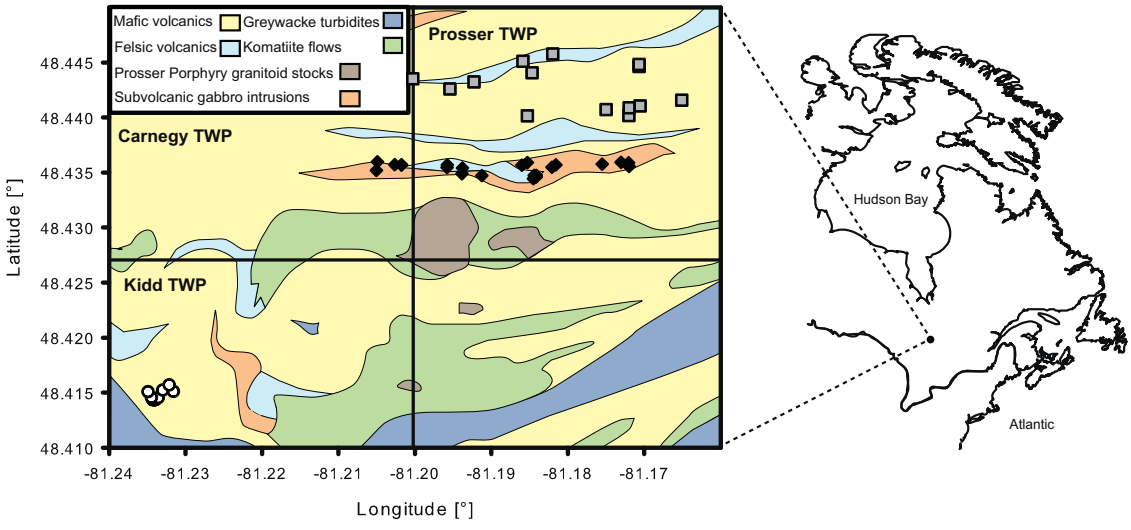

Fig. 1. Geologic map and sample locations from the sample area at Kidd Creek (modified from Bleeker et al. (1999)). The Kidd Creek area is located in the North-Eastern part of North America south of Hudson Bay. Sample locations are illustrated as grey squares (Northern Prosser horizon), black diamonds (Rusty Hill horizon) and white circles (Chance horizon).