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# Reactions of hydrothermal solutions with organic matter in Paleoproterozoic black shales at Talvivaara, Finland: Evidence from multiple sulfur isotopes

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## ABSTRACT

Stable isotopic studies of Archean–Paleoproterozoic sedimentary rocks older than 2.4 Ga have documented large mass-anomalous fractionations of sulfur isotopes ( $\Delta^{33}\text{S} = > 0 \pm 0.2\text{‰}$ ), while younger rocks record little to no anomalous fractionation of sulfur isotopes. This change from large anomalous fractionations to sulfur isotope values that fall on the terrestrial fractionation line has been proposed to represent the transition from an essentially anoxic Archean atmosphere to an oxygenated atmosphere. Here we present  $\delta^{34}\text{S}$  and  $\delta^{33}\text{S}$  data for 28 core samples from Paleoproterozoic (2.1–1.9 Ga) metamorphosed black shales and associated sulfide ores in eastern Finland. Previous  $\delta^{34}\text{S}$  studies of the Talvivaara and Outokumpu deposits of eastern Finland focused on single-grain analyses of sulfides, while this study presents data from sequentially extracted sulfur fractions (e.g., acid-soluble sulfides, chrome-reducible sulfides, elemental sulfur). The sulfur isotope results range between +16.6 and –11.6‰ for  $\delta^{34}\text{S}$ , +8.6 and –6.0‰ for  $\delta^{33}\text{S}$ , and +1.25 and –0.55‰ for  $\Delta^{33}\text{S}$ . The anomalously fractionated samples are not consistent with previous findings that large anomalous fractionations of sulfur isotopes are absent in sedimentary/metasedimentary rocks younger than 2.4 Ga. It is unlikely that Talvivaara sulfides are the products of ultraviolet photolysis of volcanic  $\text{SO}_2$  in an oxygen-poor atmosphere. Alternatively, these sulfides could in part be the products of diagenetic reactions between sediments enriched in organic matter ( $C_{\text{org}}$ ) and hydrothermal solutions rich in sulfate (i.e., thermochemical sulfate reduction). Laboratory experiments on thermochemical sulfate-reduction have shown that mass-anomalous fractionations of sulfur isotopes can be recorded in reduced-sulfur products from reactions between simple amino acids and sulfate at 150–300 °C. A thermochemical sulfate-reduction pathway for the mass-anomalous signatures in Talvivaara samples is consistent with previous genetic models proposed for the origin of the sulfur- and organic carbon-rich black shales (now schists) associated with the Talvivaara and Outokumpu ore deposits. At Talvivaara metalliferous black shales apparently were deposited under an anoxic to sulfidic marine water column. The reported multiple sulfur-isotopic data are key geological evidence for mass-anomalous fractionations of sulfur isotopes during hydrothermal alteration of fine-grained organic-rich sediments. Approximately 20% of samples in this study show large offsets in  $\Delta^{33}\text{S}$  values between different extracted sulfur fractions from the same sample, which can be explained by classical isotope effects associated with the formation of hydrothermal alteration products that predominantly are retained within the precursor fine-grained organic-rich units.

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## 1. Introduction

Major changes in Earth's atmosphere and ocean chemistry are widely thought to have occurred during the Paleoproterozoic Era (Canfield, 1998; Farquhar et al., 2000; Holland, 1984). Strong arguments have been made for a stepwise oxidation of an anoxic

terrestrial atmosphere beginning in the early Paleoproterozoic based upon multiple lines of sedimentary and geochemical evidence (Bekker et al., 2004; Canfield, 2005; Farquhar and Wing, 2003; Holland, 1994, 2004; Johnston, 2011). Additionally, studies of iron speciation, redox sensitive elements, and metal isotopes suggest that Paleoproterozoic oceans also transitioned from ferruginous ( $\text{Fe}^{2+}$ -rich) to euxinic ( $\text{H}_2\text{S}$ -rich and anoxic) water column conditions (Poulton et al., 2004, 2010; Scott et al., 2008; Shen et al., 2002, 2003; Rouxel et al., 2005). Archean sedimentary rocks commonly record large anomalous fractionations (often referred to as mass-independent fractionations; MIF) of sulfur isotopes while such

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signatures are essentially absent in Proterozoic and Phanerozoic strata which record mass-dependently fractionated (MDF) sulfur isotope values (Cates and Mojzsis, 2006; Domagal-Goldman et al., 2008; Farquhar et al., 2000, 2007; Johnston et al., 2006, 2008; Ohmoto et al., 2006; Ono et al., 2003, 2006, 2009; Papineau et al., 2005; Shen et al., 2009; Ueno et al., 2008). Mass-anomalous fractionations of sulfur isotopes are defined as deviations of  $\delta^{33}\text{S}$  and  $\delta^{36}\text{S}$  values from terrestrial fractionation lines (TFL) and are expressed as  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values that fall outside of  $0 \pm 0.2\%$  and  $0 \pm 0.4\%$  respectively (e.g., Farquhar and Wing, 2003; Watanabe et al., 2009). Latest Archean-earliest Paleoproterozoic sedimentary sulfides from Western Australia (Mount Bruce Supergroup) and Ontario, Canada (Huronian Supergroup) record moderate to small ( $\Delta^{33}\text{S} < \pm 2\%$  but  $> \pm 0.2\%$ ) mass-anomalous fractions of sulfur isotopes (Farquhar et al., 2000; Mojzsis et al., 2003; Papineau et al., 2007). By 2.3 billion years ago, however, sedimentary sulfides from South Africa (Transvaal Supergroup) only record MDF sulfur isotopes (Bekker et al., 2004; Guo et al., 2009). The disappearance approximately 2.3–2.4 billion years ago of large anomalous fractionations of sulfur isotopes (e.g.,  $\Delta^{33}\text{S} \geq \pm 2\%$ ) from sedimentary rocks containing sulfur-bearing minerals (e.g., barite and pyrite) signals the first significant accumulation of free  $\text{O}_2$  in the atmosphere (Farquhar and Wing, 2003).

Gas-phase reactions involving photolysis of sulfur dioxide ( $\text{SO}_2$ ) gas mixtures in an atmosphere devoid of  $\text{O}_2$  can produce elemental sulfur ( $\text{S}^0$ ) and/or sulfate ( $\text{SO}_4^{2-}$ ) with mass-anomalous sulfur isotope signatures leading to the hypothesis that the geologic record of mass-anomalous fractionations of sulfur represents ultraviolet photolytic reactions of volcanic sulfur aerosols in an anoxic early Earth atmosphere (Farquhar et al., 2000, 2001). Models by Pavlov and Kasting (2002) support this hypothesis and place a maximum threshold of  $\sim 10^{-5}$  present atmospheric levels of oxygen in order to preserve the mass-anomalous sulfur isotope signal in products produced from UV photolysis of  $\text{SO}_2$ . Further theoretical and experimental studies have suggested that self-shielding of atmospheric  $\text{SO}_2$ , and concentrations of other atmospheric compounds (e.g.,  $\text{O}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CS}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{OCS}$ ) are also capable of producing mass-anomalous sulfur isotopes in an Archean atmosphere (Lyons, 2007; Ueno et al., 2009; Wing et al., 2005). Recent experimental studies and theoretical models support an alternative pathway for mass-anomalous sulfur isotopic signals involving aqueous phase reactions under hydrothermal conditions (Lasaga et al., 2008; Watanabe et al., 2009).

Watanabe et al. (2009) have shown that high temperature (150–200 °C) reactions of sulfate in solution with reactive organic compounds (glycine and alanine) lead to moderate mass-anomalous fractionations ( $\Delta^{33}\text{S} = +0.1$  to  $+2.1\%$ ,  $\Delta^{36}\text{S} = -1.1$  to  $+1.1\%$ ) in reduced-sulfur products. Heterogeneous chemical reactions involving the adsorption of sulfur species onto reactive surfaces of organic compounds are inferred to be associated with thermochemical sulfate reduction. A recent laboratory study involving thermochemical sulfate reduction documents mass-anomalous fractionations ( $\Delta^{33}\text{S} = -0.03$  to  $+13.1\%$ ,  $\Delta^{36}\text{S} = -1.26$  to  $+0.10\%$ ) of sulfur products and suggests an ion-radical pair mechanism (Oduro et al., 2011). These authors attribute the mass-anomalous fractionation of the  $^{33}\text{S}$  to a magnetic isotope effect (MIE) that is expressed through the production of sulfur radicals that only affect the odd-numbered isotopes, while the mass-anomalous  $^{36}\text{S}$  documented in this study are linked to MDF effects through mixing processes (e.g., Ono et al., 2006). Regardless of a constrained mechanism(s), thermochemical sulfate reduction processes have clearly been shown to impart mass-anomalous fractionations on sulfur species produced in laboratory settings. In natural environments containing sulfur and organic compounds, thermal processes have been suggested as a mechanism

for formation of sulfur radicals (e.g., Lewan, 1998; Tomic et al., 1995).

Here we present  $\delta^{34}\text{S}$  and  $\delta^{33}\text{S}$  data from 28 samples of drill cores from Paleoproterozoic (2.1–1.9 Ga) metasedimentary black shales (schists) that record moderate–minor mass-anomalous fractionations of sulfur isotopes. Previous  $\delta^{34}\text{S}$  studies of the Talvivaara and Outokumpu sulfide deposits of eastern Finland have focused on single grain analyses of sulfides (e.g., Loukola-Ruskeeniemi, 1999; Mäkelä, 1974) while this study presents data from sequentially extracted sulfur fractions (acid-soluble sulfides, chromium-reducible sulfides, elemental sulfur). Papineau et al. (2005) previously analyzed sulfide minerals for  $\delta^{34}\text{S}$  and  $\delta^{33}\text{S}$  and found no mass-anomalous  $\Delta^{33}\text{S}$  signatures in Paleoproterozoic rocks from these deposits in Finland, although they collected only six samples mostly from outcrops as part of a larger study of the 600 Ma period after the Paleoproterozoic “Snowball Earth” events. Our new multiple sulfur isotope data are evaluated along with previously published geochemical and geologic evidence for hydrothermal fluid interactions with organic-rich sediments in these riftogenic marine basins in the Kainuu and Outokumpu areas (e.g., Eilu, 2012; Loukola-Ruskeeniemi, 1995, 1999, 2011; Loukola-Ruskeeniemi and Heino, 1996; Loukola-Ruskeeniemi and Lahtinen, 2013; Peltonen et al., 2008). These newly documented  $\Delta^{33}\text{S}$  anomalies fall mostly within the range of previously published  $\Delta^{33}\text{S}$  values for laboratory TSR experiments (Oduro et al., 2011; Watanabe et al., 2009). The results of our study reveal the first geologic evidence supporting mass-anomalous fractionations during thermochemical sulfate reduction processes.

## 2. Geologic setting

### 2.1. Black schists in the Kainuu–Outokumpu region, eastern Finland

Kainuu–Outokumpu region is located in the central part of the Fennoscandian Shield, near the Archean–Proterozoic boundary (Fig. 1). In the metamorphosed black-shale units associated with sulfide occurrences and deposits in the Kainuu–Outokumpu region, the median concentration of organic carbon ( $C_{\text{org}}$ ) varies from 5% to 10%, and the concentration of sulfur from 4% to 13% (Loukola-Ruskeeniemi 1999). Multiple studies have characterized the textures, mineralogy, and geochemistry of black schists in the Kainuu region and associated mining prospects (Kontinen, 2012; Loukola-Ruskeeniemi, 1991, 1995, 1999; Loukola-Ruskeeniemi and Heino, 1996; Loukola-Ruskeeniemi and Lahtinen, 2013; Loukola-Ruskeeniemi et al., 1991). Tectonic deformation has both thinned and thickened the black schist units, but 50–120 m is an average thickness in drill cores. The geological setting and the principal rock types differ along the north–south transect of the Kainuu–Outokumpu province. In the northern part of Kainuu, at Melalahti, thick black schist units occur together with phyllite, dolomite and quartzite. In the Outokumpu area, C- and S-rich black schist units are associated with serpentinite, calc-silicate rocks, dolomite-rich and fine-grained quartz rocks, and associated Cu–Co–Zn sulfide ore deposits and occurrences.

Rocks in the Kainuu–Outokumpu region have undergone green schist to amphibolite facies metamorphism, which impacts on the mineralogy of black schists. The occurrence of the mineral assemblage antigorite–olivine–tremolite in the Jormua area, north of Talvivaara, indicates from 480 °C to 530 °C (at 2–4 kb) as the peak metamorphic temperatures (Peltonen et al. 1996). In the Outokumpu area black schists have undergone amphibolite facies metamorphism with peak temperatures of  $\sim 630$  °C (Peltonen et al., 2008). The predominant sulfides in the Kainuu–Outokumpu black schists are pyrite and pyrrotite with minor sphalerite, chalcopyrite, pentlandite, and galena also occurring in mineralized

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