Sulfur isotope behavior during metamorphism and anatexis of Archean sedimentary rocks: a case study from the Ghost Lake batholith, Ontario, Canada

Claire E. Bucholz[1*], Joseph A. Biasi[1], Patrick Beaudry[2], and Shuhei Ono[2]
[1]California Institute of Technology, Pasadena, CA 91125
[2]Massachusetts Institute of Technology, Cambridge, MA 02139
*cbucholz@caltech.edu

SUBMITTED TO EARTH and PLANETARY SCIENCE LETTERS
REVISION #1

ABSTRACT

Recycling of surface-derived sulfur into the deep earth can impart distinct sulfur isotope signatures to magmas. The details of sulfur transfer from sedimentary rocks to magmas (and ultimately igneous rocks) through metamorphism and devolatilization and/or partial melting, however, is difficult to trace. To understand this process in detail we studied multiple-sulfur isotope compositions of sulfides in the Archean (*c.* 2685 Ma) Ghost Lake batholith (GLB) and its surrounding host metasedimentary rocks of the Superior Craton (Ontario, Canada) by high spatial resolution secondary ion mass spectrometry, complemented by high-precision gas source isotope ratio mass spectrometry measurements. The GLB comprises strongly peraluminous biotite+cordierite, biotite+muscovite, and muscovite+garnet+tourmaline granites to leucogranites, which are thought to represent the partial melts of surrounding metagreywackes and metapelites. The metasedimentary rocks display a range of metamorphic grades increasing from biotite-chlorite (280-380ºC) at ~5 km away from the GLB to sillimanite-K-feldspar grade (~660ºC) immediately adjacent to the batholith, thus providing a natural experiment to understand sulfur isotope variations from low- to high-grade Archean sedimentary rocks, as well as granites representative of their partial melts.

We find that metasedimentary sulfide $\delta^{34}S$ values increase with progressive metamorphism at most 2-3‰ (from -1‰ up to +1 to +2‰). An increase in $\delta^{34}S$ values in pyrrhotite during prograde metamorphism can be explained through Rayleigh fractionation during pyrite desulfidation reactions. Pyrite from all but one of the granite samples preserve $\delta^{34}S$ values similar to that of the high-grade metasedimentary rocks, indicating that partial melting did not result in significant fractionation of $\delta^{34}S$. The exception to this is one granite sample from a part of the batholith characterized by abundant metasedimentary inclusions. This sample contains

pyrite with heterogeneous and low $\delta^{34}S$ values (down to -16‰) which likely resulted from incomplete homogenization of sulfur between the granitic melt and metasedimentary inclusions. Small (several tenths of a permil), mostly positive $\Delta^{33}S$ are observed in both the metasedimentary rocks and granites.

Our results suggest that Archean strongly peraluminous granites could be a high-fidelity archive to quantify the bulk sulfur isotope composition of the Archean siliciclastic sediments. Further, our findings indicate that subduction of reduced sulfur-bearing sediments in the Archean with $\delta^{34}S$ at or near 0‰ should result in release of sulfur-bearing fluids in the mantle wedge with similar values (within a few permil). S-MIF (if initially present in Archean surface material) may be preserved during this process. However, the absence of S-MIF in igneous rocks does not preclude assimilation of Archean sedimentary material as either S-MIF may not be originally present in the Archean sedimentary sulfur and/or homogenization or dilution could obscure any S-MIF originally present in assimilated Archean sediments.

1. Introduction

Atmospheric oxygen levels increased throughout Earth's history with the largest increase in O_2 levels occurring during the "Great Oxidation Event" (GOE, ~2.4-2.3 Ga; Canfield, 2004) from $<10^{-5}$ to 1-10% of the present atmospheric level. One of the most distinctive chemical fingerprints of low atmospheric O_2 levels is the presence of mass-independent fractionation (MIF) of sulfur isotopes in Archean and earliest Paleoproterozoic sedimentary sulfide and sulfate arising from SO_2 photodissociation in a low-pO_2 atmosphere (see review of Ono, 2017; Fig.

45 1a,b). Although the details of the gas phase atmospheric chemistry leading to non-zero $\Delta^{33}S$[1] are
46 not fully understood (*c.f.*, Ono et al., 2017), a leading model for the Archean sulfur cycle is that
47 reduced and elemental sulfur species acquired positive $\Delta^{33}S$, whereas oxidized sulfur (sulfate)
48 carried the complementary negative $\Delta^{33}S$ (*e.g.,* Farquhar and Wing, 2003; Halevy et al., 2010).
49 Similarly, sulfur isotopes in igneous rocks have been used as tracer of assimilation of
50 oxidized or reduced sedimentary sulfur. For example, magnetite-series, or relatively oxidized,
51 granitoids have positive bulk-rock $\delta^{34}S$ values of +1 to +9‰, whereas ilmenite-series granitoids
52 have predominantly negative values between -11 and +1‰ (*e.g.*, Ishihara and Sasaki, 1989). The
53 positive $\delta^{34}S$ of magnetite-series granitoids was interpreted as a result of incorporation of sulfur
54 derived from subducted sulfate-bearing sediments or seawater, whereas the negative $\delta^{34}S$ of
55 ilmenite-series granitoids was attributed to assimilation of sulfur from reduced graphite- and
56 sulfide-bearing sediments. Multiple sulfur isotopes have also been measured in igneous rocks as
57 a tracer of Archean sulfur in magmas. For example, Bekker et al. (2009) found non-zero $\Delta^{33}S$ in
58 sulfides from Archean komatiite-hosted Fe-Ni sulfide deposits and concluded that the komatiite
59 magmas gained sulfur from Archean seafloor hydrothermal sulfides and sulfur-rich shales (Fig.
60 1c). Similarly, metamorphosed ultramafic sills, gabbros, and tonalites from the >3.8 Ga
61 Nuvvuagittuq Greenstone Belt (Quebec) have $\Delta^{33}S$ values from -0.03 to 0.26‰, consistent with
62 having mostly mantle-derived sulfur ($\Delta^{33}S$=0), but also a minor contribution from surrounding
63 metasedimentary rocks (Thomassot et al., 2015; Fig. 1c). Similarly, positive $\Delta^{33}S$ have been
64 observed in Proterozoic igneous rocks such as the Bushveld Complex of South Africa
65 (Penniston-Dorland, 2008; 2012; Magalhães et al., 2018; 2019) and granitoids from Australia

[1] S isotope ratios are expressed as $\delta^{X}S = \{(^{X}S/^{32}S)_{sample}/(^{X}S/^{32}S)_{CDT} - 1\}*1000$ (‰), where x is 33, 34, or 36 & CDT is Canyon Diablo meteorite troilite (Ding et al., 2001). $\Delta^{x}S$ is the ‰ deviation from the mass dependent relationship: : $\Delta^{x}S = 1000\ [\ln\left(\frac{\delta^{x}S}{1000} + 1\right) - \theta \ln\left(\frac{\delta^{34}S}{1000} + 1\right)]$. θ = 0.515 for ^{33}S & 1.90 for ^{36}S (for discussion of Δ definition see Ono, 2017).

(LaFlamme et al., 2018; Selvaraja et al., 2017; Fig. 1c). S-MIF has also been observed in magmatic sulfides in modern ocean island basalts (OIB) from Mangaia, Cook Islands (Cabral et al., 2013) and Pitcairn Island (Delavault et al., 2016). For these OIB samples, both $\delta^{34}S$ and $\Delta^{33}S$ values are mostly negative (Fig. 1c) and interpreted as evidence for deeply subducted Archean altered oceanic crust. (We note, however, that the majority of sulfur isotope studies of OIBs have observed $\Delta^{33}S = 0$ [*e.g.*, Discovery/Shona: Labidi et al., 2013; Samoa: Labidi et al., 2015; Dottin et al., 2020; Canary: Beaudry et al., 2018; Fig. 1c]). In contrast to some OIB, S-MIF observed in sulfide inclusions in diamonds exhibit primarily positive $\Delta^{33}S$ values (Farquhar et al., 2002; Thomassot et al., 2009; Smit et al., 2019; Fig. 1c). Based on these findings, it has been suggested that the material in some OIB source regions represents a complementary oxidized ($\Delta^{33}S<0$) sulfur reservoir (through sulfate reduction during ocean-floor basalt alteration) to that of the reduced ($\Delta^{33}S>0$) subcontinental lithospheric source of diamonds (Cabral et al., 2013).

However, our understanding of sulfur transfer from Archean surface reservoirs to the igneous rock records remains limited in that existing multiple sulfur isotope data for igneous materials are from samples which represent a mixture of different reservoirs (*i.e.*, mantle and Archean sediment/oceanic crust). In addition, the process of sulfur transfer from sedimentary rocks to magmas is poorly understood. During metamorphism, partial melting, and/or assimilation, desulfidation of sedimentary pyrite produces pyrrhotite and sulfur-bearing fluids (Ferry, 1981; Tomkins, 2010). Thermodynamic calculations and experiments indicate that this reaction begins at ~75-200ºC and subsequently evolves with increasing temperature along the pyrrhotite-pyrite buffer (Toulmin and Barton, 1964). The loss of sulfur from pyrite or pyrrhotite to fluids can drive several per mil fractionations between the $\delta^{34}S$ of residual sulfide and fluid, which may be preserved in the sulfur isotope composition of melts formed through partial melting or assimilation

of metasedimentary rocks. Although sulfur transfer from sedimentary rock to melt should not disturb the original sedimentary $\Delta^{33}S$, non-zero $\Delta^{33}S$ can be diluted by external sulfur or homogenized during metamorphism (*e.g.*, Cui et al., 2018). Consequently, a magma assimilating S-MIF-bearing sedimentary sulfur, may or may not preserve S-MIF signals.

If $\Delta^{33}S$-$\delta^{34}S$ variations are to be used in igneous rocks to trace contamination by Archean sedimentary material, this process must be understood in a fundamental way. Here we present a case study of the Ghost Lake batholith, an Archean strongly peraluminous granite (SPG; *i.e.*, bulk-rock molar Al/(2Ca-1.67P+Na+K)>1.1) and its host metasedimentary rocks. The Al-rich compositions of SPGs indicate derivation predominantly (if not completely) through the partial melting of metasedimentary rocks (see discussion in Bucholz and Spencer, 2019) and therefore are a useful archive to understand how sulfur isotopes from sedimentary rocks are transferred to the igneous rock record. We analyzed sulfur isotopes for sulfides from both metasedimentary rocks representative of the granite source and from the granite itself. We interpret these results in the context of metamorphic grade, modeling of devolatilization reactions, and sulfur transfer between high temperature fluids and melts.

2. Geologic setting

The Ghost Lake batholith (GLB) is situated in the Sioux Lookout terrane at the Winnipeg River-Wabigoon subprovince boundary of the Superior Province (Fig. 2a). The Sioux Lookout terrane comprises (a) metasedimentary (Zealand/Minnitaki/Warclub Units) and metavolcanic assemblages that were deposited at ~2730-2700 Ma (Blackburn et al., 1991) and (b) a 150-km-long belt of peraluminous granite plutons, including the GLB, which is the largest (~220 km^2 in areal extent) (Breaks and Moore, 1992). The Zealand Unit is characterized by east-striking

112 foliations, a range in metamorphic grades (Fig. 2a-c), and zones of incipient migmatization
113 (Breaks and Moore, 1992; Fig. 2d). Metamorphic grade in the metasedimentary units increases
114 northward from the Wabigoon subprovince with mineral isograds of chlorite±biotite, andalusite,
115 garnet, sillimanite-muscovite, and sillimanite-K-feldspar (Breaks and Moore, 1992; Fig. 2a). The
116 metamorphic gradient calculated based on mineral assemblages and thermobarometry increases
117 steeply northward (50ºC/km) from the low-grade Wabigoon subprovince (~200ºC) to the
118 margins of the GLB (>700ºC) at a constant pressure of ~0.3 GPa (Breaks and Moore, 1992). On
119 the west-northwest batholith margins, clastic sedimentary rocks were metamorphosed
120 sufficiently as to partially melt (Fig. 2d). In contrast, host rocks to the east and south contain
121 mineral assemblages characteristic of the sillimanite-muscovite zone, but do not preserve
122 evidence for incipient melting (Fig. 2a).
123 The GLB consists of eight units comprising a volumetrically-dominant,
124 biotite(±cordierite±muscovite) granite (GLB-1/-2 of Breaks and Moore, 1992), lesser amounts of
125 locally garnet-bearing biotite+muscovite granite (GLB-3), and highly evolved,
126 tourmaline+garnet+muscovite-bearing pegmatitic granitic facies (GLB-4 to -8) found primarily
127 in the eastern lobe of the GLB. Samples from units GLB-1, -2, and -4 were selected for study.
128 The western and central part of the GLB is weakly foliated and contains zones with abundant
129 inclusions of metasedimentary rocks and restitic material (Fig. 2a,f). To the east, the intensity of
130 foliation and abundance of the inclusions decrease to the point that the batholith is either massive
131 or preserves original magmatic layering. However, locally on the batholith's eastern margin,
132 there are zones rich in partially melted, sedimentary inclusions (Fig. 2e).
133 A detailed examination of the petrology and bulk-rock chemistry of the GLB was
134 presented by Breaks and Moore (1992), who proposed the following petrogenetic model.

Greywackes and mudstones (the Zealand unit) were deposited as turbidites in an arc-proximal basin between 2730-2700 Ma. Subsequently, during collision between an arc (the Wabigoon subprovince) and a microcontinent (the Winnipeg River subprovince), the sediments were metamorphosed under high-temperature, low-pressure conditions resulted in anatexis and widespread production of peraluminous granitic melts (*c.* 2685 Ma). The metasedimentary rocks preserved along the margins of the GLB are thought to be representative of the source rock for the batholith.

3. Analytical and methods

Petrographic descriptions of both metasedimentary and granitic samples are given in the Supplementary Material. Bulk-rock major and trace elements were measured via X-ray fluorescence (XRF) for pseudosection construction and are given in Table S1. Sulfide and silicate mineral major and minor elements were analyzed via electron microprobe analysis (EMPA). Mineral compositions are reported in Table S2 and S3. Sample average sulfide analyses are given in Table 2. XRF and EMPA analytical methods and pseudosection construction details are given in the Supplementary Material.

3.1 Sulfur isotope analysis

3.1.1 Secondary ion mass spectrometry

Sulfur isotopes (^{32}S, ^{33}S, ^{34}S) of sulfide separates (see Supplemental Material) were analyzed on a Cameca 7f-GEO ion microprobe (Caltech). A primary Cs^+ beam of ~3 nA rastered over an area of ~20x20 µm during pre-sputtering (90 s) and then over a 5x5 µm area during data collection was used. As the 7f-GEO lacks a multi-collection setup, ^{32}S was measured on one

158 Faraday cup and ^{33}S and ^{34}S were measured on a second Faraday cup sequentially, in rapid peak-
159 jumping mode. 30 cycles of sequential mass measurements were collected per spot analysis. A
160 mass resolving power of ~3900 was used to resolve ^{33}S from ^{32}SH. Sample analyses were
161 bracketed by standard measurements every 15-20 measurements. During analysis of pyrite, we
162 measured three different pyrite standards; Balmat ($\delta^{34}S$ = 16.4‰; Kozdon et al., 2010), Ruttan
163 ($\delta^{34}S$=1.2‰; Crowe and Vaughan, 1996), and Orocampa pyrite ($\delta^{34}S$=3.41‰, $\delta^{33}S$=1.74; these
164 values differ from those of Fischer et al. (2014) which were found to be in error during this
165 study). During analysis of pyrrhotite we measured Anderson pyrrhotite ($\delta^{34}S$=1.4±0.2‰; Crowe
166 and Vaughan, 1996) and Orocampa pyrite. Raw isotope ratios were then corrected for
167 instrumental mass fractionation (IMF, see Supplementary Material for details) using Orocampa
168 pyrite and Anderson pyrrhotite as primary standards.
169 In-run precision (2σ, over 30 cycles on the same spot) were ~0.02‰ for $\delta^{34}S$ and ~0.06‰
170 for $\delta^{33}S$. External precision, defined as the 1σ of multiple (3-6) adjacent measurements of
171 standards was $\delta^{34}S$ = 0.06-0.55‰, $\delta^{33}S$ = 0.13-0.58‰, and $\Delta^{33}S$ = 0.13-0.56‰. Full analyses of
172 standards and unknowns (both uncorrected and corrected for IMF) are in Tables S3 and S4.
173
174 3.2.2 Isotope ratio mass spectrometry
175 Separated sulfides from 7 samples were reacted in a chromous chloride ($CrCl_2$) solution
176 to extract acid volatile sulfur (*e.g.,* pyrrhotite) and chromium reducible sulfur (*e.g.,* pyrite)
177 species following Canfield et al. (1986). The reaction was performed under an N_2 atmosphere for
178 2 hours and the evolved H_2S gas was trapped in a zinc acetate solution and precipitated as zinc
179 sulfide (ZnS). Silver nitrate ($AgNO_3$) was then added to recover silver sulfide solids (Ag_2S),
180 which were centrifuged and then dried at 80°C and weighed. The Ag_2S precipitates weighed

between 0.16 to 2.68 mg (Table S5) and were fluorinated for over 8 h at 300°C. The produced SF_6 was purified with a gas chromatograph by sequentially going through a column packed with molesieve 5 Å, followed by a column packed with HayeSep Q. The purified SF_6 gas was transferred to the Thermo-electron MAT 253 isotope ratio mass spectrometer (IRMS) at MIT, where ion beams of $^{32}SF_5^+$, $^{33}SF_5^+$, $^{34}SF_5^+$ and $^{36}SF_5^+$ were measured, as previously described (Ono et al., 2006; 2012).

Replicate analyses of reference sulfide material (IAEA-S1) by Ono et al. (2012) yielded -0.30±0.26‰, 0.100±0.014‰, and -0.57±0.19‰ for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$, respectively (n=28, 2σ) for 2 mg Ag_2S. Fluorination of small IAEA-S1 samples (40 to 130 μg Ag_2S, N=13) by Fortin et al. (2019) yielded standard deviations (2σ) of 0.43, 0.03, and 0.54‰ for $\delta^{34}S$, $\Delta^{33}S$ and $\Delta^{36}S$, respectively. The overall precision of isotope ratio analyses is between those values (*i.e.*, 0.26 to 0.43‰ for $\delta^{34}S$), with larger standard deviation for smaller samples. During our analyses, our IAEA-S1 bracketing standards (2 mg Ag_2S) yielded an average of -0.26±0.20‰, 0.093±0.004‰, and -0.56±0.06‰ for $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$, respectively (n = 3, 2σ), in agreement with Ono et al. (2012). Mass-spectrometer precisions, evaluated by repeated (n=7) measurement cycles, are from 0.01-0.15 ‰ for $\delta^{34}S$, 0.01-0.04 ‰ for $\Delta^{33}S$ and 0.04-0.5 ‰ for $\Delta^{36}S$ (all 1σ), generally increasing for smaller samples (Table S5).

4. Results

4.1 Sulfide major and minor element compositions

The only observed sulfide mineral in the granites is pyrite (Fig. 3b). In the metasedimentary rocks, one biotite-chlorite grade sample (SP-18-10) and one sillimanite-K-feldspar grade sample (SP-18-27) contain pyrite as the dominant sulfide phase. Pyrite in the

latter sample likely formed during retrogression of pyrrhotite upon cooling (Craig and Volkes, 1993). All other metasedimentary samples contained pyrrhotite (Fig. 3a) as the primary sulfide with stoichiometries ranging from $Fe_{0.88}S$ to $Fe_{0.94}S$. No systematic variation in stoichiometry was observed with increasing metamorphic grade. Minor chalcopyrite was observed in a few metasedimentary samples (Fig. 3a). Otherwise, Ni, Cu, and Zn were present at <0.2 wt.% in all sulfides.

4.2 Pressure-temperature estimates – thermobarometry and pseudosections

A maximum pressure during metamorphism of ~0.4 GPa is inferred from the presence of andalusite in the andalusite- and garnet-grade samples (Fig. 4). In the high-grade metamorphic zones, metamorphic pressures are constrained to be below 0.35 GPa based on the intersection of the univariant reaction curves muscovite + plagioclase + quartz = K-feldspar + Al_2SiO_5 + H_2O and the water-saturated peraluminous granite solidus (Holtz et al., 1992, Fig. 4). Evidence for this constraint comes from the coexistence of sillimanite and K-feldspar in metapelitic rocks lacking evidence for partial melting.

The increase in metamorphic gradient northward is primarily a reflection of increasing temperature. Three metasedimentary samples from the biotite-chlorite zone contain prehnite/pumpellyite indicating temperatures of ~275-380ºC. Minimum temperatures of the rocks of the andalusite isograd are defined by the reaction of pyrophyllite = andalusite + quartz + H_2O, corresponding to 400ºC at 0.3 GPa and maximum temperatures of ~550ºC are constrained by the reaction andalusite = sillimanite (Fig. 4). Garnet-biotite thermometry (Holdaway, 2000) from four samples above the garnet isograd yielded temperatures of 510-585ºC (Table 1). Metamorphic temperatures above the first sillimanite isograd (sillimanite+muscovite) are

227 constrained by the reactions andalusite = sillimanite (~550ºC) and muscovite + plagioclase +
228 quartz = K-feldspar + Al_2SiO_5 + H_2O (~625 ºC, Thompson and Tracy, 1979) at 0.3 GPa (Fig. 4).
229 Samples in the sillimanite-K-feldspar zone crystallized between 625ºC (see constraint for K-
230 feldspar-muscovite samples) and the water-saturated peraluminous granite solidus (660 ºC, Holtz
231 et al., 1992).
232 Best temperature estimates at 0.3 GPa via pseudosection analysis confirms the constraints
233 above (Table 1, Supplemental Material). Briefly, phase assemblages of biotite+chlorite-,
234 andalusite-, garnet-, and sillimanite-K-feldspar-grade metasedimentary rocks are reproduced
235 over a range of 280-380ºC, 420-550ºC, and ~660ºC, respectively.
236
237 *4.3 SIMS sulfur isotope analysis*
238 4.3.1 Note on IMF correction for pyrrhotite
239 Well-characterized, homogeneous, matrix-matched standards are critical for precise and
240 accurate SIMS analysis (Kozdon et al., 2010). Pyrrhotite presents a particular challenge in that it
241 is non-stoichiometric with a generalized formula of $Fe_{1-x}S$ (x = 0-0.2). Anderson pyrrhotite, the
242 standard used in this study, has a reported major element composition of $Fe_{0.88(\pm0.01)}S$ (Kozdon et
243 al., 2010) which we confirmed (average measured values: Fe = 59.58±0.32 wt.%, S = 39.98±0.29
244 wt.%, Fe/S = 0.88±0.01, all errors 1σ). Pyrrhotite from our samples, however, displays a range
245 of Fe/S values from 0.88 to 0.94, raising the question whether the Anderson pyrrhotite is an
246 appropriate matrix-matched standard. To assess whether our sample pyrrhotite ionized and
247 sputtered similarly to the standard pyrrhotite, we compared yields (defined as $^{32}S^-$ counts per
248 second per nA of primary beam current) of the standard and unknowns (Fig. S9). For the
249 majority of pyrrhotite-bearing samples (~75%), the $^{32}S^-$ yields fell within the range of Anderson

pyrrhotite yields from the same analytical session, supporting the assumption that the standards and unknowns were sputtering and ionizing in a similar fashion. In addition, these samples yielded the same values within uncertainty of the IRMS data. However, for 3 samples (see Table 2), the unknown pyrrhotite $^{32}S^-$ yields were either higher or lower than that of the Anderson pyrrhotite, suggesting potentially different matrix effects. Therefore, for these latter samples (indicate in Table 2) there is uncertainty in the accuracy of the corrected $\delta^{34}S$ and $\delta^{33}S$ values. However, $\Delta^{33}S$ values are robust even with non-matrix matched standards/samples.

Additionally, in 5 samples, $^{32}S^-$ SIMS yields were correlated with raw $^{34}S/^{32}S$ ratios suggesting strong matrix effects during the ionization and sputtering, potentially due to mixed phases present in the sulfides resulting from incomplete breakdown of pyrite to pyrrhotite or retrograde conversion of pyrrhotite to pyrite. Although we report data for these samples, corrected $\delta^{34}S$ and $\delta^{33}S$ may not be accurate as we were unable to confidently construct an empirical IMF correction (see Table 2). Due to these uncertainties, we only discuss pyrrhotite SIMS data where (a) yields were similar to Anderson pyrrhotite and (b) no correlation between $^{32}S^-$ yields with $^{34}S/^{32}S$ ratios were observed.

4.3.2 Sulfides from metasedimentary rocks and granites

Pyrrhotite from 7 biotite-chlorite grade samples display a range of $\delta^{34}S$ values of -2.5 to 1.3‰ with an average of -0.7±0.8‰ (1σ, Fig. 5a). Only two samples from the andalusite isograd (SP-16-36, SP-16-42) yielded robust SIMS $\delta^{34}S$ values with sample averages of 2.5±0.2‰ and -2.6±0.4‰ (1σ), respectively (Fig. 5b). Garnet and K-feldspar-sillimanite grade samples have pyrrhotite $\delta^{34}S$ values between -2.1 to +1.3‰ (Fig. 5c,d). $\Delta^{33}S$ values for the majority of analyzed sulfides are within uncertainty of zero (±0.4 to 1.0‰, 2σ).

Pyrite from the three granite samples have sample average $\delta^{34}S$ values of 0.6±0.6, 1.2±0.3, and 0.7±0.1‰ (1σ) (Fig. 5e, Fig. 6a). Pyrite from one granite sample (SP-16-22) displays isotopically light and heterogeneous inter-grain $\delta^{34}S$ values from -0.5 to -16.4‰. $\Delta^{33}S$ values for most analyzed sulfides were within 2σ uncertainty of zero, but are mostly positive (Fig. 6a).

4.4 IRMS sulfur isotopes

$\delta^{34}S$ values of sulfides increase with increasing metamorphic grade (see circles in Fig. 5), from -1.1 and -2.0‰ in the biotite-chlorite and andalusite-grade samples to 1.1 to 1.7‰ in the garnet and K-feldspar—sillimanite grade samples. $\delta^{34}S$ values in pyrite from the two analyzed granite samples are 0.5 and 1.7‰ (1σ). $\Delta^{33}S$ values for the granites and the metasedimentary rocks vary from -0.09 to +0.43‰ (Fig. 6 and 7). For example, biotite-chlorite grade sample SP-18-8 has $\Delta^{33}S$ of 0.43±0.03‰ and both granites have small, positive $\Delta^{33}S$ (+0.08 and 0.16‰, Fig. 6).

5. DISCUSSION

5.1 Comparison of SIMS and IRMS data

The $\delta^{34}S$ and $\Delta^{33}S$ determined via SIMS and IRMS are consistent with $\delta^{34}S$ within 1‰ and $\Delta^{33}S$ within 0.5‰ of each other (Fig. 7). Exceptions to this are for sulfides from the higher grade (garnet and K-feldspar—sillimanite) samples where the IRMS data are offset to heavier $\delta^{34}S$ values (by 1-2 ‰, *c.f.*, SP-18-22 and SP-18-11, Fig. 7). This discrepancy is likely due to the difficulties of analyzing pyrrhotite via SIMS (see section 4.3.1). Due the uncertainties with the

295 SIMS pyrrhotite data in the high-grade samples, we consider the bulk IRMS data to be most
296 reliable.
297
298 *5.2 Sulfur isotope fractionation during metamorphic devolatilization*
299 Metamorphic reactions involving the liberation of a fluid phase, particularly those
300 occurring at low temperatures, can drive large fractionations (≥1 to 10s ‰) of light stable
301 isotopes (*c.f.,* Rumble, 1982). Compared to other major fluid-mobile species, fractionation of
302 sulfur isotopes during metamorphism has been comparatively less studied (*e.g.*, Hall et al., 1988;
303 Oliver et al., 1992; Alirezaei and Cameron, 2001; Wagner and Boyce, 2006) and dominantly
304 through bulk (whole-rock or separated sulfide) analyses of natural samples [though see Alirezaei
305 and Cameron (2001) and Wagner and Boyce (2006) as examples of in-situ studies]. In addition,
306 these studies focused on either the effects of diagenesis (*i.e.*, pyrite formation and re-
307 precipitation; Wagner and Boyce, 2006), high-grade metamorphic rocks (Alirezaei and Cameron,
308 2001), retrograde metamorphism (Hall et al., 1988), or sulfidic black shales (Oliver et al., 1992).
309 The main sulfide reaction during prograde metamorphism is decomposition of pyrite to
310 pyrrhotite beginning at ~200ºC (lower greenschist facies) and completing at ~400ºC (upper
311 amphibolite facies) (Toulmin and Barton, 1964; Ferry, 1981; Tomkins, 2010). Two classes of
312 reactions may be involved in the reduction of sulfur and oxidation of another phase during pyrite
313 decomposition to pyrrhotite (see discussion of Ferry, 1981). First, there are those that require
314 iron addition to the sulfide mineral from either a free fluid phase:
315
316 $$2FeS_2 + 2FeCl_{2,f} + 2H_2O_f + C \rightarrow 4FeS + 4HCl_f + CO_{2,f} \qquad \text{(Eq. 1)}$$
317

or a coexisting oxide or silicate phase:

$$2FeS_2 + 2FeO_{oxide/silicate} + C \rightarrow 4FeS + CO_{2,f} \quad \text{(Eq. 2)}$$

where the subscript *f* indicates a component in a free fluid. Both Equations 1 and 2 involve oxidation of reduced carbon (*i.e.,* graphite) to CO_2. Second, there are reactions involving loss of sulfur to a fluid phase:

$$2FeS_2 + 2H_2O_f + C \rightarrow 2FeS + 2H_2S_f + CO_{2,f} \quad \text{(Eq. 3)}$$

$$2FeS_2 + CH_{4,f} \rightarrow 2FeS + 2H_2S_f + C \quad \text{(Eq. 4)}$$

Although Ferry (1981) determined that sulfur loss to fluid (Eqs. 3 and 4) predominated during pyrite decomposition using bulk-rock Fe/S ratios and Fe/Mg ratios in co-existing biotite, that study focused on graphitic sulfide-rich schists where the majority of iron and sulfur in the rocks was contained within sulfides. In the relatively sulfide-poor schists studied here, sulfides are a minor phase (<5 modal %) and pyrite breakdown reactions are neither the dominant control on bulk-rock nor mineral compositional trends. Therefore, we are unable to constrain the specific pyrite decomposition reaction. However, field studies (Ferry, 1981) and modeling (Tomkins, 2010) have demonstrated the importance of sulfur loss to a fluid phase during dehydration reactions resulting from low pressure—high temperature metamorphism. For example, chlorite breakdown and H_2O release during greenschist to amphibolite facies metamorphic conditions

drives pyrite breakdown because sulfur addition to the free fluid phase is required to maintain equilibrium fluid compositions of H_2S, SO_2, and H_2O (Tomkins, 2010).

Although we cannot pinpoint the reaction resulting in pyrrhotite formation in our rocks, we model the effects of sulfur-loss on the isotopic composition of metamorphic sulfides to quantify maximum possible effects. At the low oxygen fugacity (f_{O_2}) and pH characteristic of graphite-bearing metapelites, fluids will be H_2S-rich under metamorphic conditions (Poulson and Ohmoto, 1989). For example, a COHS-bearing fluid in equilibrium with graphite, pyrite, and pyrrhotite at 300 to 500ºC and 0.3 GPa will be dominated by H_2O, H_2S, and CH_4. For this reason, we do not calculate fluid speciation along a prograde path. We model sulfur isotope fractionation during prograde desulfidation (Eq. 3 or 4) assuming an open system involving three sulfur-bearing phases (H_2S, FeS_2, and FeS; Kajiwara et al., 1981):

$$\ln\left(R_{FeS_2}\right) - \ln\left(R^0_{FeS_2}\right) = \left[\frac{\alpha_1 - \alpha_2}{2} - 1\right] * \ln\left(X\right) \quad \text{(Eq. 5)}$$

where X is the extent of reaction expressed in terms of the molecular fraction of residual pyrite, R^0 and R are $^{34}S/^{32}S$ isotope ratios of pyrite initially and at reaction extent X (0 to 1), and α_1 and α_2 are the fractionation factors between H_2S-FeS_2 and FeS-FeS_2, respectively, defined as:

$$\alpha_1 = \frac{R_{H_2S}}{R_{FeS_2}} \text{ (Eq. 6a)}$$

$$\alpha_2 = \frac{R_{FeS}}{R_{FeS_2}} \text{ (Eq. 6b)}$$

Temperature-dependent values of α_1 and α_2 used in the model are given in Table S6 (Ohmoto and Goldhaber, 1997). Desulfidation is assumed to follow mass dependent fractionation laws and therefore ^{33}S is not considered in the model. An initial pyrite $\delta^{34}S$ value of -1.4‰ was used based on the lowest sample-average $\delta^{34}S$ value from the biotite-chlorite grade. The full model is available in Table S6.

Figure 8 shows the results of desulfidation modeling for temperatures of 200, 300, and 400ºC. As H_2S and FeS in equilibrium with pyrite are depleted in ^{34}S, pyrite becomes progressively heavier as the reaction proceeds, whereas FeS and H_2S produced from the reaction are initially lighter than the initial pyrite (X = 0-0.6). For example, at 200ºC, the first pyrrhotite produced through desulfidation is depleted by 1.5‰ compared to the initial pyrite. At reaction completion at 300-400ºC, both H_2S and pyrrhotite are isotopically heavier than initial pyrite reaching values of 0-2‰ (+2.6-4.6‰ above that of the initial pyrite). (Note: α_1 values used in this modeling are < 1, however Syverson et al. (2015) re-measured α_1 at 350ºC and found it to be > 1, which would result in lower $\delta^{34}S$ values in pyrite than H_2S and reversing the sign of our model results, *i.e.*, producing more negative residual pyrrhotite values. Thus, the Syverson et al. α_1 may not apply here.)

As discussed above, our SIMS and IRMS datasets, while mostly in agreement, demonstrate more significant differences for the high-grade (garnet to sillimanite-grade) samples, with the IRMS $\delta^{34}S$ values being higher than respective SIMS values (Fig. 7). The SIMS data suggests that prograde metamorphism did not significantly disturb the $\delta^{34}S$ of sulfides in the metasedimentary rocks with most samples being within 1-2‰ of 0 (Fig. 5). In contrast, our limited, but more precise IRMS dataset demonstrates a shift to heavier isotopic values in the garnet and K-feldspar—sillimanite grade samples ($\delta^{34}S$ = +1-2‰) by 2-3‰ from the biotite-

385 chlorite and andalusite grade samples ($\delta^{34}S$ = -1 to -2‰). This observation can be explained
386 through removal of isotopically light H_2S during prograde metamorphism which would increase
387 residual pyrrhotite $\delta^{34}S$ values by 3-4‰ at high grades (Fig. 8). It is also possible that there was
388 pre-metamorphic $\delta^{34}S$ heterogeneity among samples. Although we are unable to rule out this
389 possibility, among the 7 biotite-chlorite grade samples analyzed, most analyses (~93%) have
390 $\delta^{34}S < 0.5$‰. Last, $\Delta^{33}S$ shows no systematic trends with metamorphic grade, varying within
391 0.5‰ of 0 (Fig. 7), suggesting that S-MIF signatures were heterogeneous, but broadly conserved
392 during prograde metamorphism.
393
394 *5.3 Transfer of sulfur from metasedimentary rocks to granitic melts during anatexis*
395 Three of the four analyzed granite samples have $\delta^{34}S$ values heavier (by 1-2‰) than that
396 of the biotite-chlorite grade metasedimentary sulfides, but similar values to that of the $\delta^{34}S$ IRMS
397 values of pyrrhotite from high-grade (garnet and K-feldspar sillimanite) sedimentary rocks,
398 suggesting that the $\delta^{34}S$ of the granites reflect that of high-grade metasedimentary rocks affected
399 by metamorphic desulfidation reactions (see section 5.2). In reduced systems, where
400 desulfidation is driven primarily by the decomposition of pyrite to pyrrhotite, this will drive
401 positive, but small (on the order to +2-3‰) fractionations upon reaction completion. Importantly,
402 however, the granites preserve positive $\Delta^{33}S$ within the range of values observed in their
403 sedimentary source rocks (IRMS $\Delta^{33}S$ of 0.08 and 0.16‰, Fig. 6 and 7b). To our knowledge,
404 this is the first study demonstrating non-zero $\Delta^{33}S$ in Archean granitic rocks (*sensu stricto*). Only
405 a handful of Archean igneous rocks have been shown to have non-zero $\Delta^{33}S$, including sulfides
406 from komatiite-hosted Ni deposits ($\Delta^{33}S$ = -1.0 to +2.6; Bekker et al., 2009) and ultramafic sills,

gabbros, and tonalites from Nuvvuagittuq Greenstone Belt ($\Delta^{33}S$ = -0.03 to +0.18; Thomassot et al., 2015; Fig. 1c).

Granite sample SP-16-22 is an outlier, displaying negative and heterogeneous *in-situ* $\delta^{34}S$ (0 to -16‰). This sample is from part of the GLB characterized by abundant metasedimentary inclusions (Fig. 2a,f). On a macroscopic level this indicates significant heterogeneity in the granite and also, potentially, incomplete homogenization of the sulfur between the metasedimentary rocks and granitic melt. During assimilation of metasedimentary host rock, the metasedimentary sulfides break down upon heating and release H_2S (Eq. 3 & 4). (H_2S – as opposed to SO_2 – would be the dominant gas phase under the low f_{O_2} of formation of the GLB; Bucholz et al., 2018; Ohmoto, 1972; Poulson and Ohmoto, 1989). H_2S is transferred from the fluid to the melt through the following reaction:

$$H_2S_f + O^{2-}_{melt} = H_2O_f + S^{2-}_{melt} \qquad \text{(Eq. 7)}$$

At oxygen fugacities near the graphite-CO buffer characteristic for the GLB (Bucholz et al., 2018) sulfide (S^{2-}) in a hydrous melt may be complexed as either SH^-, H_2S, or FeS (*e.g.,* Klimm et al., 2012). The low, heterogeneous $\delta^{34}S$ values in SP-16-22 as compared to the other granites is likely due to fractionation between H_2S_{fluid} and reduced sulfur species in the melt. Although not constrained for rhyolitic melts at low (<900ºC) temperatures, existing experimental data suggests that $\alpha(H_2S_{fluid} - S^{2-}{}_{melt})$ is >1 for basalt and andesite at 1030-1050ºC (summarized in Fiege et al., 2015). Therefore, the $\delta^{34}S$ of the fluid phase will be higher than the sulfur dissolved in the melt. Figure 6b shows the $\delta^{34}S$ fractionation between H_2S_{fluid} and $S^{2-}{}_{melt}$ using empirical fractionation factors of Fiege et al. (2015) (their Eq. 8) for basaltic and andesitic

melts extrapolated to 650-900ºC. The $\delta^{34}S$ fractionation between H_2S_{fluid} and S^{2-}_{melt} at 1030ºC is 4.6-5.0‰ and will increase at lower temperatures (Fiege et al., 2015). These calculations demonstrate that H_2S in the fluid may be 5-10‰ heavier than S^{2-} in the melt over the temperature range expected for the crystallization of a hydrous granitic melt. Therefore, the isotopically light and heterogeneous nature of the sulfides may be the result of incomplete homogenization between isotopically light H_2S derived from pyrite decomposition in the metasedimentary inclusions and the granitic melt prior to solidification. S^{2-} diffusion in hydrous (7 wt.% H_2O) rhyolitic melts is several orders of magnitude slower than other volatile species (Baker and Rutherford, 1996), which would serve to preserve sulfur isotopic heterogeneity in a melt during assimilation. For example, at 800ºC sulfur requires ~10^3 years to equilibrate over 10 cm in a hydrous rhyolitic melt (using diffusivities of Baker and Rutherford, 1996). Notably, diffusion induced fractionation of ^{34}S and ^{32}S is minimal in basaltic melts (*i.e.*, the diffusivities of ^{34}S and ^{32}S are similar; Fortin et al., 2019) and, if we assume that this finding can be applied for high-silica melts, the intrasample $\delta^{34}S$ variability in sulfides is likely not due to diffusive fractionation.

5.4 SPGs as a record of the bulk siliciclastic Archean sedimentary sulfur reservoir

This work demonstrates that the sulfur isotopic composition of SPGs mirrors the $\delta^{34}S$ of their high-grade metasedimentary source rocks (within ~1‰) and is similar to that of low grade source rocks, shifted at most +2-3‰ (Fig. 5). Prograde pyrite breakdown results in residual sulfide in metasedimentary rocks that have higher $\delta^{34}S$ than the original pyrite. This elevated $\delta^{34}S$ is then transferred to the granitic melts during partial melting. Although heterogeneous and low $\delta^{34}S$ in one granitic sample suggests inefficient homogenization of sulfur may occur, most pyrite from the granites display homogeneous values in agreement with bulk sulfide $\delta^{34}S$ via

IRMS. Thus, $\delta^{34}S$ of SPGs should broadly reflect that of their source sediments and inhomogeneity can be screened for through in-situ analyses of sulfides.

Second, small (tenths of ‰) positive $\Delta^{33}S$ observed in the metasedimentary rocks are also observed in the GLB granites, suggesting the transfer and preservation of S-MIF through metamorphism and partial melting. As a cautionary note, however, the absence of S-MIF in igneous rocks does not preclude assimilation of Archean sedimentary material (although this has been previously implied, *c.f.* LaFlamme et al. 2018; Smit et al. 2019). This can arise in several instances: (1) The majority of Archean sedimentary sulfides do not preserve significant S-MIF (Fig. 1a,b) and therefore partial melting or assimilation of these sources would not result in S-MIF in magmatic products; (2) The partial melting/assimilation of a sedimentary rock package with both positive and negative $\Delta^{33}S$ could result in a bulk $\Delta^{33}S$ of 0 in the melt; and (3) Dilution by external non-MIF-bearing sulfur could obscure S-MIF imparted to the magmas by sedimentary assimilation.

Our observations demonstrate that Archean SPGs provide a useful archive for understanding the Archean sulfur cycle. As Archean SPGs are generated under reducing conditions similar to that of the GLB (Bucholz et al., 2018), we suggest that the $\delta^{34}S$ and $\Delta^{33}S$ of Archean SPGs could provide an estimate of the bulk siliciclastic source rock from which they were derived. A survey of sulfur isotopes of global Archean SPGs (*c.f.* localities in Bucholz and Spencer, 2019) could provide an alternative archive to sedimentary rocks in that they average out small spatial heterogeneities often sampled in sedimentary studies. The SPG sulfur isotope record would be particularly useful in light of studies suggesting that Archean crust is not mass balanced in terms of sulfur with its bulk $\Delta^{33}S$ being skewed to positive values (Farquhar and Wing, 2003; Reinhard et al., 2013) instead of being similar to that of bulk Earth ($\Delta^{33}S = 0$;

476 Labidi et al., 2013). The idea that the Archean crust has a bulk composition $\Delta^{33}S > 0$ is based on
477 compilations of $\Delta^{33}S$ in Archean sedimentary rocks that are skewed towards positive values
478 (*e.g.*, Johnston et al., 2011). The complementary negative $\Delta^{33}S$ reservoir has been suggested to
479 be deeply subducted hydrothermally-altered oceanic crust that acquired its sulfur from the
480 oceanic sulfate reservoir (Cabral et al., 2013; Farquhar et al., 2002). In contrast, Torres et al.
481 (2018) analyzed multiple sulfur isotopes of surface and ground waters draining bedrock of the
482 Superior craton and found that these waters had an average sulfur isotopic composition
483 equivalent to that of the bulk Earth ($\Delta^{33}S \approx 0$) suggesting that on average the bulk Archean crust
484 was mass balanced. Similarly, SPGs would provide a more direct, integrated record of Archean
485 crustal sulfur over large volumes of supracrustal rocks, and could serve as an archive that isolates
486 the bulk Archean sedimentary reservoir, rather than a mixture of igneous (*i.e.*, mafic volcanic
487 rocks and granitoids) and sedimentary rocks that define Archean terranes.
488
489 *5.5 Implications for using sulfur isotopes as a tracer of Archean sedimentary material in the*
490 *mantle*
491 One of the most exciting recent applications of sulfur isotopes in the igneous record is the
492 identification of S-MIF in mantle-derived igneous rocks: sulfides from some ocean island basalts
493 (Cabral et al., 2013; Delavault et al., 2016; green dots in Fig. 1c) and diamonds (Farquhar et al.,
494 2002; Cartigny et al., 2009; Thomassot et al., 2009; Smit et al. 2019; red dots in Fig. 1c), as well
495 as in bulk-rock analyses of Proterozoic plutonic rocks (Selvaraja et al., 2017; LaFlamme et al.,
496 2018; blue dots in Fig. 1c). These observations have been interpretted to suggest that sulfur
497 processed through the Archean atmosphere was transferred into the deep Earth through
498 subduction. Our specific case study interrogates the transfer of sedimentary sulfur to the igneous

499 rock record (*i.e.*, through direct partial melting of Archean sedimentary rocks to produce SPGs)
500 to understand this process in its most fundamental form. We demonstrate that during
501 metamorphism and partial melting within the upper crust, reduced Archean metasedimentary
502 rocks and their derivative granites should preserve (within a few ‰) the original $\delta^{34}S$ and $\Delta^{33}S$
503 of their protoliths if not modified by an external sulfur source.
504 Assuming subduction (or a variant of it) operated in the Archean, subducted altered
505 oceanic crust and sediments would have been relatively reduced as compared to present day
506 (*e.g.*, Evans, 2012; Stolper and Bucholz, 2019) and the main reservoir of sulfur in subducting
507 slabs would be pyrite in sediments or volcanogenic deposits and magmatic pyrrhotite in mid-
508 ocean ridge basalts (or gabbros). Thus, sulfur transfer to the mantle wedge would occur through
509 pyrite/pyrrhotite decomposition and H_2S release (Jégo and Dasgupta, 2013). As this process
510 results in relatively little fractionation (at most a few per mil) at elevated temperatures (>200ºC,
511 see section 5.2), subduction of Archean sedimentary (and igneous) sulfides which have $\delta^{34}S$ at or
512 near 0‰ (Fig. 1b) should result in release of H_2S in the mantle wedge with a similar value.
513 Residual sulfides that were then deeply subducted would have a similar to slightly heavier $\delta^{34}S$.
514 Our study also suggests that S-MIF (if initially present) should be preserved during
515 devolatilization and partial melting as long as it is not diluted by an external source of sulfur.
516 Although some studies have suggested that subducted Archean slabs would carry a negative
517 $\Delta^{33}S$ signature due to sulfate incorporation (*e.g.,* Cabral et al., 2013; Delavault et al., 2016),
518 sulfate concentrations in the Archean ocean were low (<200 μmol) (Canfield and Farquhar,
519 2009) and consequently sulfur concentrations in hydrothermally altered oceanic crust derived
520 from oceanic sulfate were also low. Alternatively, in situations where pyrite-bearing sediment

fluxes to subduction zones were low, Archean arc magmas or slab melts may have had sulfur isotopic compositions similar to that of the mantle ($\delta^{34}S \approx -1$; $\Delta^{33}S = 0$; Labidi et al., 2013).

Therefore, Archean subduction likely transferred distinct sulfur isotopic and redox signatures to arc-related magmas as compared to modern day. In the Archean, primitive arc basalts or slab melts were likely relatively reduced (*i.e.,* similar to mid-ocean ridge basalts (MORB) or potentially more reduced; Stolper and Bucholz, 2019) and characterized by $\delta^{34}S$ near 0 and possibly non-zero $\Delta^{33}S$. In contrast, present day arc basalts are generally oxidized compared to MORB due to subduction of Fe^{3+}- and sulfate-bearing sediments and hydrothermally altered oceanic crust (*c.f.*, Evans, 2012) and have variable, though generally positive $\delta^{34}S$ (and $\Delta^{33}S = 0$). Although it is beyond the scope of this paper to fully discuss modern day sulfur cycling in subduction zones, the positive $\delta^{34}S$ have been interpreted as evidence of sulfur transfer to the mantle wedge through subduction of sulfur derived from the oceanic sulfate pool (*c.f.*, Wallace and Edmonds, 2011). In addition, sulfur isotope fractionation during sulfide/sulfate metamorphism and fluid release in modern subducting slabs is potentially more significant (as compared to reduced slabs in the Archean) due to the present of multiple sulfur redox species in minerals and fluids (Walters et al., 2019; Li et al., 2020).

6. Conclusions

We demonstrate that during metamorphism and partial melting, reduced Archean metasedimentary rocks and their derivative granites should closely retain the original sulfur isotope composition of their protoliths if not modified by an external sulfur source. $\delta^{34}S$ values from the GLB and surrounding metasedimentary rock, as well as modeling results indicate that prograde metamorphic pyrite desulfidation reactions can drive residual pyrrhotite to isotopically

heavier values by at most 2-3‰ over a temperature range of 200-400ºC. Furthermore, the $\delta^{34}S$ values of pyrite from SPGs of the GLB closely resemble that of pyrrhotite in their high-grade metasedimentary source rocks. One exception to this is a granite sample demonstrating intra-sample pyrite sulfur isotope disequilibrium likely resulting from incomplete homogenization between sulfur derived from a metasedimentary-derived fluid and granitic melt.

Sulfides from both the granites and the metasedimentary rocks preserve similar, non-zero $\Delta^{33}S$ values. Notably, however, $\Delta^{33}S$ values are within several tenths of a permil of 0 and only identifiable with high-precision IRMS analyses. Importantly, however, the absence of S-MIF in igneous rocks does not exclude the assimilation of Archean sedimentary material. Igneous rocks without S-MIF, but with Archean surface-derived sulfur could form through a variety of non-exclusive processes: (1) assimilation or partial melting of Archean sulfur with $\Delta^{33}S$=0; (2) partial melting/assimilation of sulfur with a bulk $\Delta^{33}S$ of 0; and (3) dilution by external sulfur with zero $\Delta^{33}S$.

SPGs are a potential archive of the bulk sulfur isotopic composition of Archean silicilastic sedimentary rocks averaged over large volumes. Further, mass transfer of sulfur from the sedimentary to igneous rock record explored here is likely applicable to subduction scenarios. In the Archean sulfur transfer from the slab to the mantle wedge would occur through pyrite/pyrrhotite decomposition and H_2S release. As this process results in relatively small fractionation (at most a few per mil) at elevated temperatures, subduction of Archean sedimentary (and igneous) sulfides which have $\delta^{34}S$ at or near 0‰ should result in release of sulfur in the mantle wedge with a similar value. S-MIF (if initially present in the subducted Archean surface material) should be preserved during this process as long as it is not diluted by external sulfur (*e.g.*, from the mantle).

Acknowledgements

We thank Madeline Lewis and Allyson Trussell for help collecting samples, Yunbin Guan for assistance with SIMS analyses, and Gareth Izon for assistance with the IRMS analyses. C. Bucholz thanks Fred Breaks for spending time in the field introducing her to the Ghost Lake batholith, John Eiler for discussion of sulfur isotope analyses via SIMS, and Doug Crowe and Woody Fischer for generously providing sulfide standard materials. This work was supported by NSF grant EAR-1943629 awarded to C. Bucholz. We are grateful for the comments of two anonymous reviewers which help to clarify and improve the presentation of this work.

580 REFERENCES

581 Alirezaei, S., Cameron, E.M., 2001. Variations of sulfur isotopes in metamorphic rocks from Bamble
582 Sector, southern Norway: a laser probe study. Chemical Geology 181, 23–45. doi:10.1016/S0009-
583 2541(01)00266-2

584 Beaudry, P., Longpré, M.A., Economos, R., Wing, B.A., Bui, T.H. and Stix, J., 2018. Degassing-induced
585 fractionation of multiple sulphur isotopes unveils post-Archaean recycled oceanic crust signal in
586 hotspot lava. Nature Communications 9(1), 1-12.

587 Bekker, A., Barley, M.E., Fiorentini, M.L., Rouxel, O.J., Rumble, D., Beresford, S.W., 2009.
588 Atmospheric Sulfur in Archean Komatiite-Hosted Nickel Deposits. Science 326, 1086–1089.
589 doi:10.1126/science.1177742

590 Blackburn, C.E., Johns, G.W., Ayer, J.A., Davis, D.W., 1991. The Wabigoon Subprovince, in: Geology
591 of Ontario, The Wabigoon Subprovince. Geology of Ontario. Ontario Geological Survey, pp. 303–382.

592 Breaks, F.W., Moore, J.M., 1992. The Ghost Lake Batholith, Superior Province of Northwestern Ontario:
593 A Fertile, S-Type, Peraluminous Granite - Rare-Element Pegmatite System. Canadian Mineralogist 30,
594 835–875.

595 Bucholz, C.E., Spencer, C.J., 2019. Strongly Peraluminous Granites across the Archean–Proterozoic
596 Transition. Journal of Petrology 60, 1299–1348. doi:10.1093/petrology/egz033

597 Bucholz, C.E., Stolper, E.M., Eiler, J.M., Breaks, F.W., 2018. A Comparison of Oxygen Fugacities of
598 Strongly Peraluminous Granites across the Archean–Proterozoic Boundary. Journal of Petrology 59,
599 2123–2156. doi:10.1093/petrology/egy091

600 Cabral, R.A., Jackson, M.G., Rose-Koga, E.F., Koga, K.T., Whitehouse, M.J., Antonelli, M.A., Farquhar,
601 J., Day, J.M.D., Hauri, E.H., 2013. Anomalous sulphur isotopes in plume lavas reveal deep mantle
602 storage of Archaean crust. Nature 496, 490–493. doi:10.1038/nature12020

603 Canfield, D.E., 2004. The Early History of Atmospheric Oxygen. Annual Reviews in Earth and Planetary
604 Sciences, 33, 1–36. doi:10.1146/annurev.earth.33.092203.122711

605 Canfield, D.E., Farquhar, J., 2009. Animal evolution, bioturbation, and the sulfate concentration of the

oceans. PNAS 106, 8123–8127. doi:10.1073/pnas.0902037106

Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M., Berner, R.A., 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. Chem. Geol. 54, 149–155. https://doi.org/10.1016/0009-2541(86)90078-1.

Cartigny, P., Farquhar, J., Thomassot, E., Harris, J.W., Wing, B., Masterson, A., McKeegan, K. and Stachel, T., 2009. A mantle origin for Paleoarchean peridotitic diamonds from the Panda kimberlite, Slave Craton: evidence from ^{13}C-, ^{15}N-and ^{33},^{34}S-stable isotope systematics. *Lithos*, *112*, pp.852-864.

Craig, J.R. and Vokes, F.M., 1993. The metamorphism of pyrite and pyritic ores: an overview. Mineralogical Magazine, 57(386), 3-18.

Crowe, D.E., Vaughan, R.G., 1996. Characterization and use of isotopically homogeneous standards for in situ laser microprobe analysis of $^{34}S/^{32}S$ ratios. American Mineralogist 81, 187–193. doi:10.2138/am-1996-1-223

Cui, H., Kitajimai, K., Spicuzza, M.J., Fournelle, J.H., Ishida, A., Brown, P.E., Valley, J.W., 2018. Searching for the Great Oxidation Event in North America: A Reappraisal of the Huronian Supergroup by SIMS Sulfur Four-Isotope Analysis. Astrobiology 18, 519–538. doi:10.1089/ast.2017.1722

Delavault, H., Chauvel, C., Thomassot, E., Devey, C.W., Dazas, B., 2016. Sulfur and lead isotopic evidence of relic Archean sediments in the Pitcairn mantle plume. PNAS 113, 12952–12956. doi:10.1073/pnas.1523805113

Dottin III, J.W., Labidi, J., Lekic, V., Jackson, M.G. and Farquhar, J., 2020. Sulfur isotope characterization of primordial and recycled sources feeding the Samoan mantle plume. Earth and Planetary Science Letters 534, 116073.

Evans, K.A., 2012. The redox budget of subduction zones. Earth-Science Reviews 113, 11–32. doi:10.1016/j.earscirev.2012.03.003

Farquhar, J., Wing, B., 2003. Multiple sulfur isotopes and the evolution of the atmosphere. Earth and Planetary Science Letters 213, 1–13.

Farquhar, J., Wing, B.A., McKeegan, K.D., Harris, J.W., Cartigny, P., Thiemens, M.H., 2002. Mass-

632 Independent Sulfur of Inclusions in Diamond and Sulfur Recycling on Early Earth. Science 298,
633 2369–2372. doi:10.1126/science.1078617
634 Ferry, J.M., 1981. Petrology of graphitic sulfide-rich schists from south-central Maine: an example of
635 desulfidation during prograde regional metamorphism. American Mineralogist 66, 908–930.
636 Fiege, A., Holtz, F., Behrens, H., Mandeville, C.W., Shimizu, N., Crede, L.S., Göttlicher, J., 2015.
637 Experimental investigation of the S and S-isotope distribution between H_2O–S ± Cl fluids and basaltic
638 melts during decompression. Chemical Geology 393-394, 36–54. doi:10.1016/j.chemgeo.2014.11.012
639 Fischer, W.W., Fike, D.A., Johnson, J.E., Raub, T.D., Guan, Y., Kirschvink, J.L. and Eiler, J.M., 2014.
640 SQUID–SIMS is a useful approach to uncover primary signals in the Archean sulfur
641 cycle. Proceedings of the National Academy of Sciences 111(15), 5468-5473.
642 Fortin, M.A., Watson, E.B., Stern, R.A. and Ono, S., 2019. Experimental characterization of diffusive and
643 Soret isotopic fractionation of sulfur in a reduced, anhydrous basaltic melt. Chemical Geology 510, 10-
644 17.
645 Halevy, I., Johnston, D.T. and Schrag, D.P., 2010. Explaining the structure of the Archean mass-
646 independent sulfur isotope record. Science 329(5988), 204-207.
647 Hall, A.J., Boyce, A.J., Fallick, A.E., 1988. A Sulphur Isotope Study of Iron Sulphides in the Late
648 Precambrian Dalradian Easdale Slate Formation, Argyll, Scotland. Mineral. Mag. 52, 483–490.
649 doi:10.1180/minmag.1988.052.367.06
650 Holdaway, M.J., 2000. Application of new experimental and garnet Margules data to the garnet-biotite
651 geothermometer. American Mineralogist 85, 881–892. doi:10.2138/am-2000-0701
652 Holtz, F., Johannes, W., Pichavant, M., 1992. Effect of excess aluminium on phase relations in the system
653 Qz-Ab-Or: experimental investigation at 2 kbar and reduced H_2O-activity. Eur.J.Mineral. 4, 137–152.
654 Ishihara, S., Sasaki, A., 1989. Sulfur isotopic ratios of the magnetite-series and ilmenite-series granitoids
655 of the Sierra Nevada batholith—A reconnaissance study. Geology 17, 788–791. doi:10.1130/0091-
656 7613(1989)017<0788:SIROTM>2.3.CO;2

Jégo, S., Dasgupta, R., 2013. Fluid-present melting of sulfide-bearing ocean-crust: Experimental constraints on the transport of sulfur from subducting slab to mantle wedge. Geochimica et Cosmochimica Acta 110, 106–134. doi:10.1016/j.gca.2013.02.011

Johnston, D.T., 2011. Multiple sulfur isotopes and the evolution of Earth's surface sulfur cycle. Earth Science Reviews 106(1-2), 161-183.

Kajiwara, Y., Sasaki, A., Matsubara, O., 1981. Kinetic sulfur isotope effects in the thermal decomposition of pyrite. Geochem. J. 15, 193–197. doi:10.2343/geochemj.15.193

Klimm, K., Kohn, S.C., Botcharnikov, R.E., 2012. The dissolution mechanism of sulphur in hydrous silicate melts. II: Solubility and speciation of sulphur in hydrous silicate melts as a function of fO2. Chemical Geology 322-323, 250–267. doi:10.1016/j.chemgeo.2012.04.028

Kozdon, R., Kita, N.T., Huberty, J.M., Fournelle, J.H., Johnson, C.A., Valley, J.W., 2010. In situ sulfur isotope analysis of sulfide minerals by SIMS: Precision and accuracy, with application to thermometry of ~ 3.5 Ga Pilbara cherts. Chemical Geology 275, 243–253. doi:10.1016/j.chemgeo.2010.05.015

Labidi, J., Cartigny, P., Moreira, M., 2013. Non-chondritic sulphur isotope composition of the terrestrial mantle. Nature 501, 208–211. doi:10.1038/nature12490

Labidi, J., Cartigny, P. and Jackson, M.G., 2015. Multiple sulfur isotope composition of oxidized Samoan melts and the implications of a sulfur isotope 'mantle array'in chemical geodynamics. Earth and Planetary Science Letters 417, 28-39.

LaFlamme, C., Fiorentini, M.L., Lindsay, M., Bui, T.H., 2018. Atmospheric sulfur is recycled to the crystalline continental crust during supercontinent formation. Nature Communications 9, 4380.

Li, J.L., Schwarzenbach, E.M., John, T., Ague, J.J., Huang, F., Gao, J., Klemd, R., Whitehouse, M.J. and Wang, X.S., 2020. Uncovering and quantifying the subduction zone sulfur cycle from the slab perspective. Nature Communications 11(1), 1-12.

Magalhães, N., Penniston-Dorland, S., Farquhar, J. and Mathez, E.A., 2018. Variable sulfur isotope composition of sulfides provide evidence for multiple sources of contamination in the Rustenburg Layered Suite, Bushveld Complex. Earth and Planetary Science Letters 492, 163-173.

683 Magalhães, N., Farquhar, J., Bybee, G., Penniston-Dorland, S., Rumble III, D., Kinnaird, J. and
684 McCreesh, M., 2019. Multiple sulfur isotopes reveal a possible non-crustal source of sulfur for the
685 Bushveld Province, southern Africa. Geology 47(10), 982-986.
686 Ohmoto, H., Goldhaber, M.B., 1997. Isotopes of sulfur and carbon, in: Barnes, H.L. (Ed.), Geochemistry
687 of Hydrothermal Ore Deposits. John Wiley & Sons, pp. 491–559.
688 Oliver, N.H.S., Hoering, T.C., Johnson, T.W., Rumble, D., III, Shanks, W.C., III, 1992. Sulfur isotopic
689 disequilibrium and fluid-rock interaction during metamorphism of sulfidic black shales from the
690 Waterville-Augusta area, Maine, USA. Geochimica et Cosmochimica Acta 56, 4257–4265.
691 doi:10.1016/0016-7037(92)90266-L
692 Ono, S., 2017. Photochemistry of sulfur dioxide and the origin of mass-independent isotope fractionation
693 in Earth's atmosphere. Annual Reviews of Earth and Planetary Sciences 45, 301–329.
694 doi:10.1146/annurev-earth-060115-012324
695 Ono, S., Wing, B., Johnston, D., Farquhar, J. and Rumble, D., 2006. Mass-dependent fractionation of
696 quadruple stable sulfur isotope system as a new tracer of sulfur biogeochemical cycles. *Geochimica et*
697 *Cosmochimica Acta*, *70*(9), pp.2238-2252.
698 Ono, S., Keller, N.S., Rouxel, O., Alt, J.C., 2012. Sulfur-33 constraints on the origin of secondary pyrite
699 in altered oceanic basement. Geochim. Cosmochim. Acta 87, 323–340.
700 https://doi.org/10.1016/j.gca.2012.04.016
701 Penniston-Dorland, S.C., Wing, B.A., Nex, P.A., Kinnaird, J.A., Farquhar, J., Brown, M. and Sharman,
702 E.R., 2008. Multiple sulfur isotopes reveal a magmatic origin for the Platreef platinum group element
703 deposit, Bushveld Complex, South Africa. Geology 36(12), 979-982.
704 Penniston-Dorland, S.C., Mathez, E.A., Wing, B.A., Farquhar, J. and Kinnaird, J.A., 2012. Multiple
705 sulfur isotope evidence for surface-derived sulfur in the Bushveld Complex. Earth and Planetary
706 Science Letters 337, 236-242.
707 Poulson, S.R., Ohmoto, H., 1989. Devolatilization equilibria in graphite-pyrite-pyrrhotite bearing pelites
708 with application to magma-pelite interaction. Contrib Mineral Petrol 101, 418–425.

doi:10.1007/BF00372215

Reinhard, C.T., Planavsky, N.J., Lyons, T.W., 2013. Long-term sedimentary recycling of rare sulphur isotope anomalies. Nature 497, 100–103. doi:10.1038/nature12021

Rumble, D., 1982. Stable isotope fractionation during metamorphic devolatilization reactions. Reviews in Mineralogy and Geochemistry 10(1), 327-353.

Selvaraja, V., Fiorentini, M.L., LaFlamme, C.K., Wing, B.A. and Bui, T.H., 2017. Anomalous sulfur isotopes trace volatile pathways in magmatic arcs. Geology 45(5), 419-422.

Smit, K.V., Shirey, S.B., Hauri, E.H., Stern, R.A., 2019. Sulfur isotopes in diamonds reveal differences in continent construction. Science 364, 383–385. doi:10.1126/science.aaw9548

Stolper, D.A., Bucholz, C.E., 2019. Neoproterozoic to early Phanerozoic rise in island arc redox state due to deep ocean oxygenation and increased marine sulfate levels. PNAS 116, 8746–8755. doi:10.1073/pnas.1821847116

Syverson, D.D., Ono, S., Shanks, W.C. and Seyfried Jr, W.E., 2015. Multiple sulfur isotope fractionation and mass transfer processes during pyrite precipitation and recrystallization: an experimental study at 300 and 350ºC. Geochimica et Cosmochimica Acta 165, 418-434.

Thomassot, E., Cartigny, P., Harris, J.W., Lorand, J.P., Rollion-Bard, C., Chaussidon, M., 2009. Metasomatic diamond growth: A multi-isotope study (^{13}C, ^{15}N, ^{33}S, ^{34}S) of sulphide inclusions and their host diamonds from Jwaneng (Botswana). Earth and Planetary Science Letters 282, 79–90. doi:10.1016/j.epsl.2009.03.001

Thomassot, E., O'Neil, J., Francis, D., Cartigny, P. and Wing, B.A., 2015. Atmospheric record in the Hadean Eon from multiple sulfur isotope measurements in Nuvvuagittuq Greenstone Belt (Nunavik, Quebec). Proceedings of the National Academy of Sciences 112(3), 707-712.

Thompson, A.B., Tracy, R.J., 1979. Model systems for anatexis of pelitic rocks: II. Facies Series Melting and Reaction in the System CaO-$KAlO_2$-$NaAlO_2$-Al_2O_3-SiO_2-H_2O Contrib Mineral Petrol 70: 429-438.

Tomkins, A.G., 2010. Windows of metamorphic sulfur liberation in the crust: Implications for gold

deposit genesis. Geochimica et Cosmochimica Acta 74, 3246–3259. doi:10.1016/j.gca.2010.03.003

Torres, M.A., Paris, G., Adkins, J.F., Fischer, W.W., 2018. Riverine evidence for isotopic mass balance in the Earth's early sulfur cycle. Nature Geosciences 11, 661–664. doi:10.1038/s41561-018-0184-7

Toulmin, P., III, Barton, P.B., Jr., 1964. A thermodynamic study of pyrite and pyrrhotite. Geochimica et Cosmochimica Acta 28, 641–671. doi:10.1016/0016-7037(64)90083-3

Wagner, T., Boyce, A.J., 2006. Pyrite metamorphism in the Devonian Hunsrück slate of Germany: Insights from laser microprobe sulfur isotope analysis and thermodynamic modeling. American Journal of Science 306, 525–552.

Wallace, P.J. and Edmonds, M., 2011. The sulfur budget in magmas: evidence from melt inclusions, submarine glasses, and volcanic gas emissions. Reviews in Mineralogy and Geochemistry, 73(1), 215-246.

Walters, J.B., Cruz-Uribe, A.M. and Marschall, H.R., 2019. Isotopic compositions of sulfides in exhumed high-pressure terranes: implications for sulfur cycling in subduction zones. Geochemistry, Geophysics, Geosystems *20*(7), 3347-3374.

752 **FIGURE CAPTIONS**

753

754 **Figure 1**: Comparison of triple S isotope data of this study with sedimentary and selected igneous studies.
755 A) $\Delta^{33}S$ versus $\delta^{34}S$ for Archean sedimentary sulfides (compilation of Johnston (2011). B)
756 Histograms of $\delta^{34}S$ (left panel) and $\Delta^{33}S$ (right panel) for same compilation shown in A. C) $\Delta^{33}S$
757 versus $\delta^{34}S$ for sulfides from various studies including: Archean komatiite-hosted Fe-Ni sulfide
758 deposits (Bekker et al., 2009); meta-igneous ultramafic, gabbroic, and tonalitic rocks (Thomassot et
759 al., 2015); bulk-rock data for Proterozoic (~1620-1820 Ma) Moorarie and Durlacher Supersuites
760 (plutonic rocks) from the Capricorn orogen in Australia (LaFlamme et al., 2018); pegmatites and
761 tonalites from the Glenburgh arc (2.0 Ga), Australia (Selvaraja et al., 2017); range of bulk-rock and
762 sulfide data from the 2.06 Ga Bushveld Complex (blue field; Penniston-Dorland et al., 2008; 2012;
763 Magaelhães et al., 2018; 2019); sulfide inclusions in diamonds (Farquhar et al., 2002; Cartigny et al.,
764 2009; Thomassot et al., 2009; Smit et al., 2019); sulfide inclusions in olivines, clinopyroxene, or
765 spinel from ocean island basalts (Cabral et al., 2013; Delevault et al., 2016; Beaudry et al., 2018);
766 bulk-rock data for OIBs and hot spots (Labidi et al., 2013; 2015; Dottin et al., 2020). Depleted MORB
767 end-member is from Labidi et al. (2013). The method of analysis is given in legend – SIMS or IRMS.
768 Error bars were omitted for clarity, but vary widely by study and analysis type and the reader is
769 referred to the original references for more detail. Broadly, however, reported SIMS measurements
770 have 2σ $\delta^{34}S$ uncertainties from tenths to >1‰ and 2σ $\Delta^{33}S$ uncertainties of 0.1-0.4‰. Corresponding
771 values for IRMS measurements are several 0.1-0.6‰ and <0.01 to 0.09‰, respectively.

772

773 **Figure 2**: (A) Geologic map of the Ghost Lake batholith (GLB) modified from Breaks and Moore, 1992.
774 Sample prefixes of "SP-" are omitted for clarity. Hatched area indicates inclusion rich zone of
775 batholith. Unit GLB-8 described in text is not shown as it comprises 3-8 cm pegmatitic dikes. (B-F)
776 field photos from the GLB. Hammer head is 13.5 cm long. Locations where photos were taken are
777 shown as yellow stars in (A). (B) cm-scale cordierite porphyroblasts aligned along foliation from

metapelite above the andalusite isograd (photo location: N49º45'55.6" W093º06'46.9") (C) metapelite and metagraywacke beds above the andalusite isograd. Andalusite porphyroblasts occur in the metapelites, but not in the metagreywackes (photo location: N49º46'49.8" W092º49'46.1"). Sharpie is 14 cm long. (D) Biotite+plagioclase+quartz gneiss with fine-grained leucosomes above sillimanite-K-feldspar isograd (photo location: N49º48'54.9", W093º09'34.6") (E) biotite-rich metapelite with nebulous boundary with pegmatitic granite (photo location: N49º50'50.9", W092º41'31.0") (F) coarse-grained biotite-muscovite granite with biotite-rich metapelitic inclusion and late-stage tourmaline-bearing dikes (photo location: N49º48'53.7", W092º57'04.7")

Figure 3: Photomicrographs of A) pyrrhotite (po) and chalcopyrite (ccp) in sample SP-18-11 a metagreywacke from the sillimanite-K-feldspar isograd and B) pyrite in sample E19-8 a biotite+muscovite granite. Images are reflected light and red circle highlight sulfides.

Figure 4: Pressure-temperature conditions of metamorphism for the Zealand metasedimentary unit. Isograds shown in different colors. The granite solidi are from Holtz et al. (1992). The pyrophyllite dehydration reaction is from Kerrick (1968) and the muscovite dehydration reaction is from Thompson and Tracy (1979). Mineral abbreviations: AS = aluminosilicate, Kfs = K-feldspar, Ky = kyanite, Mu = muscovite, Pl = plagioclase, Prl = pyrophyllite, Q = quartz, Sil = sillimanite, f = fluid.

Figure 5: Histograms of $\delta^{34}S$ (‰) of sulfides from biotite-chlorite (A), andalusite (B), garnet (C), and K-feldspar—sillimanite (D) grade metamorphic rocks and peraluminous granite samples (E). Histograms show $\delta^{34}S$ values obtained via SIMS. (Note: only samples for which SIMS data could be confidently corrected to a matrix matched standards are shown.) Colored horizontal bars show average plus one standard deviation in $\delta^{34}S$ values for specific samples. Circles show $\delta^{34}S$ values obtained via IRMS for seven samples.

Figure 6: A) $\Delta^{33}S$ versus $\delta^{34}S$ of pyrite from peraluminous granites. Grey symbols indicate SIMS values (with 1σ) and black symbols indicate IRMS values. B) Calculated fractionation between H_2S in a fluid and S^{2-} in a melt based on rhyolite fractionation factors given in Fiege et al. (2015) over the range of 650-900ºC. For example, an H_2S-bearing fluid with a $\delta^{34}S$ value of 0‰ will be in equilibrium with S^{2-} in a rhyolitic melt with a $\delta^{34}S$ value of approximately -10‰ at 650ºC.

Figure 7: Comparison of $\delta^{34}S$ (A) and $\Delta^{33}S$ (B) obtained via SIMS and IRMS. For SIMS values, sample average value is shown with 1σ standard deviation on average.

Figure 8: Results of Rayleigh fractionation modeling for $\delta^{34}S$ during pyrite desulfidation (Eq. 8). Calculated for 200, 300, and 400 ºC (left to right panels). Fractionation factors from Ohmoto and Goldhaber (1997). Initial pyrite value (red line) at -1.4‰ is based on lower limit observed in chlorite-grade samples. Shifting the initial pyrite value to a higher value would shift modeled curves upwards by an equal amount. Gray bar indicates the range of $\delta^{34}S$ of sulfides (as obtained via IRMS) observed in garnet- and K-feldspar-sillimanite grade metasedimentary rocks.