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1 **Influence of high marine Ca/SO<sub>4</sub> ratio on alteration of submarine basalts at**  
2 **2.41 Ga documented by triple O and Sr isotopes of epidote**

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43 **ABSTRACT**

44 Over the course of Earth's history, marine sulfate concentrations have been increasing in response  
45 to long-term atmospheric oxygenation. In contrast to modern oceans, where abundant sulfate  
46 precipitates in hot oceanic crust as anhydrite, Precambrian oceans contained much less (~0-10  
47 mM) sulfate, so that submarine hydrothermal systems were comparatively poor in anhydrite. As a  
48 step towards exploring the role of chemical evolution of seawater solutes, we investigate the  
49 reaction between basalt and seawater that took place at the ca. 2.43-2.41 Ga Vetreny Belt (Karelia  
50 craton, NW Russia) using fluid inclusion and multi-isotope measurements complemented by  
51 reactive transport and static aqueous-mineral equilibrium calculations. Using fluid inclusion  
52 measurements by LA-ICP-MS, we constrain the Sr concentration in the least modified fluids at  
53 the and address the effect of phase separation. Then, we complement the previous  $\delta^{18}\text{O} - \Delta^{17}\text{O}$   
54 datasets with new  $^{87}\text{Sr}/^{86}\text{Sr}$  measurements performed on ancient epidote from the Vetreny Belt and  
55 modern (0-6 Ma) oceanic epidote from Reykjanes, Iceland and the drilling site 504B in the eastern  
56 Pacific Ocean. The ancient epidote with  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$  of 0.7029-0.7041 and  $\Delta^{17}\text{O}$  of -0.06 to 0.00  
57 ‰ is best explained by a relatively high fraction (~90%) of marine Sr that was delivered from  
58 contemporaneous seawater without significant removal by early anhydrite. Using Monte-Carlo  
59 simulation of a dual-porosity model, we constrain the range of possible exchange trajectories based  
60 on the variability of physical parameters (porosity, fluid flow velocity, fracture spacing,  
61 recrystallization rates). Further, we use a series of static equilibrium seawater-basalt reaction  
62 calculations with emphasis on the possible range of Ca/SO<sub>4</sub> values at 2.41 Ga. Our calculations  
63 demonstrate that co-existing quartz and epidote in absence of feldspars represent equilibrium with  
64 less-evolved hydrothermal fluids. Consequently, equilibrium assemblage of quartz and epidote  
65 provide an insightful archive for marine Sr. High Ca/SO<sub>4</sub> ratio of seawater (>>1) and low  
66 concentration of anhydrite in submarine systems of the contemporaneous oceans promote a higher  
67 fraction of seawater Sr to be permanently stored in silicates of altered oceanic crust, while modern  
68 altered oceanic crust is depleted in radiogenic Sr due to partitioning into anhydrite, which partly  
69 returns into the ocean upon cooling.

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71 Keywords: triple oxygen isotopes, marine sulfate, altered oceanic crust, epidote, mineral-  
72 aqueous equilibrium modeling

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## 79 1. INTRODUCTION

80 Over time scales exceeding 10 Ma, the composition of the Earth's oceans is modulated  
81 by delivery and removal of major elements. Driven by exchange reactions with oceanic crust,  
82 hydrothermal circulation of seawater serves both as a sink and a source in budgets of many  
83 major elements. The composition of exchanged fluids released at submarine vents (i.e. black  
84 smokers) is considered to be rock-buffered with limited influence of seawater dissolved load  
85 (e.g. Berndt et al. 1989). However, the long-term changes of seawater concentrations driven by  
86 other factors such as continental weathering can modify the pathways that marine elements  
87 undergo during reactive transport within oceanic crust (Kump and Seyfried, 2005; Antonelli et  
88 al., 2017). In turn, the chemical signature acquired by altered oceanic crust is translated into the  
89 composition of fluids released at subduction zones. On billion-year timescale, one of the most  
90 prominent changes that affected seawater composition is the rise of sulfate. The overall rise of  
91 atmospheric  $pO_2$  levels over geological time promoted an increase in oxidized marine species,  
92 particularly sulfate, which is intimately tied to the increasing oxidative capacity of terrestrial  
93 sulfide weathering (Holland, 1984; Canfield, 1998; Farquhar and Wing, 2003; Kah et al., 2004).

94 While chemical transfer between seawater and mid-ocean ridge basalts establishes a first-  
95 order control on the composition of the terrestrial ocean, the effect of secular rise of marine  
96 sulfate on alteration of oceanic crust is still poorly understood. In this contribution we focus on  
97 the effect of anhydrite precipitation during reactive circulation of seawater within hot oceanic  
98 crust. The high sulfate concentration of modern seawater causes precipitation of anhydrite  
99 ( $CaSO_4$ ) during early stages of seawater-basalt reactions, distributing seawater-derived Ca and S  
100 in the upper section of altered oceanic crust (Fig. 1; Mills et al., 1998; Teagle et al., 1998).  
101 Consequently, the fluids that reach high-temperature alteration zones of oceanic crust are  
102 depleted in marine sources of these elements.

103 Strontium is an element geochemically similar to Ca and is commonly found in anhydrite  
104 in trace amounts (e.g. Teagle et al., 1998). Thus, the origin of elements incorporated in the

105 budgets of hydrothermal fluids and altered oceanic crust can be traced by Sr isotope  
106 compositions that ranges from  $^{87}\text{Sr}/^{86}\text{Sr}$ -enriched modern seawater ( $^{87}\text{Sr}/^{86}\text{Sr} = \sim 0.7092$ ) to  $^{87}\text{Sr}$ -  
107 depleted modern oceanic basalts ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.702\text{-}0.703$ ). This Sr isotope distinction is  
108 commonly used to trace seawater-derived fluxes based on measurements of submarine vent  
109 fluids and altered rocks (e.g. Bickle and Teagle 1992; Alexander et al. 1993; Gillis et al. 2005;  
110 Turchyn et al. 2013). In addition, the  $^{87}\text{Sr}/^{86}\text{Sr}$  measured in epidote has also been used to  
111 indirectly trace saturation of fluids with anhydrite (Antonelli et al., 2017). For context, the  
112 marine Ca and  $\text{SO}_4$  concentration estimates and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of marine carbonates are  
113 shown in Fig. 2.

114 This idea of feedbacks between marine Ca,  $\text{SO}_4$  and Sr concentrations has been explored  
115 previously for the Phanerozoic seawater using the submarine hydrothermal record (Coogan,  
116 2009; Turchyn et al., 2013; Antonelli et al., 2017) for which both  $^{87}\text{Sr}/^{86}\text{Sr}$  of seawater and major  
117 element solute concentrations are reconstructed. In particular, Antonelli et al. (2017) highlighted  
118 that the evolving marine Ca/ $\text{SO}_4$  ratio governs the amount of marine Sr incorporated into  
119 anhydrite vs. silicates in the oceanic crust using the  $^{87}\text{Sr}/^{86}\text{Sr}$  of oceanic epidotes (see Figs. 1 and  
120 2). Similar to the present study, Turchyn et al. (2013) combined O and Sr isotope measurements  
121 from Cambrian, Ordovician and Cretaceous ophiolites, pointing out that the elevated  $^{87}\text{Sr}/^{86}\text{Sr}$   
122 values of epidotes formed when marine sulfate was around 10 mM, much lower than  
123 contemporaneous marine Ca concentrations. It is important to note that anhydrite itself is rarely  
124 preserved in relicts of ancient oceanic crust due to its high solubility in cold water (<150 °C).  
125 Thus, the high-temperature Sr-bearing silicates can be informative of the marine  $\text{SO}_4$  and Ca  
126 concentrations. Compared to the Phanerozoic, it is obvious that in the Precambrian, before the  
127 first appearance of evaporitic sulfates at  $\sim 2.4\text{-}2.3$  Ga (Schröder et al., 2008), low-sulfate seawater  
128 would result in anhydrite-poor submarine systems (Kump and Seyfried, 2005). However,  
129 evidence of this has not been studied using actual submarine altered rocks.

130 We further explore low sulfate seawater-basalt reactions that took place in the early  
131 Paleoproterozoic using the well-preserved 2.41 Ga hydrothermally altered basalts from the  
132 Vetreny Belt of the Baltic (Fennoscandian) Shield, Russia. Using the lithologies that reflect areas  
133 of voluminous seawater flow through the ancient hydrothermal system, we study the influence of  
134 low sulfate concentration on the isotope systematics of high temperature altered rocks. Given  
135 that the solute concentrations of contemporaneous seawater are not reliably known, we use the Sr  
136 isotope record of these rocks as an indirect reflection of the Ca/SO<sub>4</sub> ratio. However, unlike the  
137 marine sedimentary record, high-temperature alteration minerals that form within oceanic crust  
138 are not straightforward indicators of seawater composition due to the rock-buffered reactions.  
139 Thus, we acknowledge that hydrothermally altered rocks cannot compare in accuracy to the  
140 sedimentary record because they do not reflect marine solute concentrations directly. On the  
141 other hand, the isotope signals recorded in hydrothermally altered rocks may be more robust  
142 when compared to the sedimentary record due to the low solubility and chemical resilience of  
143 high-temperature silicates. Consequently, hydrothermally altered rocks can inform us of the  
144 pathways taken by elements during alteration of oceanic crust, a process that dominates  
145 concentration and isotope budgets of many elements. Below we outline the strategy to  
146 deconvolute the ancient seawater signature from altered rocks using fluid inclusion  
147 measurements, multi-isotope ratios and modeling approaches.

#### 148 **1.1 Fluid inclusion measurements combined with the $\delta^{18}\text{O}$ — $\Delta^{17}\text{O}$ — $^{87}\text{Sr}/^{86}\text{Sr}$ approach**

149 We apply fluid inclusion measurements, and multiple isotope ratios,  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ , and  
150  $^{87}\text{Sr}/^{86}\text{Sr}$ , to constrain the isotopic signature of ancient hydrothermal fluids and initial seawater  
151 recorded within the alteration silicate minerals of submarine basalts. We specifically focus on the  
152 effect of precipitation of anhydrite, removal and delivery of marine Sr into the altered oceanic  
153 crust using a resilient Ca-silicate, epidote. Epidote forms in zones of focused upward flow at  
154 temperatures around 300 °C and is thought to reflect the marine Sr-pathways within altered  
155 oceanic crust (Alt et al., 1996; Gillis et al., 2005; Harris et al., 2015). Thus, we use fluid

156 inclusion elemental measurements to constrain the concentrations of Sr in ancient fluids and to  
157 recognize what processes could have affected the initial marine concentrations (i.e. phase  
158 separation). Further, we present several new  $^{87}\text{Sr}/^{86}\text{Sr}$  measurements of the 2.41 Ga and recent  
159 (0-6 Ma) oceanic epidote. These relatively young epidotes were extracted from the 6 Ma altered  
160 oceanic crust drilled at the ODP site 504B in the eastern Pacific Ocean and from the modern  
161 geothermal system at Reykjanes, Iceland (boreholes RN12 and RN17B). These new Sr isotope  
162 measurements are then combined with the previously published triple O isotope values in the  
163 same samples (Zakharov and Bindeman, 2019; Zakharov et al., 2019b). We specifically target  
164 epidote's triple O isotope ratios because the small fractionation factor between the mineral and  
165  $\text{H}_2\text{O}$  enables us to provide a close estimate of the O isotope ratio in the fluids. Traditionally used  
166  $\delta^{18}\text{O}$  value alone does not provide sufficient information on the isotope composition of the  
167 ancient fluids since both temperature and water-rock ratio affect the  $\delta^{18}\text{O}$  value of epidote within  
168  $\pm 1$  ‰ ( $1000\ln\alpha_{\text{epidote-water}}$  between -1 and +1 at 300-400 °C; Matthews et al. 1983; Zheng 1993).  
169 Using the  $\Delta^{17}\text{O}$  values of epidote, defined as  $10^3 \cdot \ln(\delta^{17}\text{O} \cdot 10^{-3} + 1) - 0.528 \cdot 10^3 \cdot \ln(\delta^{18}\text{O} \cdot 10^{-3} + 1)$ ,  
170 we rely on the O isotope fractionation between water and epidote, namely  $\Delta^{17}\text{O}_{\text{water}} - \Delta^{17}\text{O}_{\text{epidote}}$   
171 being minimal. Due to distinctly different O isotope compositions of mantle-derived rocks ( $\delta^{18}\text{O}$   
172 = ca. 6 ‰;  $\Delta^{17}\text{O} = -0.05 \pm 0.01$  ‰), seawater ( $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  very close to 0 ‰) and meteoric  
173 waters (negative  $\delta^{18}\text{O}$  and positive  $\Delta^{17}\text{O}$ ), epidote is a useful tracer of fluid-rock exchange  
174 reactions. Its  $\Delta^{17}\text{O}$  value must be very close to that of the fluids, within analytical uncertainty  
175 (i.e.  $\pm 0.01$  ‰), due to the relatively small mass-dependent fractionation at 300-400 °C (Hayles  
176 et al., 2018). This effect was demonstrated using the  $\Delta^{17}\text{O}$  measurements of geothermal fluids  
177 and co-existing epidote from modern hydrothermal systems of Iceland and altered oceanic crust  
178 (Zakharov et al., 2019b). Thus, the combined  $\delta^{18}\text{O} - \Delta^{17}\text{O} - ^{87}\text{Sr}/^{86}\text{Sr}$  values of epidote allows us  
179 to directly trace the evolution of ancient submarine fluids without the need to correct for the  
180 temperature- or composition-dependent (i.e. epidote-clinozoisite; Matthews et al. 1983)  
181 fractionation. Further, due to the difference in concentrations of Sr and O contained in rocks and

182 fluids, the concomitant change in the  $\delta^{18}\text{O} - \Delta^{17}\text{O} - {}^{87}\text{Sr}/{}^{86}\text{Sr}$  values of epidote is then used to  
183 trace the reactive exchange between seawater and basalt. The shapes of the isotope exchange  
184 trajectories reflect the physical parameters of reactive seawater circulation (DePaolo and Getty,  
185 1996; DePaolo, 2006) and can be used to constrain the Sr concentrations through geological time  
186 (Turchyn and DePaolo, 2019). We use two modeling approaches, static equilibrium and reactive  
187 transport, to narrow down the possible concentrations of marine Sr and the Ca/SO<sub>4</sub> ratio at 2.41  
188 Ga.

## 189 **1.2 Geological setting**

190 The hydrothermally altered section of komatiitic basalts of the Vetreny Belt originated  
191 from the voluminous subaqueous eruption of high-Mg lavas (several km thick) during rifting of  
192 the Karelia craton, a part of the Baltic Shield (Puchtel et al., 1996, 1997, 2016; Zakharov and  
193 Bindeman, 2019; Kulikov et al., 2010; Mezhelovskaya et al., 2016). The summarized and  
194 simplified structure of the Vetreny Belt along with some representative sample photographs are  
195 shown in Figures 3 and 4. The overall stratigraphic context includes the lower part of the basin  
196 that is filled with early Paleoproterozoic (Sumian) sedimentary and volcano-sedimentary  
197 formations (Toksha, Kirichi, Kalgachi and Kozhozero suites) comprising sandstones,  
198 conglomerates, turbidites and dolostones (Kulikov et al., 2010). The upper part of the belt is  
199 composed of voluminous, several km-thick komatiities, komatiitic basalts and andesitic basalts  
200 that form differentiated flows and pillow lavas. Coeval mafic dikes and small intrusions cut the  
201 cratonic basement rocks and are also present within the volcanic rocks of the belt. One such  
202 intrusion named Ruiga is exposed in the northern part of the belt and is notably differentiated  
203 into peridotites and gabbros (see Fig. 4). In this study, we mainly focus on the seawater isotope  
204 signatures recorded in the hydrothermally altered varieties of the komatiitic basalts (Fig. 3). We  
205 also use samples of the sedimentary carbonates from the Kozhozero suite underlying the  
206 komatiitic basalts with the goal to capture the near-contemporaneous seawater isotope  
207 composition. This suite comprises marls, stromatolitic dolomites, marbles with micaceous shales



208 and sandstones (Mezhelovskaya et al., 2016). In this study we assume that these sedimentary  
209 formations as well as the subaqueous pillow basalts reflect deposition in a shallow marine basin;  
210 however the details of sedimentation setting are not well established. We further rely on other  
211 contemporaneous basins of the Karelia craton and of the nearby Kola craton that have been  
212 interpreted to record sedimentation in shallow marine or glacial-marine environment at ~2.4 Ga  
213 (Ojakangas et al., 2001; Hanski and Melezhik, 2013).

214 The age of the komatiitic basalts is constrained by multiple geochronological studies. The  
215 underlying Kirichi suite of andesites is dated to  $2437 \pm 3$  Ma by high-precision isotope dilution  
216 thermal ionization mass spectrometry (ID-TIMS) zircon measurements (Puchtel et al., 1997). We  
217 consider this to be the maximum age of the Kozhozero sedimentary rocks that include the  
218 carbonate unit analyzed for this study. The minimum age for the komatiitic basalts is constrained  
219 by the precise  $2407 \pm 6$  Ma Re-Os isochron for whole-rock samples, olivine and chromite  
220 separates (Puchtel et al., 2016). Using ID-TIMS, a single zircon extracted from a differentiated  
221 komatiitic basalt flow yielded the age of  $2405 \pm 6$  Ma (Mezhelovskaya et al., 2016). The  
222 subvolcanic intrusions are likely of similar age, as indicated by a Sm-Nd isochron measured in  
223 the Ruiga intrusion ( $2390 \pm 50$  Ma; Kulikov et al., 2008) and by the upper intercept produced by  
224 measurements of three discordant zircons ( $2415 \pm 15$  Ma; Mezhelovskaya et al., 2016). Thus, the  
225 komatiitic basalts are 2.41 Ga, while together with the carbonates of the Kozhozero suite they are  
226 constrained to between 2.43 and 2.41 Ga.

227 The preservation of the Vetreny Belt komatiitic basalt has been demonstrated previously  
228 with geochemical investigations of unaltered volcanic glass, olivine phenocrysts and pristine  
229 spinifex textures (Puchtel et al., 1996, 2001, 1997, 2016). The hydrothermally altered section of  
230 the Vetreny Belt is also exceptionally well-preserved as demonstrated by presence of  
231 undeformed pillow structures, delicate alteration of hyaloclastites and pillow rinds with original  
232 textures, and by internally consistent quartz-epidote O isotope and fluid inclusion thermometry  
233 (Zakharov and Bindeman, 2019). The epidotes measured for  $^{87}\text{Sr}/^{86}\text{Sr}$  are the same as in the

234 studies of Zakharov and Bindeman (2019) and Zakharov et al. (2019), encompassing samples  
235 from the Vetreny Belt and recent altered oceanic crust. New bulk rock measurements of the  
236 Vetreny Belt formations are from: a) altered section of Ruiga intrusion used for conventional  
237  $\delta^{18}\text{O}$  values; b) the Lava Lake flow, a locality near Lev Gora containing least-altered basaltic  
238 rocks (see Fig.4) used for conventional  $\delta^{18}\text{O}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  values (sample description in Puchtel  
239 et al. 1996); c) underlying carbonates of the Kozhozero suite used for  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ . This  
240 wide range of samples is used to trace the contribution of marine isotope signals for both O and  
241 Sr, following the scheme introduced in the Section 1.1.

### 242 **1.3 The record of marine sulfate in the early Paleoproterozoic**

243 Since the ultimate purpose of this study is to assess anhydrite saturation in hydrothermal  
244 fluids as a consequence of evolving marine solutes, we must first review the current state of  
245 marine sulfate reconstructions for the Precambrian. We focus particularly on the early  
246 Paleoproterozoic, a period of dynamic change in atmospheric chemistry and sulfate  
247 concentrations. Modern oceans contain 28 mM sulfate, ~8 % of the total dissolved load (Berner  
248 and Berner, 1996), while the Phanerozoic (0.54 Ga to now) concentrations oscillated between 10  
249 and 30 mM (see recent review Turchyn and DePaolo, 2019). This contrasts with the marine  
250 sulfate levels before the initiation of oxidative weathering at ~2.43- 2.42 Ga (Gumsley et al.,  
251 2017; Warke et al., 2020). Before this transition, termed the Great Oxidation Event (hereinafter  
252 the GOE), Archean seawater likely contained < 1mM sulfate (Holland, 1984; Canfield, 1998;  
253 Habicht et al., 2002; Farquhar and Wing, 2003; Kah et al., 2004; Jamieson et al., 2013; Crowe et  
254 al., 2014). The first occurrence of evaporitic sulfates at ca. 2.4-2.3 Ga suggests that marine  
255 sulfate concentration reached at least ~2.5 mM shortly after or during the GOE (Bekker et al.,  
256 2001; Schröder et al., 2008; Crockford et al., 2019). Further, recent reconstructions based on  
257 sedimentary sulfate, sulfide, and carbonate-associated sulfate spanning from ~2.0 Ga to 0.6 Ga  
258 suggest the marine sulfate from 2 to 10 mM (Halverson and Hurtgen, 2007; Blättler et al., 2018a,  
259 2020; Turner and Bekker, 2016; Fig. 2). On the other hand, multiple studies suggest much lower

260 sulfate concentrations (0-5 mM) in the Paleo- and Mesoproterozoic and micromolar  
261 concentrations in the Archean based on absence of thick bedded massive sulfate evaporates, and  
262 minimal sulfur isotope fractionation between pyrite and carbonate associated sulfate (e.g.  
263 Fakhraee et al., 2019; Kah et al., 2004; Scott et al., 2014). Thus, the 2.41 Ga Vetreny Belt rocks  
264 occupy a peculiar place in the marine sulfate record, as they could have interacted with seawater  
265 containing a wide and growing range of sulfate concentrations. Conservatively, we rely on the  
266 timing of the first appearance of evaporitic sulfate at ~2.4-2.3 Ga (Schröder et al., 2008;  
267 Crockford et al., 2019) that likely occurred around the same time or after the formation of the  
268 Vetreny Belt. Consequently, we explore the hypothesis in which marine sulfate was low (~1  
269 mM), reflecting generally high Ca/SO<sub>4</sub> ratios and, thus, limiting anhydrite precipitation in  
270 equilibrium with hydrothermal fluids. As we show later in the paper, the difference between  
271 choosing 1 to 10 mM sulfate as the initial marine concentration does not affect out  
272 interpretations significantly, due to consistently high Ca/SO<sub>4</sub> ratios. To support this, we explore a  
273 wide range of marine sulfate concentrations between 1 and 28 mM, and marine Ca between 10  
274 and 40 mM.

## 275 **2. METHODS**

### 276 **2.1 Sr isotope measurements**

277 Strontium isotope ratios (<sup>87</sup>Sr/<sup>86</sup>Sr) were measured using the Nu Plasma HR  
278 multicollector inductively-coupled-plasma mass-spectrometer (MC-ICP-MS) hosted at the  
279 Geology Department of the University of Illinois, Urbana-Champaign. Silicate samples were  
280 dissolved with concentrated HF and HNO<sub>3</sub> in Teflon beakers, while carbonates were treated with  
281 concentrated HCl and HNO<sub>3</sub>. After removing an aliquot of the solution for Rb and Sr  
282 concentration determination, the majority of the dissolved sample was loaded onto 200 µl Sr  
283 spec column for Sr purification. The sample was introduced to the mass spectrometer using an  
284 Aridus II desolvator. Standard NIST SRM 987 was run between every 3 samples and two other  
285 standards, Eimer and Amend and an in-house modern coral were run every 6 samples. All

286 samples and the two secondary standards were corrected for offsets in  $^{87}\text{Sr}/^{86}\text{Sr}$  between the  
287 measured ( $0.71040 \pm 0.00001$ ; mean  $\pm 1\sigma$ ;  $n = 10$ ) and nominal values of NIST SRM987  
288 ( $0.71034 \pm 0.00026$ ). This correction results in accurate measurements for Eimer and Amend  
289 ( $0.70804$ ) and modern coral ( $0.70918$ ). The reproducibility of each sample is conservatively  
290 estimated as  $\pm 0.00003$ .

291 The Rb and Sr concentrations were determined using a Thermo iCAP-Q ICP-MS.  
292 Quantification involved external calibration lines and admixed internal standards for drift. The  
293 uncertainty on the Rb/Sr ratios is conservatively estimated as  $\pm 10\%$  of the mean.

## 294 **2.2 Conventional O isotope measurements**

295 The  $\delta^{18}\text{O}$  values were determined in several amphibole separates and whole rock samples  
296 ( $n = 7$ ) of altered gabbros from the Ruiga subvolcanic intrusion. The analyses were performed at  
297 the University of Oregon Stable Isotope Laboratory vacuum line using laser-assisted fluorination  
298 in the presence of  $\text{BrF}_5$  to liberate  $\text{O}_2$  from silicates. The product  $\text{O}_2$  was subsequently purified  
299 through a series of cryogenic traps held at liquid  $\text{N}_2$  temperature and a mercury diffusion pump.  
300 The gas was converted to  $\text{CO}_2$  gas and subsequently analyzed with a MAT 253 mass  
301 spectrometer in dual-inlet mode. The average uncertainty on the  $\delta^{18}\text{O}$  determination was  $\pm 0.1$   
302 ‰. The accuracy of the analysis was monitored with the in-house standard UOG (University of  
303 Oregon Garnet standard;  $\delta^{18}\text{O} = 6.52\%$  VSMOW). A powdered sample of unaltered komatiitic  
304 basalt was analyzed using an airlock sample chamber. This allowed us to introduce and  
305 fluorinate one sample at the time avoiding high blanks due to the reactivity of powdered  
306 samples.

307 In addition, we measured C and O isotope composition of the two sedimentary carbonate  
308 samples from the Kozhozero suite. The analysis was conducted using the GasBenchII device  
309 connected to the DeltaXP mass spectrometer located at the University of Lausanne, Switzerland.  
310 The procedure is outlined in (Spötl and Vennemann, 2003). Briefly, powdered samples (100-300  
311  $\mu\text{m}$ ) were reacted with phosphoric acid at  $70\text{ }^\circ\text{C}$ . The product  $\text{CO}_2$  was separated from other

312 components using a gas chromatographic column and analyzed in the mass spectrometer for  $\delta^{13}\text{C}$   
313 and  $\delta^{18}\text{O}$  values. The reproducibility of  $\pm 0.06$  and  $0.08$  ‰, respectively, was monitored by  
314 analyzing an in-house standard.

### 315 **2.3 Fluid inclusions measurements by LA-ICP-MS**

316 The chemical compositions of quartz-hosted fluid inclusions were measured using LA-  
317 ICP-MS at the Department of Earth Sciences of ETH Zurich (Switzerland). We used a Perkin  
318 Elmer NexION 2000 fast-scanning quadrupole ICP-MS connected to the ETH-prototype GeoLas  
319 laser ablation system equipped with a Coherent Compex Pro 102F Excimer ArF (193 nm) laser  
320 source. For this study, we used assemblages of  $\sim 10$ -micron quartz-hosted fluid inclusions  
321 abundantly present in samples VB8A and GO22. These are the same samples that host epidote  
322 used for the isotope measurements (see Fig. 3E). The fluid inclusions consist of polyphase brines  
323 containing a liquid, a gas bubble and a halite crystal, frequently associated with vapor-like  
324 inclusions. Only the former yielded quantifiable signals upon ablation. We targeted tight clusters  
325 of brine inclusions showing very similar phase proportions that were therefore assigned as fluid  
326 inclusion assemblages ( $n = 13$  in VB8A and  $n = 10$  in GO22).

327 The sample chips were set in a custom-made, small volume (ca.  $1\text{ cm}^3$ ) and fast-washout  
328 stainless steel ablation chamber, mounted on an optical microscope equipped with a CCD  
329 camera. Gas blanks and system contamination were minimized following the cleaning and setup  
330 recommended by Schlöglöva et al. (2017). The ablation chamber was fluxed with He (ca. 1  
331 L/min) as carrier gas to which was admixed make-up Ar (ca.  $1\text{ L}\cdot\text{min}^{-1}$ ) downstream of the  
332 ablation chamber, prior to introduction in the plasma. The ICP-MS was optimized for maximum  
333 sensitivity on the whole mass range and low oxide rate formation ( $^{248}\text{ThO}^+ / ^{232}\text{Th}^+ < 0.5\%$ ).

334 The NIST SRM610 glass (Jochum et al., 2011) was used as external standard for  
335 quantification of most elements, except S, Cl and Br that were calibrated against the Sca-17  
336 scapolite standard (Seo et al., 2011). Both were analyzed with laser spot diameter of  $40\text{ }\mu\text{m}$ ,  
337 repetition rate of 10 Hz, energy density of ca.  $7\text{ J cm}^{-1}$  and a ca. 1 min measurement consisting

338 of 30 s gas blank followed by 30 s ablation. For fluid inclusions, analyses were performed with a  
 339 laser repetition rate of 10 Hz, energy density of ca. 15 to 20 J cm<sup>-2</sup>, variable spot sizes set as to  
 340 completely ablate the entire inclusion (see Heinrich et al. (2003) for details) and an ablation  
 341 duration of ca. 1 min. The spot diameter was slowly incremented to the desired size using an  
 342 opening aperture, to prevent quartz cracking (Gognon et al., 2003). Intensities for the following  
 343 isotopes were acquired in peak jumping mode: <sup>7</sup>Li, <sup>11</sup>B, <sup>23</sup>Na, <sup>25</sup>Mg, <sup>27</sup>Al, <sup>29</sup>Si, <sup>34</sup>S, <sup>35</sup>Cl, <sup>39</sup>K,  
 344 <sup>42</sup>Ca, <sup>55</sup>Mn, <sup>57</sup>Fe, <sup>63</sup>Cu, <sup>66</sup>Zn, <sup>75</sup>As, <sup>79</sup>Br, <sup>85</sup>Rb, <sup>88</sup>Sr, <sup>133</sup>Cs, <sup>137</sup>Ba, and <sup>208</sup>Pb with a dwell time of 10  
 345 ms except for Na, Al, Si, K, Sr and Ba (5 ms), corresponding to a total sweep time of 0.224 s.

346 Data processing was performed with the Matlab-based SILLS program (Guillong et al.,  
 347 2008). The fluid inclusion signals were corrected for contributions from the host quartz using a  
 348 SiO<sub>2</sub> content of 99.9 wt.% as internal standard. Spectra were only selected for element  
 349 quantification if the ablation of the FI was controlled (i.e. not breached at the onset of ablation)  
 350 and when the FI peak was clearly distinguishable from the surface contamination peak; Pettke et  
 351 al., 2012). Over 100 inclusions were analyzed, of which 88 gave useable signals.

## 352 **2.4 Reactive transport model in dual-porosity medium**

353 We undertake reactive transport modeling of water-rock isotope exchange in a dual-  
 354 porosity system (DePaolo, 2006) since we use epidote measurements from filled fractures and  
 355 veins, where both advective and diffusive transport occurs. The model is used to calculate  
 356 simultaneous shifts of Sr and triple O isotope ratios experienced by hydrothermal fluids. The  
 357 principal equation includes diffusion, advection and reaction terms that add (dissolution) or  
 358 consume (precipitation) chemical species:

$$359 \quad \rho_f \frac{\partial \phi C_f}{\partial t} = \rho_f D \frac{\partial}{\partial x} \left( \frac{\partial \phi C_f}{\partial x} \right) - v \rho_f \frac{\partial \phi C_f}{\partial x} + \sum_i R_{di} C_{si} - \sum_j R_{pj} K_j C_f \quad (1),$$

360 where  $C$  is concentration of element in the fluid and solid (subscript  $f$  and  $s$  respectively),  $\rho$  and  $\phi$   
 361 denote density and porosity,  $D$  is ionic diffusivity,  $v$  is fracture fluid velocity,  $K$  is distribution

362 coefficient for solid/fluid. The terms  $R$  describe rates of dissolution (subscript  $d$ ) and rates of  
 363 precipitation (subscript  $p$ ) of species  $i$  and  $j$ .

364 The equation can be re-written for a fractured medium, where fluid transport occurs via  
 365 advection along fractures and diffusion in the low-porosity matrix. Combining dissolution and  
 366 precipitation into one term yields recrystallization rate (denoted  $R$ ) expressed in  $\text{g}\cdot\text{g}^{-1}\cdot\text{yr}^{-1}$ , i.e.  
 367 grams of alteration material forming per grams of original rock in a year. As explained in  
 368 DePaolo, 2006, the steady-state assumption of the dual porosity model is a good starting point  
 369 for demonstrating possible trajectories of combined isotope shifts. The application of such  
 370 assumptions is justified by the relative longevity of hydrothermal systems and by our inability to  
 371 make safe assumptions about how and why the isotopic ratio of incoming/discharging fluids  
 372 changed with time, when only the final product (hydrothermally altered rocks) can be analyzed.  
 373 In the steady-state formulation of the model, the fluid isotopic ratios change with distance ( $x$  in  
 374 meters). The rate of change of isotopic ratio in fracture fluid ( $r_f$ ) with the distance is described as  
 375 (eq. 28 in DePaolo, 2006):

$$376 \quad \frac{dr_f(x)}{dx} = \frac{8D\phi_m}{\phi_f v_f b d} [r_s - \alpha r_f(x)] \sum_{n_{\text{odd}}} (1 + n^2 \pi^2 \frac{L^2}{b^2})^{-1} \quad (2),$$

377 where  $D$  is ionic diffusivity of a species (e.g. self-diffusion of  $\text{H}_2\text{O}$ ,  $\text{Sr}^{2+}$ ),  $\phi$  is porosity in the  
 378 matrix,  $v_f$  velocity of the fracture fluid,  $\phi_f$  porosity of the fracture (always equals 1),  $b$  is fracture  
 379 spacing and  $d$  is fracture width. The variable  $L$  (reactive length) derives from the relationship  
 380  $(D\rho_{\text{fluid}}\phi C_{\text{fluid}}/R\rho_{\text{rock}}(1-\phi)C_{\text{rock}})^{1/2}$ , where  $\rho$ ,  $\phi$ ,  $C$  denote density, rock porosity and concentration of  
 381 an element of interest. The fractionation factor  $\alpha$  is an equilibrium fractionation factor. For Sr,  $\alpha$   
 382 is unity, i.e. no fractionation occurs, while O isotope fractionation can be described as  $^{18/16}\alpha$   
 383  $=1.002$  for high-temperature bulk rock- $\text{H}_2\text{O}$  fractionation of  $^{18}\text{O}/^{16}\text{O}$  ratio. Fractionation of  
 384  $^{17}\text{O}/^{16}\text{O}$  follows the relation  $^{17/16}\alpha = ^{18/16}\alpha^\theta$  for, where  $\theta$  is mass-dependent exponent appropriate  
 385 for high-temperature fractionation of triple O isotope ratios, e.g. 0.529 (Matsuhisa et al., 1978;  
 386 Pack and Herwartz, 2014).

387           The results of steady-state dual porosity model are dependent on the poorly constrained  
388 physical parameters such as reaction rates, fluid velocity, fracture spacing, and porosity ( $R$ ,  $v_f$ ,  $b$   
389 and  $\phi$ ). These path-integrated variables are especially difficult to measure directly and perhaps  
390 should not be constrained by single values. The effects of changing the fracture spacing ( $b$ ) and  
391 recrystallization rates ( $R$ ) were discussed previously (DePaolo, 2006; Turchyn et al., 2013;  
392 Brown et al., 2013, 2020). It is sensible to accept the average fracture spacing on the order of  
393 several meters (1 m), while the recrystallization rates vary on the order of  $0.0001 \text{ yr}^{-1}$  as  
394 constrained from short-lived isotopes in active hydrothermal systems (Kadko and Moore, 1988;  
395 Kadko et al., 2007). Further, the ground water flow convects around intrusive bodies at rates  
396 anywhere between several meters a year, up to  $\sim 100 \text{ m/yr}$  (Norton, 1978; Wood and Hewett,  
397 1982; Hayba and Ingebritsen, 1997). Here we perform Monte-Carlo simulation of the isotopic  
398 shift using ranges of values listed in the Table 1. The isotopic shifts were calculated at  $\sim 200\text{m}$  ( $x$   
399 in Eq. 2) 2000 times randomly picking variables from the uniform distributions within specified  
400 ranges. This value of  $x$  is used because it successfully reproduces the isotope shifts measured in  
401 modern-day oceanic hydrothermal fluids (see Discussion).

## 402 **2.5 Mineral aqueous equilibrium calculations and Sr isotope balance**

403           All calculations of seawater-basalt reaction with different concentrations of marine  $\text{SO}_4$   
404 and Ca were simulated following the same steps as described below allowing for convenient  
405 comparison. The starting seawater compositions for modern seawater-basalt reaction is taken  
406 from (Berner and Berner, 1996). For all other reactions, we modified the initial seawater by  
407 taking different  $\text{SO}_4$  and Ca concentrations with the Mg concentration set to 45 mM. This  
408 number is close to the average estimate of Mg concentration in the seawater throughout the  
409 Phanerozoic (see Turchyn and DePaolo, 2019). The rest of solutes are left at the same  
410 concentrations compensating the charge by  $\text{Cl}^-$ . We acknowledge that seawater solutes in the  
411 Precambrian are not reconstructed as reliably as for the Phanerozoic owing to the absence of



412 suitable record, however using these values allows us to make a realistic comparison of the effect  
413 of variable calcium/sulfate ratio.

414 We perform seawater-basalt reactions using the program CHIM-XPT (Reed et al., 2010)  
415 to simulate a set of titration experiments in which small amount of basalt is incrementally added  
416 to 1020 g (1L) of seawater and the solution is then allowed to achieve equilibrium concentrations  
417 of aqueous species and minerals. A realistic order of events is simulated via following steps: 1)  
418 reaction of small amount of basalt (5 g) at 150 °C and 400 bar and removal of solid phases at the  
419 end; 2) reaction with another 5g of basalt at 350 °C and 500 bar and removal of solid phases at  
420 the end; 3) titration of basalt until aqueous concentrations become dominated by equilibrium  
421 with basalt. At this stage, albite and microcline molar quantities exceed other minerals. This  
422 configuration is intended to reproduce hydrothermal system in which seawater first heats up to  
423 ~150 °C with precipitation and removal of anhydrite and other oversaturated phases as they  
424 occupy empty spaces, vesicles and pores, yet with minimal participation of basaltic material (Alt  
425 et al., 1996; Fisher, 1998). Next, fluid moves through hot wall rock, precipitating minerals at  
426 higher temperature and pressure (350 °C and 500 bar), leaving the minerals behind in a  
427 permeable upper crust. Then fluid reacts with basalts at low water-rock ratios. The water-rock  
428 ratio (W/R) in these calculations is used as a measure of titration progress; it is calculated from  
429 dividing the amount of initial seawater (1020 g) by the mass of titrated basalt. Thus, step #1  
430 described above represents seawater-basalt reactions at W/R between infinity (0 g basalt added)  
431 and 204 (5 g basalt titrated).

432 The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of hydrothermal fluids are calculated from the simple mass balance  
433 calculation. The contributions are derived from titrated basalt assuming that it contains 200 ppm  
434 Sr (2.28 mmoles/g), and from the initial seawater Sr content and its isotope ratio. In calculating  
435 the modern seawater-basalt reaction, we take 87  $\mu\text{mol}/\text{kg}$  as the initial marine Sr concentration.  
436 We use the marine Sr/Ca ratio of 9  $\mu\text{mol}/\text{mmol}$  to retrieve the initial Sr concentrations in these  
437 calculations, unless specified otherwise. This is justified since the reconstructed ratios have been

438 remarkably stable at ca. 8-9  $\mu\text{mol}/\text{mmol}$  across the last 200 Ma (Coggon et al., 2010; Turchyn  
 439 and DePaolo, 2019; Zhang et al., 2020). The simple mass-balance of Sr isotopes in the  
 440 hydrothermal fluid in the initial stages of seawater-basalt reaction is expressed as:

$$441 \quad {}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{fluid}} ([\text{Sr}]_{\text{anhydrite}} + [\text{Sr}]_{\text{fluid}}) = ([\text{Sr}]_{\text{SW}} {}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{SW}} +$$

$$442 \quad [\text{Sr}]_{\text{basalt}} {}^{87}\text{Sr}/{}^{86}\text{Sr}_{\text{basalt}}) \quad (3),$$

443 where dissolved ions and anhydrite (if present) are the only Ca- and Sr-bearing species on the  
 444 left-hand side. As more basalt added, more Sr-bearing phases (e.g. epidote) appear on the left-  
 445 hand side of the equation (Eq. 3), while anhydrite is removed at steps #1 and #2 (see paragraph  
 446 above). We assume no isotope fractionation across phases on the left-hand side, thus we assume  
 447 same  ${}^{87}\text{Sr}/{}^{86}\text{Sr}$  of equilibrium fluids and minerals. The Sr concentration contained in equilibrium  
 448 anhydrite and in the fluids are then calculated from the distribution coefficient  $K_D$ :

$$449 \quad \frac{[\text{Sr}]_{\text{anhydrite}}}{[\text{Sr}^{2+}]_{\text{aqm}}} = K_D * \frac{[\text{Ca}]_{\text{anhydrite}}}{[\text{Ca}^{2+}]_{\text{aqm}}} \quad (4).$$

450 The  $[\text{Ca}]_{\text{anhydrite}}$  and total dissolved Ca contained in fluid  $[\text{Ca}^{2+}]_{\text{aqm}}$  are given by the output of the  
 451 mineral-aqueous equilibrium modeling in CHIM-XPT. To keep track of Sr concentration, we  
 452 specified a distribution coefficient between anhydrite and fluid ( $K_D$ ) expressed as  
 453  $[\text{Sr}/\text{Ca}]_{\text{anhydrite}}/[\text{Sr}/\text{Ca}]_{\text{fluid}} = 0.6$  (Mills et al., 1998; Teagle et al., 1998). Additionally, we explore  
 454 the effect of changing the  $K_D$  to 0.4 and 0.9. Such values encompass the majority of distribution  
 455 coefficients observed during rapid precipitation of anhydrite (Syverson et al., 2018).

456 Following the procedure outlined above, we performed two sets of calculations. The *first*  
 457 *set* features a detailed calculation of seawater-basalt reaction using i) modern seawater  
 458 composition as initial fluids and ii) the envisioned 2.41 Ga seawater compositions, where Ca, Sr  
 459 and  $\text{SO}_4$  concentrations were taken as 20 mmol/kg, 160  $\mu\text{mol}/\text{kg}$  and 1 mmol/kg, respectively.  
 460 This set is carried out over a wide range of W/R and with enabled computation of solid solutions.  
 461 The compositions of reactants are summarized in Table 2. The Sr concentration is taken from the  
 462 results of the fluid inclusion measurements, while  $\text{SO}_4$  represents a hypothesized value based on

463 the projected marine sulfate concentrations. In addition, we tested for the difference in using  
464 high-Mg (MgO = 12.4 wt. %) and normal mid-ocean ridge basalts (MgO = 7.8 wt. %; Table 2)  
465 as reactants in our calculations, since the Vetryny Belt rocks include abundant komatiitic basalts.

466 Since the exact concentration of sulfate in initial seawater is not reliably constructed for  
467 2.43 – 2.41 Ga seawater we also carry out *second set* of calculations using a wide range of SO<sub>4</sub>  
468 concentrations between 1 mmol/kg and 28 mmol/kg. These numbers represent the reported  
469 estimates throughout the Proterozoic and Phanerozoic sulfate concentrations (Holland, 1984;  
470 Lowenstein et al., 2003; Fakhraee et al., 2019; Blättler et al., 2020). Calcium was varied between  
471 10 and 40 mmol/kg. This set of calculations was performed across multiple seawater Ca/SO<sub>4</sub>  
472 ratios, above and below 1, for a range of W/R defined by the reaction with pristine seawater  
473 (W/R infinity) and by first appearance of epidote (W/R of ~ 50). This offers a sensitivity test for  
474 the <sup>87</sup>Sr/<sup>86</sup>Sr measurements of epidotes as a tracer of the marine Sr at variable marine Ca/SO<sub>4</sub>  
475 values. Since many calculations were performed, we disabled calculation of solid solutions.

### 476 **3. RESULTS**

#### 477 **3.1 Elemental concentrations measured in fluid inclusions**

478 The data is reported here (Tables 3 and 4) in two ways: (1) as assemblage ratios to Na  
479 (Table 3), which should be preferred for interpretation given that salinity was not directly  
480 determined; and (2) as concentrations (ppm) calculated using an average salinity of 40 wt.%  
481 NaCl equivalent (average salinity obtained for the inclusions by microthermometry) and a  
482 correction accounting for the presence of other cations as major chloride compounds (i.e. K, Ca  
483 as well as Fe and Mn for sample VB8A), determined based on the raw intensity ratios (Table 4).  
484 The Na-normalized ratios could be used to recalculate concentrations using any salinity. Further,  
485 Supplementary Table 1 contains both the results of individual fluid inclusions analyses and the  
486 calculated averages for the corresponding assemblages with corresponding uncertainty (standard  
487 deviation of the n individual inclusion signals used to calculate the average composition of the

488 assemblage). The limits of detection (LOD) listed in the Supplementary Table 1 were calculated  
489 using the method of Pettke et al., (2012) and are reported for individual inclusion analyses.

490 In this study we focus on elemental ratios that reflect modification of original seawater  
491 signature due to its reaction with basalt and due to phase separation, particularly Cl/Br, Na/K,  
492 Ca/Na and Sr/Na ratios (Fig. 5). Notably, the fluid inclusions of the two samples have distinct  
493 Cl/Br ratios; the values range mostly between 24-40 and 200-1000 for VB8A and GO22  
494 respectively. The Sr concentrations in the fluid inclusions (expressed as Sr/Na) range from  
495 0.0013 to 0.0087 in sample GO22, while the VB8A displays elevated ratios between 0.0516 and  
496 0.1526.

### 497 **3.2 $^{87}\text{Sr}/^{86}\text{Sr}$ values**

498 The  $^{87}\text{Sr}/^{86}\text{Sr}$  and Rb/Sr ratios of the Vetreny Belt epidotes, altered pillow basalts,  
499 unaltered komatiitic basalts and underlying carbonates along with modern oceanic epidotes  
500 included in this study are summarized in Figure 6 and reported in Table 5. The  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$   
501 values are calculated based on the age of lithologies of the Vetreny Belt. The mean and  
502 uncertainty include propagated errors from the maximum possible uncertainty in age ( $2.42 \pm 0.01$   
503 Ga), analytical error of isotope measurements ( $\pm 0.00003$ ) and the error in Rb/Sr ratio ( $\pm 10\%$ ),  
504 yielding a total range of uncertainties between 0.00003 and 0.00071 ( $\pm 1\sigma$ ). The  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$   
505 values of epidote are the most precise due to their low Rb/Sr (see Table 5). The Rb  
506 concentrations in epidotes are below the detection limit of  $\sim 1$  ppm. The unaltered rock samples  
507 have  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$  values in the range 0.7008-0.7016; these values are typical for the  
508 contemporaneous composition of ultramafic melts, slightly contaminated by crustal material  
509 (Puchtel et al., 1997, 2016). Altered pillow rinds and epidotes have  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$  ratios between  
510 0.7029 and 0.7042, significantly higher than that of the unaltered rock. The two samples from the  
511 underlying carbonate unit of Kozhozero suite returned Rb/Sr ratios of 0.006 and 0.016 and the  
512  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$  of 0.7045-0.7046 (Fig. 6), close to the previous measurements of marine carbonates  
513 (Fig. 1; Kuznetsov et al., 2010). We note that upon preparation of the carbonate samples, some

514 solid residue remained undissolved. Consequently, the carbonates of the Vetreny Belt require  
515 more effort to assess their origin and the integrity of marine isotope signal.

### 516 **3.3 $\delta^{18}\text{O}$ values**

517 The  $\delta^{18}\text{O}$  values of amphibole separates and whole rock samples from the Ruiga intrusion  
518 range between -0.7 and +3.0 ‰ (Table 6). They are plotted on the schematic geologic map in  
519 Figure 4. The unaltered komatiitic basalt (sample 12105; see sample 91105 in Puchtel et al.  
520 1996) returned  $\delta^{18}\text{O}$  value of +5.6 ‰. The two samples of sedimentary carbonates from the  
521 Kozhozero suite returned  $\delta^{13}\text{C}$  values of -0.95 and -1.38 ‰ and  $\delta^{18}\text{O}$  of -27.8 and -28.3 ‰  
522 VPDB. The previously measured  $\delta^{18}\text{O} - \Delta^{17}\text{O}$  values of modern and ancient samples are  
523 combined with the  $^{87}\text{Sr}/^{86}\text{Sr}$  values in Figure 7. The  $\delta^{18}\text{O}$  are plotted as the linearized notation  
524  $\delta^{18}\text{O} = 10^3 \ln(1 + \delta^{18}\text{O}/1000)$ . The triple O isotope values of ancient and modern oceanic epidote  
525 are compiled from (Zakharov and Bindeman, 2019; Zakharov et al., 2019b) and recalibrated to  
526 the VSMOW-SLAP defined scale with the San Carlos Olivine values of  $\delta^{17}\text{O} = 2.668$ ,  $\delta^{18}\text{O} =$   
527  $5.153$  and  $\Delta^{17}\text{O} = -0.049$  ‰. The value is slightly modified from (Pack et al., 2016) and  
528 represents unification of the standardization efforts (Pack et al. 2016; Wostbrock et al., 2020) by  
529 subtracting 12 ppm from the  $\delta^{17}\text{O}$  of original value. The stretching and shift are determined from  
530 the analyses of KRS-SKFS standards measured at the University of Oregon (Miller et al. 2020).  
531 The recalibration scheme is presented in Herwartz (2021) along with our previous measurements  
532 of hydrothermally altered rocks. The recalibrated values are gathered in Supplementary Table 2.

### 533 **3.4 The output of dual-porosity model and Montel-Carlo simulation**

534 The results of the dual-porosity model are presented in Figure 7. For verification of our  
535 approach, we show the result of conventional  $\delta^{18}\text{O} - ^{87}\text{Sr}/^{86}\text{Sr}$  profiles with the previously  
536 published data on hydrothermal fluids (Bach and Humphris, 1999) and epidotes measured here  
537 (Fig. 7A). In addition, we show the profiles in the  $\Delta^{17}\text{O} - ^{87}\text{Sr}/^{86}\text{Sr}$  space with modern and  
538 ancient oceanic epidote presented here. The outputs are shown as the 2D-density distributions

539 (Fig. 7) of isotope shifts produced by the ranging values of reaction rates, porosity, fluid flow  
540 and fracture spacing as constrained by previous studies (see Methods).

### 541 **3.5 Equilibrium mineral assemblages and aqueous speciation**

542 The equilibrium Ca-bearing minerals and several other selected minerals are shown in  
543 Figure 8. The total molality of dissolved species and moles of all mineral species during the  
544 reactions are shown in Figure 9. As expected, these calculations show that the abundance of  
545 anhydrite is the most noticeable difference between high- and low-sulfate seawater-basalt  
546 reactions. The fraction of marine Sr incorporated into the equilibrium minerals is expressed as  
547  $[\frac{^{87}\text{Sr}}{^{86}\text{Sr}}_{\text{mineral}} - \frac{^{87}\text{Sr}}{^{86}\text{Sr}}_{\text{basalt}}] / [\frac{^{87}\text{Sr}}{^{86}\text{Sr}}_{\text{SW}} - \frac{^{87}\text{Sr}}{^{86}\text{Sr}}_{\text{basalt}}]$ , where subscripts *SW* and *basalt*  
548 denote seawater and unaltered rock with their initial  $^{87}\text{Sr}/^{86}\text{Sr}$ . In the calculation with 1 mM  
549 sulfate and 20 mM Ca (envisioned for 2.41 Ga seawater), the maximum amount of marine Sr  
550 incorporated in epidote is 80 %. We found no significant difference in the computed  $^{87}\text{Sr}/^{86}\text{Sr}$   
551 epidote values produced by a reaction with high-Mg basalt with 12.4 wt. % MgO (see  
552 Supplementary Text 1). Meanwhile, in the modern seawater-basalt reaction, epidote contains up  
553 to 27 % marine Sr. Our results show that the possible variations in the distribution coefficient  $K_D$   
554 (Syverson et al., 2018) play a relatively minor role compared to the effect of abundant anhydrite  
555 precipitation (Fig. 8). The range of W/R where epidote is sensitive to the difference in marine  
556 sulfate concentrations is between 10 and 50. Further, we notice that in the calculation with 1 mM  
557 sulfate, the first appearance of epidote occurs at slightly higher W/R compared to the calculation  
558 with modern seawater concentration of solutes. This is due to the relatively higher concentration  
559 of aqueous Ca in sulfate-poor reaction. This translates into a higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the early-  
560 formed epidote in the low sulfate calculation. In addition, in the calculation with 1 mM sulfate,  
561 epidote is comparatively rich in the aluminous endmember, clinozoisite. Both calculations show  
562 a similar pattern of becoming more clinozoisite-rich with decreasing W/R.

## 563 **4. DISCUSSION**

564 We first need to discuss the fluid inclusion data as they allow us to directly determine the  
565 Sr concentrations in ancient hydrothermal fluids independently of the isotope data. Using those  
566 estimates, we can test for the marine Sr transfer within the 2.41 Ga hydrothermal system.

#### 567 **4.1 Constraints from fluid inclusion measurements**

568 The composition of fluids trapped in these samples resulted from the reaction of seawater  
569 with rocks at high temperature and phase separation of the fluids. Phase separation could lead to  
570 elevated Sr concentrations in hydrothermal fluids proportional to the increase in salinity (e.g.  
571 Butterfield et al., 1990). The types of fluid inclusions in these samples include both highly saline  
572 halite-saturated inclusions that homogenize to liquid, and vapor-dominated inclusions that  
573 homogenize to vapor (Fig. 5A). Therefore, to assess the effect of phase separation, we use the  
574 Cl/Br ratio as it fractionates during precipitation or dissolution of halite, since Br is  
575 incompatible. Compared to modern seawater, these brines are about 8-11 times more saline  
576 (Zakharov and Bindeman, 2019). The Cl/Br ratios in sample GO22 overlap with those of  
577 seawater, be it modern (600) or reconstructed Archean (400; De Ronde et al., 1997), which  
578 suggests that this sample hosts the least modified fluids. In contrast, the fluids hosted in VB8A  
579 were perhaps affected by more advanced halite-brine fractionation and phase separation that  
580 decreased the Cl/Br and Na/Br ratios. Further, the sample VB8A exhibits elevated concentrations  
581 of elements that have affinities with brines, like K, Ca, Fe, Mn, Zn, etc. (see Table 3). The Sr/Na  
582 ratios measured by LA-ICP-MS in sample GO22 range from 0.0013 to 0.0087 close to that of  
583 seawater, mimicking the pattern exhibited by Ca/Na ratios (Fig. 5B). The possible variations in  
584 Sr/Na caused by halite-fluid fractionation and/or phase separation would likely be within the  
585 large uncertainties of these ratios ( $\pm 37\%$  relative, on average), so that this range should be  
586 reasonably representative of seawater that underwent minimal exchange with basaltic rocks.  
587 Assuming that the seawater salinity did not change significantly through time, the corresponding  
588 Sr concentration estimated from the GO22 fluid is between 14 and 94 ppm, or 160-1073  
589  $\mu\text{mol/kg}$ , with an average of 457  $\mu\text{mol/kg}$ . This range can be interpreted as pre-phase-separation

590 Sr concentrations varying between seawater and the hydrothermal fluid, respectively. These  
591 estimated figures are realistic based on the modern and reconstructed Phanerozoic marine Sr  
592 concentrations. For example, modern seawater contains 87  $\mu\text{mol/kg}$  Sr, while the seawater Sr  
593 concentration of Cretaceous and Ordovician seawater is estimated to be  $\sim 570$   $\mu\text{mol/kg}$  (Coogan,  
594 2009; Turchyn and DePaolo, 2019). Thus, for the rest of the discussion we accept that the least  
595 modified fluid, i.e. seawater, had about 160  $\mu\text{mol/kg}$  Sr, i.e. the value least affected by phase  
596 separation and contributions from basaltic source.

#### 597 **4.2 Marine Sr recorded in epidote of the Vetreny Belt**

598 The high input of marine Sr in the hydrothermal system of the Vetreny Belt is evident  
599 from the epidote  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$  values ranging between 0.70288 and 0.70422, significantly higher  
600 than 0.701, an average value of the unaltered fresh basalt (Fig. 6). Further, the bulk altered  
601 basalts of the Vetreny Belt, including altered hyaloclastites and altered pillow rinds, also display  
602 high  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$  ratios, between 0.7029 and 0.7042, consistent with alteration at high W/R and  
603 high input of marine Sr. These values are exceptionally high and hint at seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  above  
604 0.704, close to the values of the underlying carbonates of the Kozhozero suite. However, caution  
605 is used when interpreting the carbonate samples as the record of pristine seawater value, as they  
606 were likely modified in post-depositional environment. In combination with previous  
607 investigations of the early Paleoproterozoic formations (Bekker et al., 2001, 2003; Kuznetsov et  
608 al., 2010), we suggest that the ca. 2.41 Ga seawater might have been as high as 0.7045 in  
609  $^{87}\text{Sr}/^{86}\text{Sr}$ . That would translate into  $\sim 90$  % of marine Sr incorporated into the Vetreny Belt  
610 epidote. The extent of connectivity to the global ocean could potentially affect our interpretations  
611 as the local seawater could be influenced by the cratonic runoff. Yet, the relatively long Sr  
612 residence time ( $\sim 2.5$  Ma; Hodell et al., 1990) and the circulation time ( $\sim 1500$  years; Broecker  
613 and Peng, 1982) of the modern ocean together result in its well-mixed  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, even in  
614 partially restricted basins, for example, in Red Sea (see Craig, 1966). Thus, it is logical (see



615 Discussion in Satkoski et al., 2016) to suggest that the Vetreny Belt was also representative of  
616 the global marine Sr.

617 Epidote and hydrothermally altered basalts of modern oceanic crust and ophiolites  
618 indicate that on average 20-50 % of marine Sr reaches the high-temperature alteration zones of  
619 oceanic crust (Fig. 6; Kawahata et al., 1987; Bickle and Teagle, 1992; Alt et al., 1996; Harris et  
620 al., 2015). Higher values are measured in epidote from Cretaceous and Ordovician ophiolite  
621 sequences (McCulloch et al., 1981; Bickle and Teagle, 1992; Alexander et al., 1993; Turchyn et  
622 al., 2013; Antonelli et al., 2017), coinciding with periods when oceans were low in sulfate ( $\leq 10$   
623 mM; Berner, 2004). For comparison, we show the detailed  $^{87}\text{Sr}/^{86}\text{Sr}$  systematics of the Troodos  
624 ophiolite rocks, provided in the study by Bickle and Teagle (1992), where the fraction of marine  
625 Sr reaches 60-70 % in epidotes and altered basalts. As suggested previously, these observations  
626 conform to the link between seawater Ca/SO<sub>4</sub> ratio and isotope budget of hydrothermal fluids  
627 (Fig. 3 in Antonelli et al., 2017). Thus, it appears logical that when Earth's surface had limited  
628 capability to produce abundant sulfate, namely at 2.41 Ga, and the Ca/SO<sub>4</sub> were generally high,  
629 this effect should be even more extreme, and submarine hydrothermal fluids were even more  
630 enriched in radiogenic seawater-derived Sr as depicted with the Sr isotope values of the Vetreny  
631 Belt rocks. In the following section, we test the extent of modification of original seawater  
632 signature by seawater-basalt reaction using the combined triple O and Sr isotope approach.

### 633 **4.3 Conventional $\delta^{18}\text{O}$ values and combined $\delta^{18}\text{O} - \Delta^{17}\text{O} - ^{87}\text{Sr}/^{86}\text{Sr}$ approach**

634 First, we need to point out that the conventional  $\delta^{18}\text{O}$  measurements presented here  
635 document a typical mantle value of  $\delta^{18}\text{O} = +5.6 \text{ ‰}$  (e.g. Eiler et al., 2000) in the well-preserved  
636 unaltered rocks of the Vetreny Belt. The high temperature altered plutonic section measured at  
637 the Ruiga intrusion has  $\delta^{18}\text{O}$  between  $-0.7$  and  $+3.0 \text{ ‰}$  (Fig. 4), similar to the distribution of  
638 values within modern altered oceanic crust (Alt and Teagle, 2000; Alt and Bach, 2006). The  
639  $\Delta^{17}\text{O}$  of the unaltered basalt was not measured directly, yet the variability in terrestrial mafic  
640 rocks is limited to  $-0.05 \pm 0.01 \text{ ‰}$  (Pack and Herwartz, 2014; Sharp et al., 2018; Cano et al.,

641 2020). Based on our previous fluid inclusion and O isotope thermometry measurements  
642 (Zakharov and Bindeman, 2019), the estimated triple O isotope composition of the least-  
643 modified seawater is  $\delta^{18}\text{O} = -1.7\text{‰}$  and  $\Delta^{17}\text{O}$  of around  $0\text{‰}$ , close to the values of ice-free  
644 oceans (Zachos et al., 2001). This slightly negative  $\delta^{18}\text{O}$  value explains the slightly negative  
645 values measured in the altered gabbros. The conventionally determined  $\delta^{18}\text{O}$  of the carbonates  
646 disagree with precipitation from such seawater. In fact, the measured values of ca.  $-28\text{‰}$  VPDB  
647 are lower than the values typical for carbonates of similar age (Shields and Veizer, 2002). Such  
648 low  $\delta^{18}\text{O}$  values are unlikely to reflect original deposition in marine environment and may have  
649 been caused by precipitation from either really low  $\delta^{18}\text{O}$  fluids or much higher temperature  
650 above  $300\text{ °C}$  (O'Neil et al., 1969). One potential explanation would entail diagenesis in  
651 presence of glacial meltwaters, as the early 2.44-2.41 Ga Huronian glacial episodes are nearly  
652 contemporaneous (Bekker et al., 2020) and are in fact recorded through extremely low  $^{18}\text{O}$ -  
653 depleted rocks on the Baltic Shield (Zakharov et al., 2019a). Recrystallization and alteration of  
654 original isotope signal at high temperature in the presence of meteoric waters are also among the  
655 reasons potentially responsible for such a low value (see Ryb and Eiler, 2018). Because  
656 carbonates are prone to diagenesis and recrystallization, we rely on the triple O isotope  
657 reconstructions of seawater values documented in Zakharov and Bindeman (2019).

658         Next, by comparing the  $\Delta^{17}\text{O}$ -shifts recorded by modern and ancient epidotes (Fig. 7),  
659 we note that the 2.41 Ga fluids of the Vetreny Belt likely experienced a similar amount of  
660 interaction with basalt as those in modern submarine systems. Both ancient and modern epidotes  
661 range in values between that of seawater and fluids in equilibrium with basalt, i.e. between  $-0.06$   
662 and  $0.00\text{‰}$  (Fig. 7A). This suggests that the Sr concentration of the fluid controlled the  
663 distinctly high  $^{87}\text{Sr}/^{86}\text{Sr}$  of the epidotes relative to contemporaneous seawater, not the difference  
664 in the amount of seawater-basalt exchange (Fig. 7A). The shape of multi-isotope shifts in the  
665  $\delta^{18}\text{O} - \Delta^{17}\text{O} - ^{87}\text{Sr}/^{86}\text{Sr}$  coordinates defined by epidote requires high Sr concentration in the  
666 fluid, similar to that in the rock ( $C_{\text{fluid}}/C_{\text{rock}} \approx 1$  in Eq. 2), even if we consider the effect of

667 different fracture spacing and the range of fractionation factors for epidote-H<sub>2</sub>O (Figs. 7B and  
668 7C). An average unaltered basaltic rock from the Vetreny Belt has 200 ppm Sr (Puchtel et al.,  
669 1996), therefore requiring the fluids to have around 200 ppm Sr too. This contrasts with the 7-8  
670 ppm Sr (80-90 μmol/kg) in modern seawater and its high sulfate concentration, which together  
671 results in an abrupt shift of <sup>87</sup>Sr/<sup>86</sup>Sr measured in upwelling fluids and epidotes, while their O  
672 isotope values are moderately shifted (Fig. 7B; Alexander et al. 1993; Alt et al. 1996; Coogan  
673 2009; Bach and Humphris 1999). This is also consistent with the estimated value of 160 μmol/kg  
674 (~14 ppm) that represents the fluid Sr concentration prior to phase separation.

675         We use the Monte Carlo simulations of the dual-porosity model (DePaolo, 2006) to  
676 portray possible ranges of the two-element isotope evolution of hydrothermal fluids. Overall, we  
677 find that the output of the model agrees well with the modern data, where both the isotope  
678 composition of seawater and Sr concentrations are known. We find that only limited variability  
679 in the shape of the two-element trajectories can be produced by variable reaction rates, fluid  
680 flow, fracture spacing, and porosity compared to the effects of drastically different concentration  
681 of Sr in initial seawater. Further, this modeling approach allows us to compare fluid and epidote  
682 values, as both record fluid flow in the fractured medium.

683         In summary, we consider the high <sup>87</sup>Sr/<sup>86</sup>Sr of Vetreny Belt epidote to be a result of  
684 several factors: i) initially high <sup>87</sup>Sr/<sup>86</sup>Sr values (ca. 0.7045) of seawater; ii) moderate  
685 concentration of marine Sr (~160 μmol/kg) that was subsequently increased by phase separation;  
686 and iii) absence of anhydrite at the early stages of hydrothermal circulation. Further, the  
687 consistency of the new δ<sup>18</sup>O -- Δ<sup>17</sup>O -- <sup>87</sup>Sr/<sup>86</sup>Sr data measured in epidotes from the 2.41 Ga and  
688 modern oceanic environments contributes to the long-standing debate on the isotope evolutions  
689 of seawater through time. The debate is based on the observation of consistently lower O isotope  
690 values of the early Phanerozoic and Precambrian carbonates and cherts compared to modern-day  
691 and Cenozoic counterparts (Knauth, 2005; Prokoph et al., 2008). Recent data on marine oxides  
692 also document this trend (Galili et al., 2019). The observation has been interpreted in several

693 non-exclusive ways such as alteration by low  $\delta^{18}\text{O}$  meteoric waters, smaller O isotope  
694 fractionation in hot Precambrian oceans (up to 70 °C) and/or significantly lower  $\delta^{18}\text{O}$  values of  
695 seawater, down to -15 ‰ in the Archean (Shields and Veizer, 2002; Knauth, 2005; Jaffrés et al.,  
696 2007; Prokoph et al., 2008; Zakharov et al., 2021). If one accepts the hypothesis of changing  
697 marine  $\delta^{18}\text{O}$  value, then early Paleoproterozoic cherts and carbonates indicate that seawater was  
698 ~8-9 ‰ lower than we reconstruct based on the triple O isotope approach. Our data suggests that  
699 the seawater O isotope values at 2.41 Ga were not significantly different from the Cenozoic (i.e.  
700 ice-free) hydrosphere. While it is not possible to reconstruct the ambient seawater temperature  
701 from altered basalts, we suggest that the alternative hypotheses or a combination of factors  
702 (higher seawater temperature and diagenesis) are more probable causes to the observed  
703 sedimentary trend.

#### 704 **4.4 The effect of different Ca/SO<sub>4</sub> ratios on incorporation of marine Sr**

705       Amongst redox-sensitive marine species, sulfur is abundantly present in modern seawater  
706 due to the high solubility of its oxidized form, sulfate, causing oversaturation of seawater with  
707 anhydrite at temperatures above 150 °C (Fig. 1). As explained in Antonelli et al. (2017), the  
708 marine Ca/SO<sub>4</sub> ratio determines the amount of anhydrite distributed between the low- and high-  
709 temperature parts of oceanic hydrothermal systems (Fig. 1). During periods of low sulfate  
710 concentrations, when the Ca/SO<sub>4</sub> ratios are high, above 1, the amount of anhydrite precipitation  
711 is mostly limited to the low-temperature, early stages of alteration of oceanic crust (see Fig. 8).  
712 At this stage, when sulfate is removed as anhydrite, the excess of marine Ca and Sr is  
713 incorporated further downstream into the silicate minerals of altered crust. When the Ca/SO<sub>4</sub>  
714 ratios are < 1, like in modern seawater, the excess sulfate precipitates as high-temperature  
715 anhydrite with Ca and Sr derived from mixed marine and basaltic sources, and a proportionally  
716 smaller amount of marine Sr is incorporated into the silicate minerals like epidote.

717       In our equilibrium calculations we show how the modern and envisioned 2.41 Ga  
718 seawater-basalt reactions affect the distribution of marine Sr across mineral and aqueous species.

719 In the modern-day seawater-basalt reaction, anhydrite precipitates early in the titration, at 150  
720 °C, W/R above 100, and thus, reflects  $^{87}\text{Sr}/^{86}\text{Sr}$  values close to original seawater (Fig. 8), similar  
721 to anhydrites from modern hydrothermal systems (e.g. Mills et al., 1998). The contribution of Sr  
722 derived from further reaction with basalt shifts the  $^{87}\text{Sr}/^{86}\text{Sr}$  of fluids from the high seawater  
723 value towards the low basaltic value. In our high-sulfate calculation at 350 °C, which mimics the  
724 modern high-temperature altered oceanic crust, the mineral assemblages include epidote with 10-  
725 30 % marine Sr (Fig. 8) in agreement with the modern high-temperature vent fluid and epidote  
726 values ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.702\text{-}0.704$ ; Bach and Humphris 1999; Gillis et al. 2005; Harris et al. 2015).

727 The computed 2.41 Ga seawater-basalt reaction shows that the Ca-silicates and fluids at  
728 W/R between 10 and 50 contain up to 80 % of original marine Sr. In addition, epidote in this  
729 calculation forms earlier at slightly higher W/R when compared to the high-sulfate reaction. This  
730 indicates that a high Ca/SO<sub>4</sub> ratio of seawater will promote an early capture of marine Sr by  
731 epidotes. The mineral assemblages informative of the early capture of marine Sr by epidote can  
732 be recognized by the presence of quartz but absence of feldspars, i.e. quartz-epidote veins. This  
733 provides an additional support to our sampling strategy at the Vetreny Belt and enables  
734 recognition of useful samples for the studies of paleoseawater  $\delta^{18}\text{O}$ , Ca/SO<sub>4</sub> and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios.

735 Further, the Ca/SO<sub>4</sub> ratio might have dynamically evolved in the early Paleoproterozoic,  
736 in concert with the rapid changes in oxidative capacity of weathering shortly after the GOE  
737 (Scott et al., 2008). We explore the sensitivity of the  $^{87}\text{Sr}/^{86}\text{Sr}$  epidote ratios using the simplified  
738 seawater-basalt calculation over the range of Ca/SO<sub>4</sub> ratios (*second set*, see Methods). Shown as  
739 color-coded points (Fig. 10), we calculated the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the early-forming epidote at W/R ~  
740 50. Spanning the envisioned conditions of the early Paleoproterozoic and the Phanerozoic, the  
741 resulted  $^{87}\text{Sr}/^{86}\text{Sr}$  range between 31 % and 89 % of the original seawater value (Fig. 10).

742 Qualitatively the pattern is consistent with the concentrations of seawater solutes across the  
743 Phanerozoic. However, only the Ordovician and modern epidotes match the quantitative output  
744 of our calculation within several %. Cretaceous, Jurassic and Silurian epidotes yield consistently

745 lower values than those predicted by the calculation. Importantly, our results show that the  
746  $^{87}\text{Sr}/^{86}\text{Sr}$  value of epidote is sensitive to marine  $\text{Ca}/\text{SO}_4$ , especially early in the progress of  
747 seawater-basalt interaction. The sensitivity to marine  $\text{Ca}/\text{SO}_4$  drops at low W/R because the  
748 values become overwhelmed by the basaltic signal. Thus, the lower marine Sr fraction  
749 incorporated in Cretaceous, Jurassic and Silurian can be explained by sampling epidotes that  
750 formed at lower W/R. Mechanistically, such epidote may have formed in an environment where  
751 advective transport was limited. Equilibrium fluids would have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios significantly  
752 shifted towards basaltic values as shown in the models with small fracture spacing (Fig. 7).

#### 753 **4.5 Implications for the long-term marine Sr cycle**

754 After the GOE, when marine sulfate reached several mM (Schröder et al., 2008; Blättler  
755 et al., 2018, 2020), hydrothermal circulation of seawater involved precipitation of anhydrite in  
756 considerable amount, compared to the envisioned low-sulfate Archean oceans. In the modern  
757 global geochemical balance, the dependency between anhydrite formation and removal of Ca  
758 and S from seawater is counter-balanced by the retrograde solubility of anhydrite at low  
759 temperature, below about 150 °C (see Fig. 1). However, the actual anhydrite fate likely depends  
760 on the history of individual fragments of oceanic crust, their cooling and sedimentation rates, as  
761 some anhydrite is still found in old oceanic crust (Alt et al., 2003). In addition, there is also  
762 evidence for subduction of seawater-derived sulfate into melt-generating reservoirs recorded by  
763 sulfur isotope studies of arc magmas (e.g. De Hoog et al. 2001) and eclogites (e.g. Evans et al.  
764 2014). Further, considering the global S isotope budget models, only up to ca. 35 % of oceanic  
765 burial flux is in form of sulfide (Halevy et al., 2012; Tostevin et al., 2014). Thus, some amount  
766 of anhydrite stays in the crust, even though the co-existing seawater would become  
767 undersaturated with respect to the mineral at temperatures < 150 °C. This is likely due to the  
768 decreasing permeability of oceanic crust over time (Fisher, 1998). Yet the proportion of  
769 dissolved anhydrite vs anhydrite that ‘sticks around’ is difficult to estimate. Despite this  
770 uncertainty, it is likely that at least some of Ca, Sr and S that make up hydrothermal anhydrite

771 return into the ocean. Dissolution of anhydrite is, however, unlikely to play a significant role in  
772 the isotope budget of oceanic Sr. It likely acts similarly to the diagenetic flux of Sr (Kump,  
773 1989). That is to say that the Sr is released quickly from dissolution of anhydrite with the isotope  
774 ratio similar to contemporaneous seawater. Such flux does not induce changes in the  $^{87}\text{Sr}/^{86}\text{Sr}$  of  
775 seawater, however, if this flux is large, it would buffer changes in the seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  caused  
776 by changes in continental weathering.

777         In the early Precambrian oceanic crust, when oceanic Ca/SO<sub>4</sub> ratios were very high,  
778 marine Sr should be permanently stored due to low solubility of high-temperature Ca-silicates  
779 that contain Sr as a common trace element. In envisioned Archean oceans with sub-mM sulfate  
780 concentrations, only negligible amounts of anhydrite formed, promoting a massive flux of  
781 marine Sr into the high temperature altered oceanic crust. As documented in the present study  
782 during the early Paleoproterozoic, when marine sulfate reached several mM (Schröder et al.,  
783 2008), the mechanism of Sr burial likely involved comparatively minor anhydrite. Consequently,  
784 a high fraction of marine Sr was constantly buried in the silicates of altered oceanic crust that  
785 would eventually be subducted at convergent margins. In other words, the altered oceanic crust  
786 was acting as a permanent sink for marine Sr.

787         In modern oceanic budgets, most of the Sr and Ca are from continental erosion delivered  
788 by riverine fluxes (e.g. Palmer and Edmond 1989). As for the early Paleoproterozoic, the  
789 proposed emergence of extensive landmasses (e.g. Flament et al. 2008; Bindeman et al. 2018),  
790 continental break-up, global glaciations (e.g. Young 2013) and elevated atmospheric  $p\text{CO}_2$  levels  
791 (e.g. Sheldon, 2006) at the Archean-Proterozoic boundary would have enabled the riverine  
792 delivery of Ca and Sr from eroded continental crust, while the limited oxidative capacity of  
793 atmosphere sustained a relatively diminished flux of oxidized sulfur into the ocean. We suggest  
794 that since the altered oceanic crust was acting as a permanent sink for radiogenic marine Sr, the  
795 contribution of Sr derived from continental weathering was subdued in the overall oceanic  
796 budget. This suggests that the Precambrian seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  curve would not only be a function

797 of radioactive decay of  $^{87}\text{Rb}$ , continental growth, assemblies and break-ups (e.g. Halverson et al.,  
798 2007), but also would be dependent on anhydrite saturation within altered oceanic crust. In  
799 essence, we document the evidence that the evolution in marine  $\text{Ca}/\text{SO}_4$  ratio changed the  
800 mechanisms of Sr burial. Yet, the magnitude of this effect exerted on the global Sr isotope  
801 budget is uncertain and proportional to the fraction of anhydrite that undergoes dissolution. The  
802 potentially ephemeral nature of anhydrite in modern-day oceanic crust versus permanent storage  
803 of Sr in silicates of ancient oceanic crust illustrate the importance of minimal sulfate  
804 precipitation on the oceanic Sr and Ca cycles.

## 805 **5. CONCLUSIONS**

806 We studied 2.41 Ga oceanic hydrothermally altered rocks from the Vetreny Belt, Russia  
807 that recorded interaction with seawater shortly after or during the GOE. Our study is overall  
808 consistent with a high marine  $\text{Ca}/\text{SO}_4$  ratio, above 1, comparable to the upper range of the  
809 Phanerozoic values. In summary, we found:

- 810 1. The fluid inclusion elemental ratios ( $\text{Cl}/\text{Br}$ ,  $\text{Na}/\text{Br}$ ,  $\text{Sr}/\text{Na}$ ) determined by LA-ICP-MS  
811 document near-seawater values in one sample and allow us to assess the effect of phase  
812 separation of the fluids that formed the quartz-epidote veins of the Vetreny Belt. Accounting  
813 for the salinity-increase, the reconstructed least-modified seawater had about  $160 \mu\text{mol}/\text{kg}$   
814 (or 14 ppm) Sr.
- 815 2. The  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$  values of epidote and altered basalts fall between 0.7029-0.7042 indicating  
816 a high influx of marine Sr into the high-temperature alteration zones of the Vetreny Belt.  
817 Assuming that the 2.41 Ga seawater had  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7045$ , these samples represent ~90 %  
818 marine Sr.
- 819 3. Triple O- and Sr-isotope approach combined with the reactive circulation modeling suggest  
820 that modern and ancient epidotes record similar amount of water-rock interaction and point  
821 out a difference in the behavior of Sr. Consequently, the Vetreny Belt epidote is best



822 explained by the high influx of marine Sr that was a) likely uninhibited by massive anhydrite  
823 precipitation and b) enhanced by phase separation.

824 4. Mechanistically controlled by Ca/SO<sub>4</sub> ratio in seawater, epidotes remain sensitive to marine  
825 Sr over a range of W/R between 10 and 50 as shown in our equilibrium seawater-basalt  
826 reaction calculations. Further, the calculations show that the equilibrium assemblage of  
827 quartz and epidote in absence of feldspars is particularly useful to track marine Sr. Given that  
828 the Vetreny Belt epidote reflects ~90 % marine Sr, the 2.41 Ga hydrothermal system reflects  
829 interaction between basalt and seawater with Ca and SO<sub>4</sub> concentrations ranging between 30-  
830 40 and 0-10 mM, respectively. These values represent the original marine input and the  
831 effects of phase separation.

832 5. Considering the global Sr budget, periods of high oceanic Ca/SO<sub>4</sub> were likely accompanied  
833 by an increased fraction of marine Sr permanently stored in insoluble silicates within altered  
834 oceanic crust. While some fraction of marine Sr returns into the ocean upon dissolution of  
835 anhydrite during periods of low Ca/SO<sub>4</sub>, insoluble silicates provided a long-term sink for Sr  
836 that was subsequently subducted.

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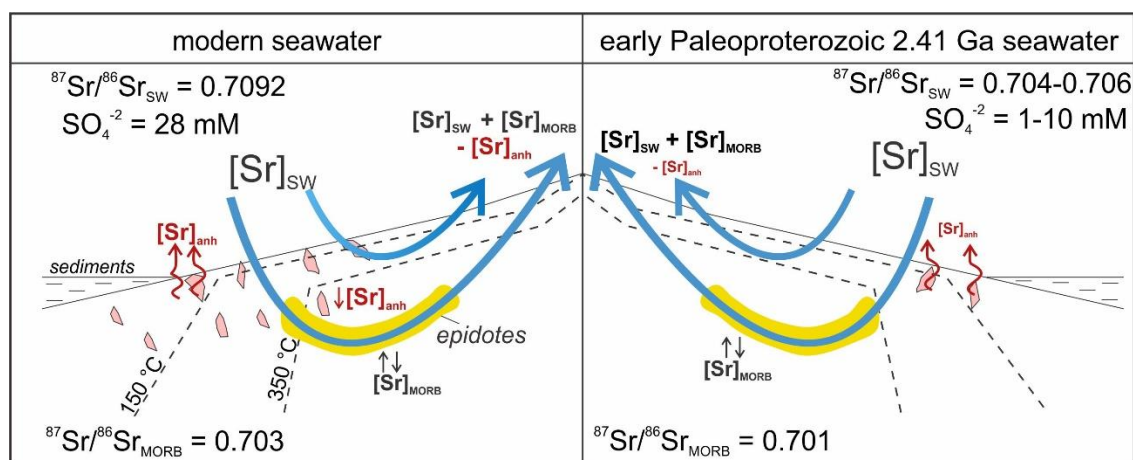
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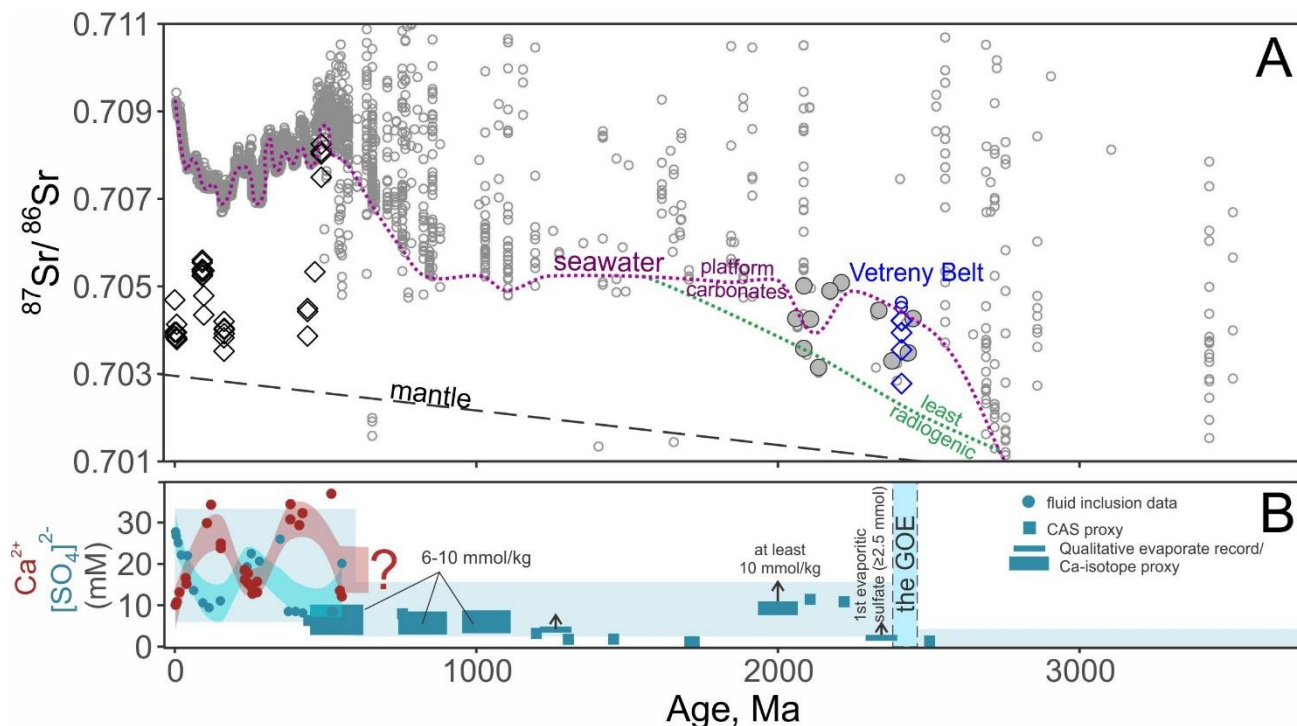
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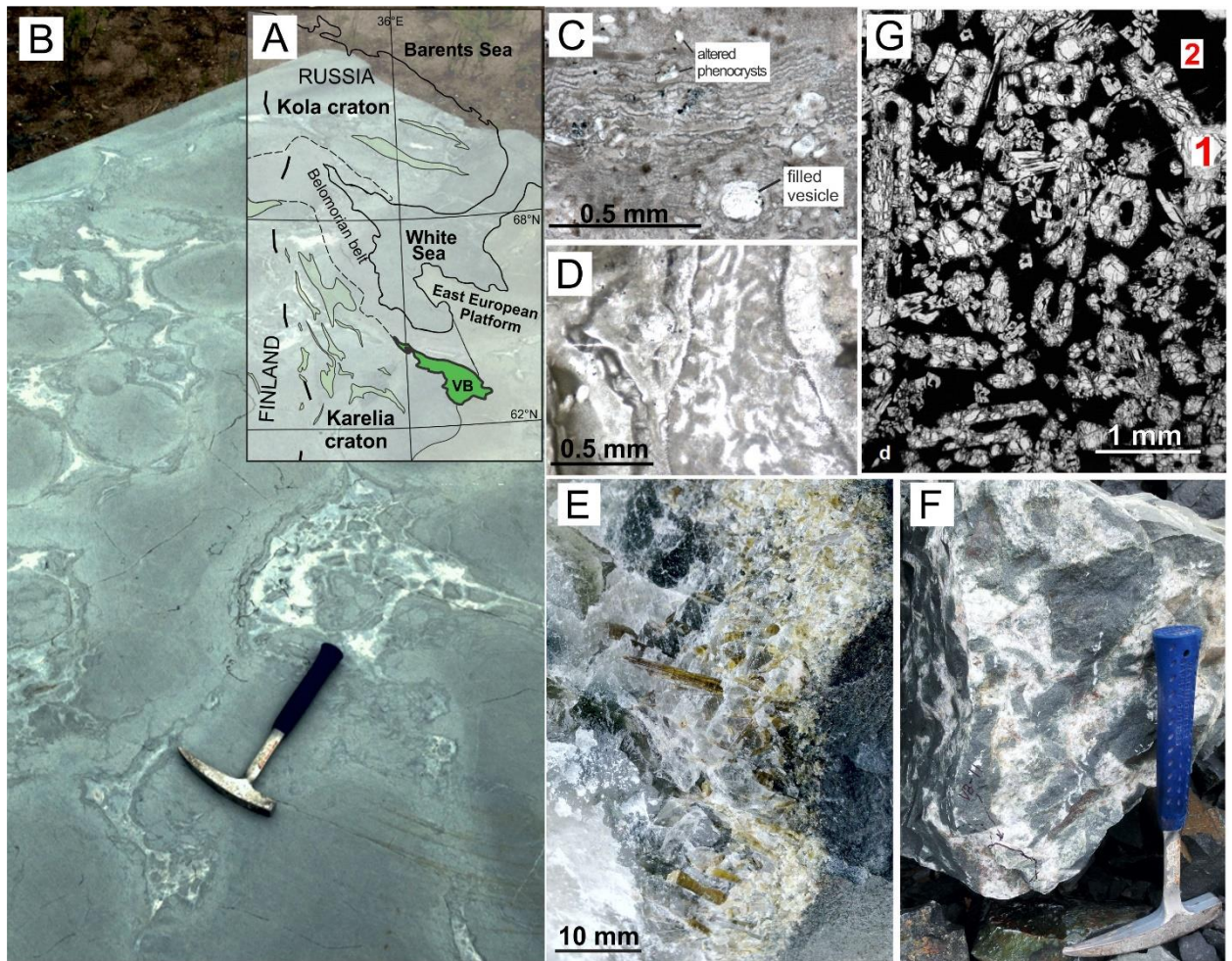
1220 **Figure 1.** Schematic illustration of Sr distribution in oceanic crust resulted from seawater-basalt  
 1221 reaction and anhydrite precipitation at mid-ocean ridges in modern (left) and the envisioned low-  
 1222 sulfate early Paleoproterozoic 2.41 Ga oceans (right). Precipitation of sulfate (shown with red-  
 1223 pink shapes) in modern and Phanerozoic hydrothermal systems removes marine Sr (shown as  
 1224  $[Sr]_{sw}$ ) from the fluids proportional to the amount of anhydrite-hosted  $[Sr]_{anh}$ . Since the early  
 1225 Paleoproterozoic (2.43-2.41 Ga) marine sulfate was likely low, the hydrothermal systems of the  
 1226 2.41 Ga Vetryny Belt were precipitating less anhydrite compared to modern systems. Thus, we  
 1227 envision that a higher fraction of  $[Sr]_{sw}$  was able to reach Ca-silicates of high-temperature  
 1228 altered oceanic crust such as epidote.

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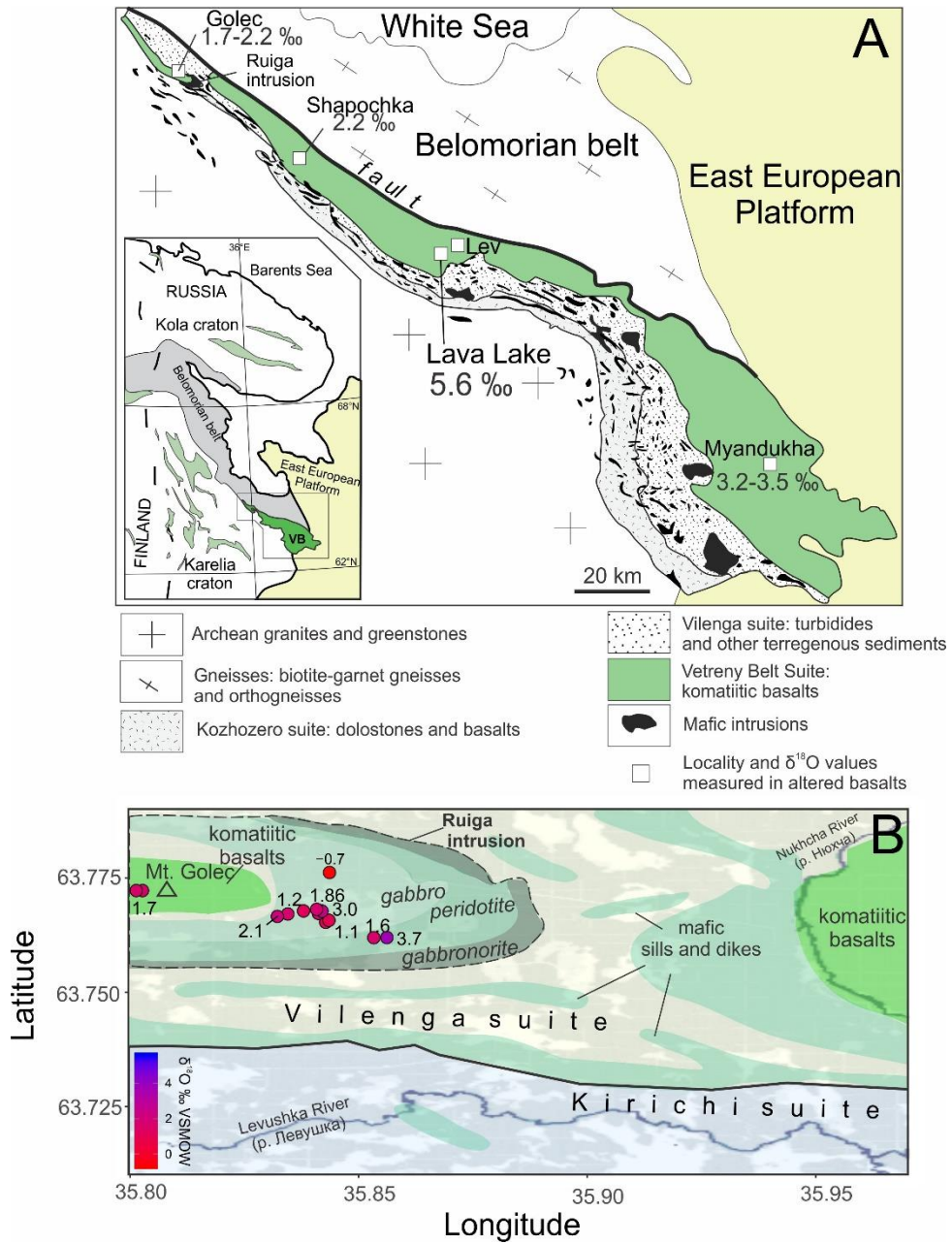
**Figure 2. A** – Strontium isotope evolution of seawater as reflected by carbonates (grey open circles; compiled from (Shields and Veizer, 2002; Prokoph et al., 2008). The early Paleoproterozoic seawater curve between 2.5 and 2.0 Ga is reconstructed from the least radiogenic samples (green dotted line Shields and Veizer, 2002) and from platform carbonates shown as the grey filled circles (Kuznetsov et al., 2010 and references therein). Oceanic epidotes (open diamonds) plot between the mantle and seawater values at respective geologic times depicting the relative contributions of marine vs basaltic Sr. The Vetreny Belt epidotes and carbonates are shown with blue diamonds and circles respectively. **B** – Marine sulfate and calcium levels over the geologic history as reconstructed in previous studies from fluid inclusion data, carbonate-associated sulfate (CAS), occurrences of evaporitic sulfate and associated Ca-isotope fractionation (Lowenstein et al., 2003; Kah et al., 2004; Canfield and Farquhar, 2009; Planavsky et al., 2012; Schröder et al., 2008; Blättler et al., 2020, 2018).



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 1250 **Figure 3.** **A** – Schematic map of the Baltic Shield showing the location of the Vetreny Belt (VB)  
 1251 within the Karelia craton. Archean greenstone belts are shown in pale green. **B** – Hydrothermally  
 1252 altered pillow basalt section exposed by a circular saw cut (locality Myandukha). The length of  
 1253 the hammer is about 30 cm for scale. **C** – Altered basaltic lava with glass hydration texture  
 1254 shown in crossed polarized light. A filled vesicle and altered phenocrysts are visible. **D** – Altered  
 1255 pillow rind with remnants of glassy shard texture. **E** – Quartz-epidote-calcite vein used for this  
 1256 study (sample VB8A). **F** – Brecciated basaltic dike cemented with quartz-epidote aggregate. **G** –  
 1257 Unaltered komatiitic basalt with olivine phenocrysts (marked 1 in red) and pristine fresh volcanic  
 1258 glass (marked 2) as seen in cross polarized light (photo adapted from Puchtel et al., 1996).

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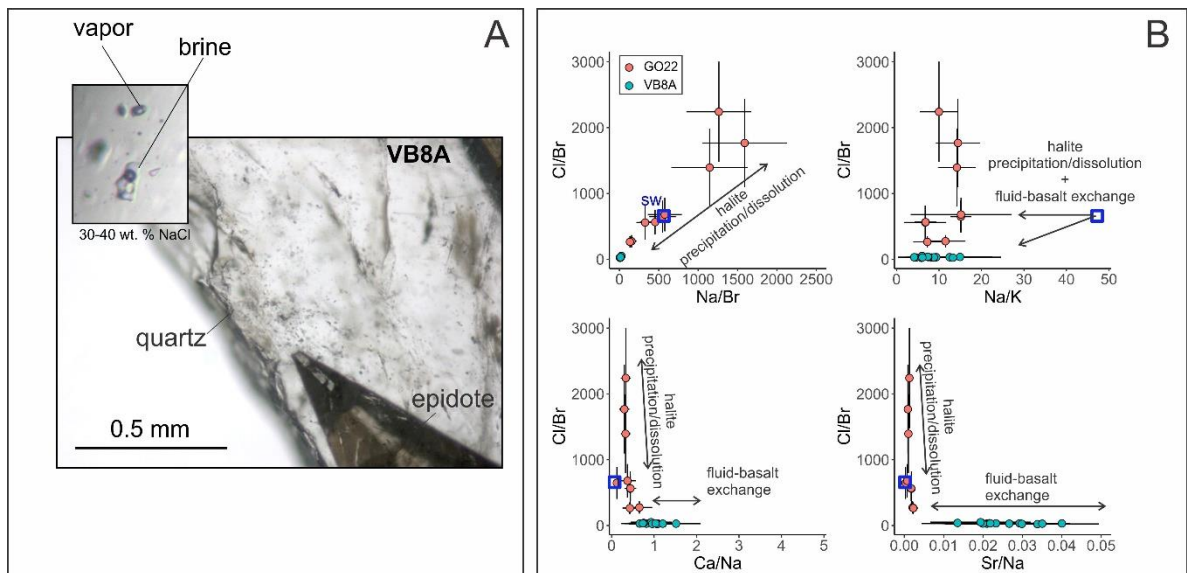
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1262 **Figure 4.** A schematic geological map of the Vetreny Belt (A) and the vicinity of Ruiga  
 1263 intrusion (B; modified from Kulikov et al., 2008) along with our δ<sup>18</sup>O sampling of altered  
 1264 gabbroids and komatiitic basalts (values from here and Zakharov and Bindeman, 2019).

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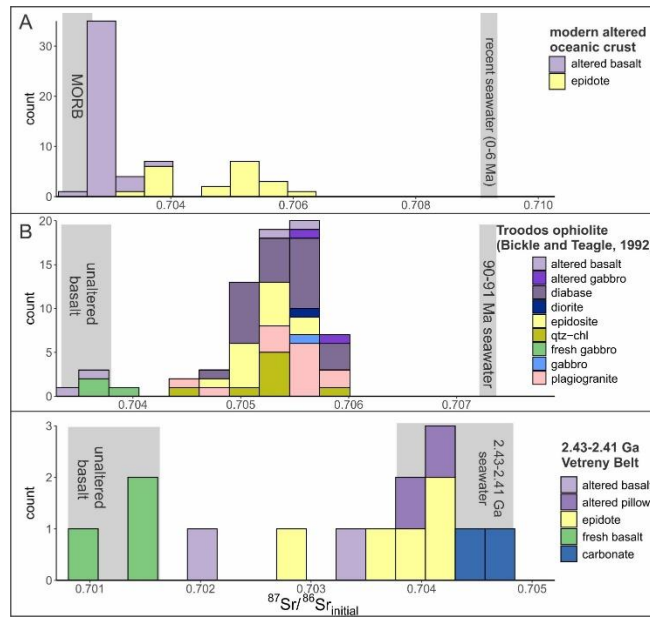


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1267 **Figure 5. A** – The photograph of sample VB8A featuring quartz hosting numerous fluid  
 1268 inclusions and an epidote crystal (labeled). The inset shows a high-salinity fluid inclusion  
 1269 (labeled “brine”) that homogenizes to liquid and a vapor-dominated fluid inclusion that  
 1270 homogenizes to vapor (labeled “vapor”). Presence of both types of inclusions indicates that the  
 1271 fluid was undergoing phase separation. **B** – The elemental ratios of fluid inclusions determined  
 1272 by LA-ICP-MS. The Cl/Br and Na/Br ratios are sensitive to precipitation or dissolution of halite,  
 1273 while Na/K, Ca/Na and Sr/Na also reflect the extent of seawater-basalt exchange. The modern  
 1274 seawater composition is shown with a blue square in each panel. We interpret the change in  
 1275 ratios in GO22 fluid inclusions chiefly as a result of halite-precipitation and dissolution yet  
 1276 moderate fluid-basalt exchange. Meanwhile, the VB8A ratios indicate halite precipitation and  
 1277 also, likely, its fractionation from the remaining fluid and subsequent phase-separation. In  
 1278 addition, elemental ratios measured in VB8A inclusions appear to be more modified due to fluid-  
 1279 basalt exchange compared to the GO22 inclusions.

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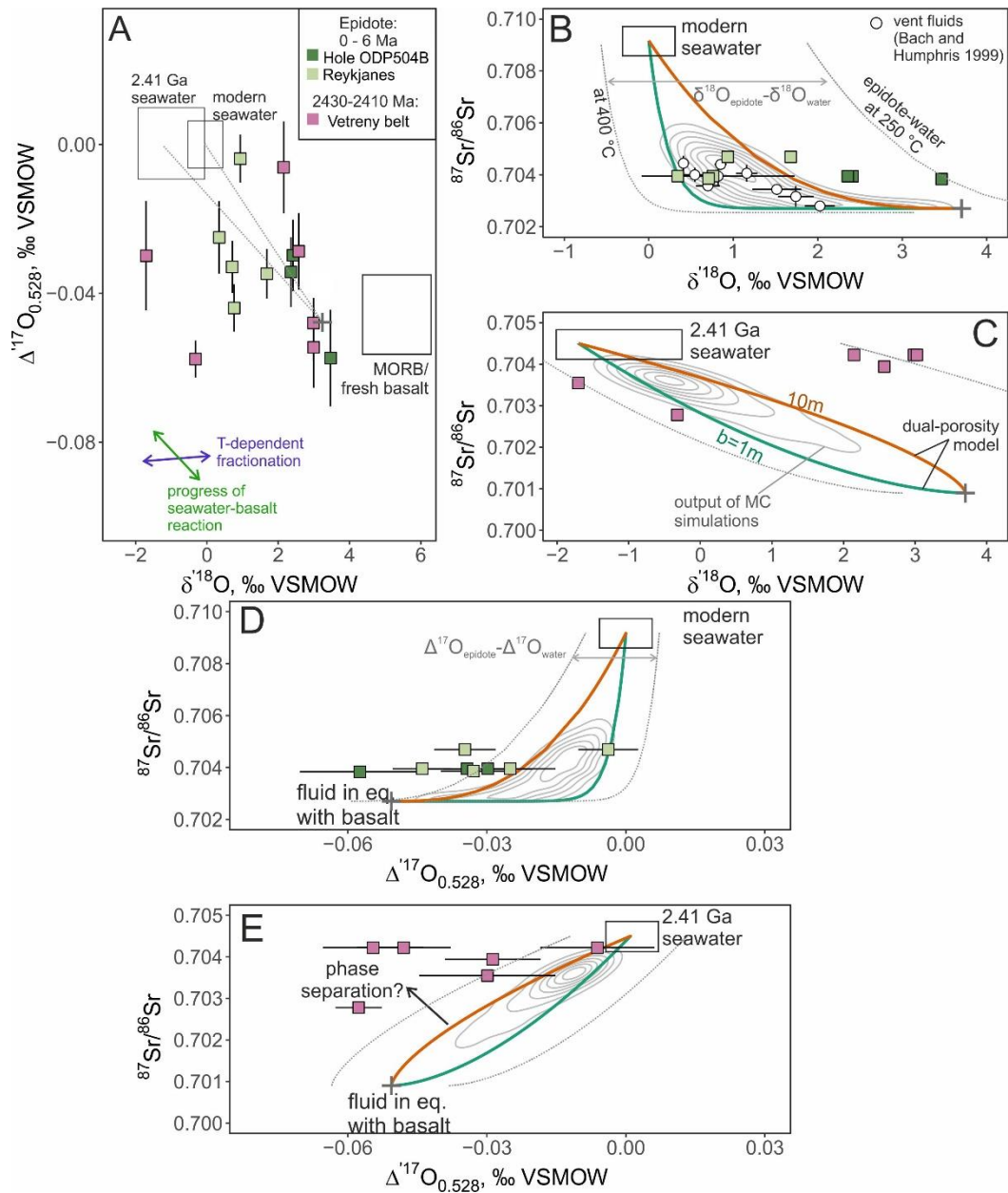


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1283 **Figure 6. A** – Stacked histograms of Sr isotope values measured in epidotes and altered basalts  
 1284 from modern oceanic crust (**A**; this study and from Kawahata et al., 1987; Alt et al., 1996; Harris  
 1285 et al., 2015), Troodos ophiolite (**B**; Bickle and Teagle, 1992; quartz-chlorite aggregates  
 1286 abbreviated to qtz-chl) and the Vetreny Belt (**C**; this study). Note the difference in the horizontal  
 1287 scale as it is adjusted so that the contemporaneous seawater and unaltered basalt (shown as mid-  
 1288 ocean ridge basalt, or MORB, for modern samples) are aligned for convenient comparison. The  
 1289  $^{87}\text{Sr}/^{86}\text{Sr}$  of the 2.43-2.41 Ga seawater is poorly constrained and thus, is shown with a wider range  
 1290 of values, encompassing contemporaneous carbonates (e.g. Kuznetsov et al., 2010) and the  
 1291 carbonates from the underlying Kozhozero suite. Fresh komatiitic basalts sampled at the lava lake  
 1292 from the Vetreny Belt represent the value of unaltered basalt.

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1295 **Figure 7. A** - The  $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$  coordinates show that modern oceanic epidotes plot in the region  
 1296 between the seawater values and fluids fully exchanged with mid-ocean ridge basalt (MORB).  
 1297 The linearized notation  $\delta^{18}\text{O} = 10^3 \ln(1 + \delta^{18}\text{O}/1000)$  is adopted. The Vetreny Belt epidotes plot in  
 1298 the same region deviating towards slightly lower  $\delta^{18}\text{O}$  fluids suggesting seawater of around -2  
 1299 ‰. The fresh unaltered basalt values are shown with the box and the corresponding high-  
 1300 temperature equilibrium fluid is shown with a cross. **B** – Modern oceanic epidotes and fluids  
 1301 (fluid values are from Bach and Humphris, 1999) plotted in  $\delta^{18}\text{O}$ - $^{87}\text{Sr}/^{86}\text{Sr}$  coordinates. Dual-  
 1302 porosity model outputs with different fracture spacings are shown with green and orange lines (1  
 1303 and 10 m, respectively). The system's  $\text{Sr}_{\text{rock}}/\text{Sr}_{\text{fluid}}$  ratio is 16 defined by modern-day  
 1304 concentrations of seawater and MORB. **C** – The Vetreny Belt epidote plotted in the same  
 1305 coordinates, with the dual-porosity model shown for a system in which the concentration ratio  
 1306  $\text{Sr}_{\text{rock}}/\text{Sr}_{\text{fluid}} = 1$ . The grey-concentric region shows the output of the Monte-Carlo (MC)

1307 simulations. The dotted lines show the limits of the equilibrium epidote compositions, i.e.  
1308  $\delta^{18}\text{O}_{\text{epidote}} - \delta^{18}\text{O}_{\text{water}}$  and envisioned  $\Delta^{17}\text{O}_{\text{epidote}} - \Delta^{17}\text{O}_{\text{water}}$ , based on the temperature range 250-400  
1309 °C (fractionation factor for  $^{18}\text{O}/^{16}\text{O}$  from Zheng, 1993). The error bars denote single grain  
1310 analyses with 1 standard error. The vent fluids plotted with bars denoting the range of values  
1311 reported in (Bach and Humphris, 1999). **D** and **E** – Modern and ancient epidote samples are  
1312 plotted in  $\Delta^{17}\text{O} - ^{87}\text{Sr}/^{86}\text{Sr}$  coordinates.

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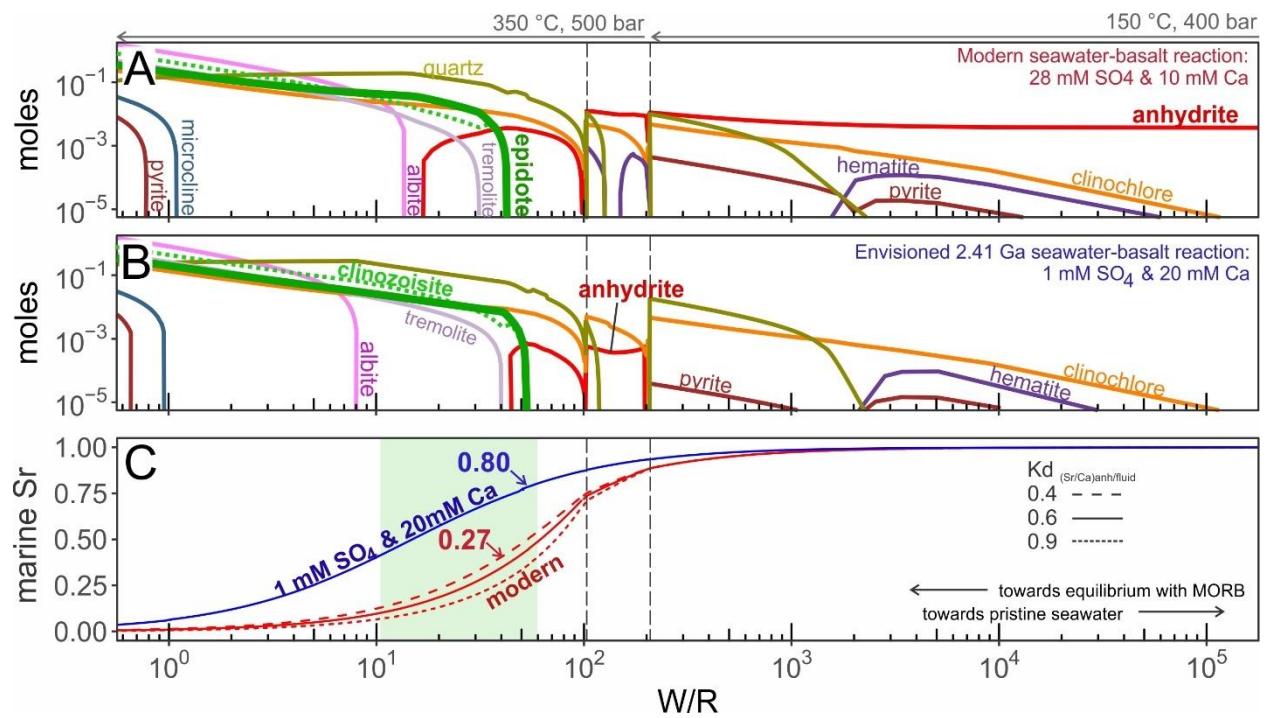
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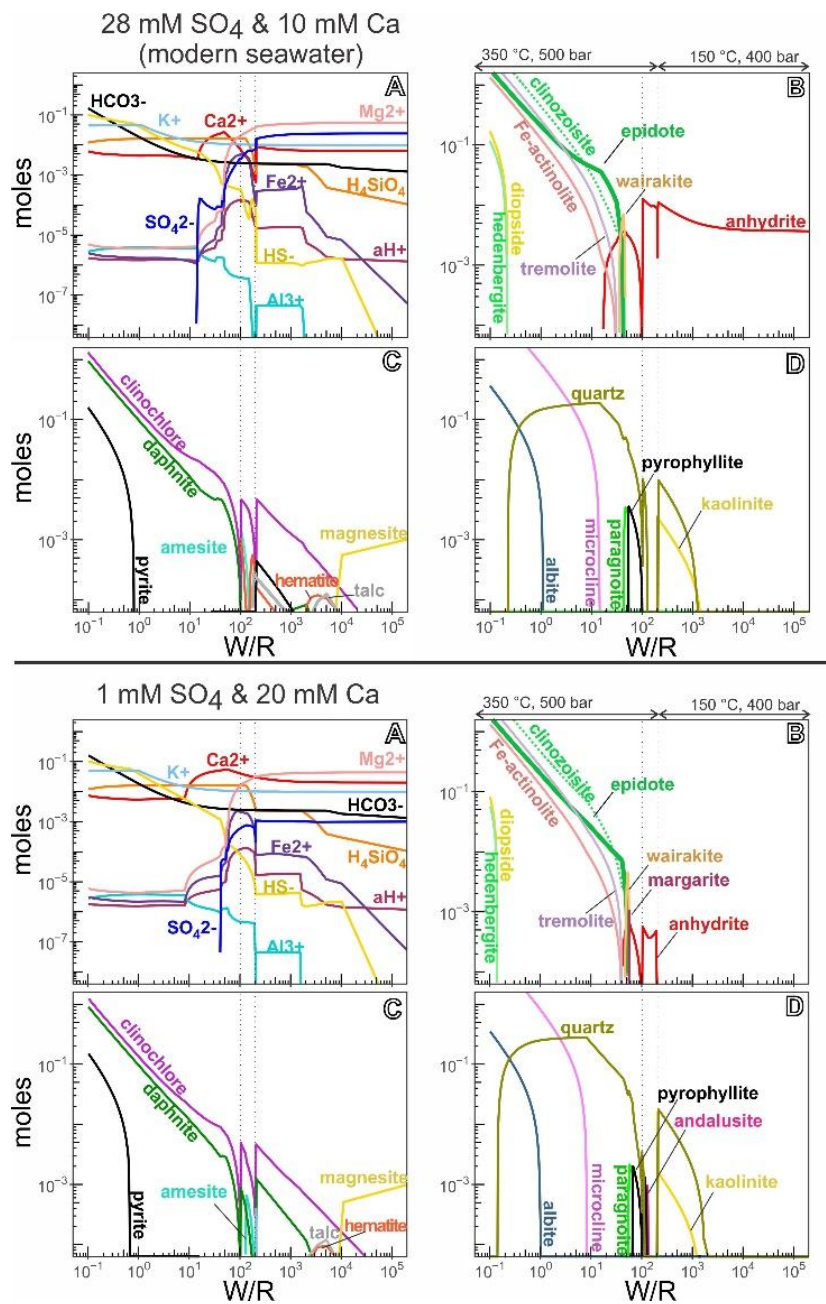
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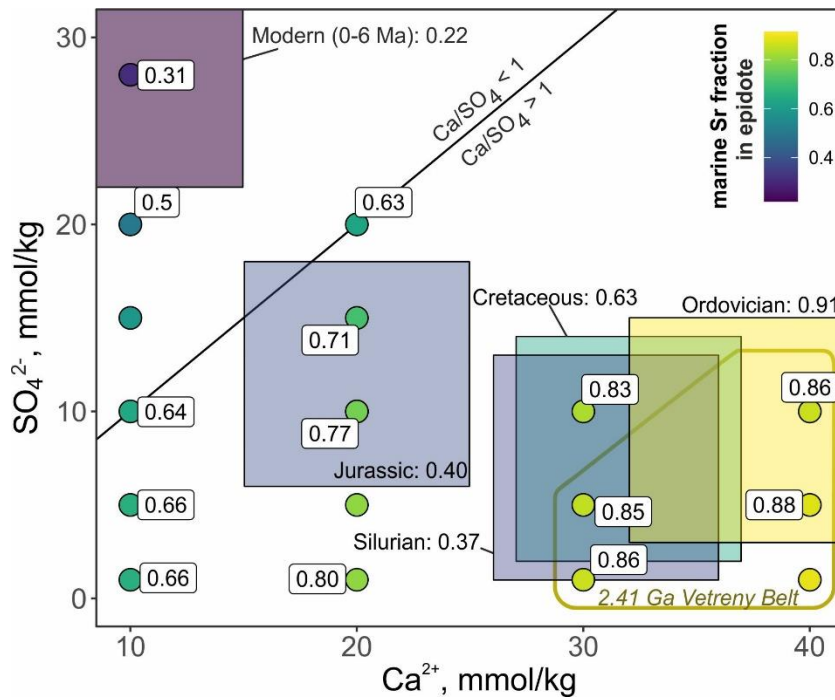
1333 **Figure 8.** Selected equilibrium mineral assemblages shown as a function of as seawater-basalt  
 1334 reaction at different water/rock (W/R) mass ratios. The calculation is carried out using the  
 1335 program CHIM-XPT (Reed et al., 2010) following the procedure outlined in Section 2.5 (*first*  
 1336 *set*). The modern seawater-basalt reaction is shown in panel (A) yielding an abundance of  
 1337 anhydrite around  $10^{-2}$  moles at high W/R. The low sulfate seawater-basalt reaction as envisioned  
 1338 at 2.41 Ga (B) exhibits considerably lower concentrations of equilibrium anhydrite ( $\sim 10^{-3}$  moles)  
 1339 at limited W/R of around 35-110. The vertical dashed lines indicate W/R ratios where  
 1340 fractionation of minerals from fluid was invoked in the calculation. C – Corresponding Sr-  
 1341 isotope shifts calculated using the Sr-Ca-partition coefficient in anhydrite  $K_D$  (see Eqs. 3 and 4).  
 1342 The isotope ratio is shown as the fraction of marine Sr, i.e.  $[\frac{87}{86}\text{Sr}/\frac{86}{86}\text{Sr}_{\text{fluid}} - \frac{87}{86}\text{Sr}/\frac{86}{86}\text{Sr}_{\text{basalt}}]/$   
 1343  $[\frac{87}{86}\text{Sr}/\frac{86}{86}\text{Sr}_{\text{sw}} - \frac{87}{86}\text{Sr}/\frac{86}{86}\text{Sr}_{\text{basalt}}]$ . The  $\frac{87}{86}\text{Sr}/\frac{86}{86}\text{Sr}_{\text{sw}} = 1$  denoting Sr-isotope composition of pristine  
 1344 seawater.



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1346 **Figure 9.** Result of the seawater-basalt equilibrium reaction calculations shown in Figure 8 with  
 1347 the complete list of aqueous and mineral species including their solid solutions. Total molalities  
 1348 of aqueous component species are shown in panels A with the exception of sodium and chlorine  
 1349 that stay almost unchanged. **B** – molar abundances of Ca-bearing minerals, including anhydrite  
 1350 and epidote. **C** - molar abundance of equilibrium Fe/Mg-bearing minerals from the same  
 1351 calculation. **D** - Molar abundance of equilibrium aluminosilicate minerals and quartz in the same  
 1352 calculation.

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1355 **Figure 10.** The outputs of seawater-basalt reaction calculations plotted as a function of marine  
 1356 Ca and SO<sub>4</sub> concentrations. Each color-coded point represents the <sup>87</sup>Sr/<sup>86</sup>Sr value of epidote  
 1357 produced in our calculations relative to the initial seawater value (pure seawater <sup>87</sup>Sr/<sup>86</sup>Sr = 1).  
 1358 Some points are labeled with numbers representing the fraction of marine Sr. The solid black  
 1359 line depicts seawater composition with Ca/SO<sub>4</sub> = 1. The large squares represent the estimated Ca  
 1360 and SO<sub>4</sub> concentrations of Phanerozoic seawater, color-coded by the <sup>87</sup>Sr/<sup>86</sup>Sr values of oceanic  
 1361 epidotes from contemporaneous ophiolites (see Fig. 2 and references within the caption). The  
 1362 highest fraction of marine Sr measured in epidote from Phanerozoic ophiolites is indicated (e.g.  
 1363 91% in an Ordovician ophiolite; Turchyn et al., 2013). The Vetreny Belt epidote records ~90 %  
 1364 marine Sr (shown as outlined field) and is most consistent with a very high Ca/SO<sub>4</sub> ratio of the  
 1365 2.41 Ga seawater.

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**Table 1.** Ranges of values used in the Monte Carlo simulation of dual porosity model

Variable	Minimum	Maximum	Units	Sources
$b$ , fracture spacing	1	10	m	DePaolo, 2006
$R$ , dissolution-precipitation rate	0.00005	0.0002	$\text{g g}^{-1} \text{ year}^{-1}$	DePaolo, 2006; Kadko et al., 2007
$v_f$ , fluid velocity	1	100	$\text{m yr}^{-1}$	Hayba and Ingebritsen, 1997
$\phi$ , matrix porosity	0.01	0.02	none	Becker, 1985

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**Table 2.** Molal concentrations of solutes in initial seawater and weight percent oxides of basaltic rock used in the mineral-aqueous equilibrium calculations.

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Ion	Concentration in modern seawater (mmol/kg)	Envisioned 2.43-2.41 Ga seawater	Initial basalt composition expressed in	Weight %
$\text{Cl}^-$	550	604*		
$\text{SO}_4^{2-}$	28	1	$\text{H}_2\text{O}$	0.21
$\text{HCO}_3^-$	2.3	-	$\text{CO}_2$	0.70
$\text{HS}^-$	$3.0 \cdot 10^{-8}$	-	$\text{FeS}$	0.30
$\text{H}_4\text{SiO}_4$	0.11	-	$\text{SiO}_2$	50.49
$\text{Al}^{3+}$	$3.0 \cdot 10^{-3}$	-	$\text{Al}_2\text{O}_3$	15.48
$\text{Ca}^{2+}$	10	20	$\text{CaO}$	11.52
$\text{Mg}^{2+}$	55	45	$\text{MgO}$	7.84
$\text{Fe}^{2+}$	$5.4 \cdot 10^{-3}$	-	$\text{FeO/Fe}_2\text{O}_3$	7.98/1.25
$\text{K}^+$	10	-	$\text{K}_2\text{O}$	0.18
$\text{Na}^+$	469	-	$\text{Na}_2\text{O}$	2.70
$\text{Sr}^{2+}$	$87 \cdot 10^{-3}$	$160 \cdot 10^{-3}$	$\text{Sr}$	200 ppm

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\* - chlorinity of seawater was adjusted to maintain neutral charge balance

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**Table 3.** Results of the fluid inclusion LA-ICP-MS measurements reported as ratios relative to Na concentration. The number of fluid inclusions within each measured assemblage is shown as # FI. Only samples with signals above detection limits are shown.

Sample	# FI	Li/Na	B/Na	Mg/Na	Al/Na	Cl/Na	K/Na	Ca/Na	Mn/Na	Fe/Na	Cu/Na	Zn/Na	Br/Na	Rb/Na	Sr/Na	Cs/Na	Ba/Na	Pb/Na
GO22-1	3		0.0017	0.0028		1.91	0.18	0.43	0.0027	0.042	0.0047			0.00031	0.0027	0.00007	0.0034	
GO22-1	3		0.0048	0.0004	0.0044	1.82	0.11	0.21	0.0015		0.0032		0.0063	0.00014	0.0013	0.00004	0.0020	0.00005
GO22-2	3		0.0030	0.0003		1.82	0.11	0.65	0.0013	0.013	0.0039	0.0008	0.0060	0.00013	0.0027	0.00003	0.0038	0.00018
GO22-2	6	0.0010	0.0021	0.0068	0.1506	1.72	0.12	0.52	0.0034	0.022	0.0074		0.0022	0.00018	0.0035	0.00005	0.0100	0.00012
GO22-2	4	0.0017	0.0028	0.0011	0.0635	1.88	0.12	0.57	0.0047	0.025	0.0098	0.0048	0.0030	0.00018	0.0040	0.00002	0.0115	0.00024
GO22-2	4		0.0038	0.0010	0.0706	2.74	0.17	0.58	0.0046	0.030	0.0077		0.0028	0.00024	0.0049	0.00005	0.0148	0.00011
GO22-3	3		0.0044	0.0016	0.0020	2.75	0.15	1.14	0.0092	0.023	0.0126		0.0224	0.00035	0.0081		0.0121	
GO22-3	3	0.0014	0.0042	0.0010	0.0010	2.64	0.25	0.76	0.0119	0.044	0.0138	0.0003	0.0106	0.00035	0.0069	0.00003	0.0323	0.00018
GO22-3	5	0.0047	0.0039	0.0009	0.0277	3.05	0.23	0.75	0.0162	0.050	0.0072		0.0259	0.00023	0.0087		0.0409	0.00088
GO22-3	4	0.0034	0.0040	0.0033	0.2203	1.92	0.25	0.77	0.0153	0.067	0.0078	0.0031	0.0076	0.00032	0.0066		0.0452	0.00121
VB8A-chip2-1	2	0.0009	0.0060	0.0022	0.0076	3.44	0.18	1.89	0.2056	0.247		0.0593	0.2358	0.00010	0.0887	0.00023	0.1474	0.05665
VB8A-chip2-1	6	0.0013	0.0021	0.0039	0.0136	4.11	0.21	1.43	0.1136	0.119		0.0423	0.3190	0.00046	0.0800	0.00039	0.1171	0.03927
VB8A-chip2-1	4		0.0056			3.46	0.11	1.30	0.1346	0.078		0.0405	0.2141	0.00026	0.0824	0.00038	0.1300	0.03667
VB8A-chip2-1	3	0.0005	0.0053			3.18	0.19	1.15	0.1621	0.174	0.0002	0.0315	0.2372	0.00049	0.0761	0.00038	0.0785	0.04671
VB8A-chip2-2	4			0.0067		3.40	0.23	1.31	0.1868	0.209		0.0445	0.2243	0.00059	0.1116	0.00052	0.1316	0.03338
VB8A-chip2-2	3		0.0091			6.02	0.37	2.65	0.1494	0.196		0.0427	0.4696	0.00187	0.1016	0.00103	0.1918	0.05110
VB8A-chip2-2	7		0.0042	0.0024	0.0046	2.79	0.23	1.32	0.0768	0.107		0.0214	0.1585	0.00069	0.0516	0.00034	0.0893	0.02019
VB8A-chip2-2	4	0.0067	0.0044	0.0054	0.0038	3.09	0.28	1.62	0.0898	0.110	0.0010	0.0229	0.1341	0.00078	0.0739	0.00037	0.0792	0.02199
VB8A-chip2-3	5		0.0048			3.14	0.14	1.28	0.1125	0.099		0.0357	0.2150	0.00040	0.0833	0.00040	0.1122	0.02913
VB8A-chip2-3	4		0.0051	0.0017	0.0099	3.56	0.13	1.67	0.1396	0.140	0.0011	0.0428	0.3146	0.00063	0.1138	0.00048	0.1463	0.04091
VB8A-chip2-3	3	0.0027	0.0020			3.97	0.29	1.87	0.1629	0.284		0.0587	0.4004	0.00149	0.1289	0.00053	0.1606	0.06562
VB8A-chip3	3	0.0426	0.0074			4.12	0.28	2.10	0.1973	0.166		0.0536	0.3229	0.00145	0.1335	0.00073	0.1710	0.05080
VB8A-chip3	2	0.0159	0.0032	0.0051		3.46	0.41	1.80	0.2687	0.279		0.0519	0.2450	0.00133	0.1526	0.00077	0.2726	0.04762

**Table 4.** Results of the fluid inclusion LA-ICP-MS measurements reported as concentrations in  $\mu\text{g/g}$  calculated based on the average salinity of the fluid inclusions measured in each sample.

Sample	# FI	Li	B	Na	Mg	Al	Cl	Br	K	Ca	Mn	Fe	Cu	Zn	Br	Rb	Sr	Cs	Ba	Pb
GO22-1	3		202	118163	328		225763	0	21703	50828	317	4987	560			36	315	7.9	406	
GO22-1	3		639	132169	52	582	240900	837	14836	28325	194		419		837	19	167	4.9	266	6.5
GO22-2	3		350	118280	36		215276	712	13260	76672	152	1553	465	100	712	15	324	3.6	451	21
GO22-2	6	116	248	118607	808	17865	203494	259	13950	61797	409	2588	874		259	22	412	6.5	1191	14
GO22-2	4	187	310	110728	119	7035	208034	336	13253	63295	520	2752	1089	531	336	20	441	2.6	1270	26
GO22-2	4		413	109135	113	7705	298996	300	18580	63438	501	3250	845		300	26	537	5.1	1610	12
GO22-3	3		399	90430	140	180	248253	2030	13364	103041	835	2087	1140		2030	32	729		1096	
GO22-3	3	135	410	97271	100	99	256936	1033	24546	73886	1153	4300	1340	32	1033	34	670	2.7	3138	17
GO22-3	5	537	449	114205	107	3159	348855	2958	26771	85421	1856	5678	817		2958	26	996		4674	101
GO22-3	4	331	385	97317	325	21441	186946	744	24230	75180	1492	6561	760	302	744	31	645		4402	118
VB8A-chip2-1	2	52	361	60394	130	460	207918	14241	10983	114214	12415	14903		3581	14241	6	5357	14	8902	3421
VB8A-chip2-1	6	97	153	73142	288	996	300839	23336	15052	104458	8310	8733		3096	23336	34	5853	29	8568	2872
VB8A-chip2-1	4		437	78048			270096	16712	8882	101551	10503	6091		3158	16712	21	6429	30	10149	2862
VB8A-chip2-1	3	42	409	76754			244461	18207	14819	88446	12438	13356	18	2419	18207	38	5840	29	6025	3585
VB8A-chip2-2	4			72370	484		245955	16236	16492	94693	13519	15143		3219	16236	43	8077	38	9524	2416
VB8A-chip2-2	3		462	50978			307021	23939	18956	134867	7614	10011		2179	23939	95	5181	52	9779	2605
VB8A-chip2-2	7		324	76597	181	351	213893	12141	17747	100736	5885	8176		1642	12141	53	3952	26	6839	1546
VB8A-chip2-2	4	485	319	71840	387	271	222330	9632	20360	116479	6454	7910	71	1648	9632	56	5306	26	5690	1580
VB8A-chip2-3	5		417	86570			271896	18609	11785	110829	9737	8535		3091	18609	35	7211	34	9710	2522
VB8A-chip2-3	4		380	75028	128	741	266756	23601	9616	125195	10476	10507	82	3211	23601	47	8537	36	10974	3070
VB8A-chip2-3	3	190	141	70152			278367	28090	20363	131198	11426	19926		4116	28090	104	9043	37	11270	4603
VB8A-chip3	3	2712	473	63598			262249	20537	17785	133525	12548	10556		3409	20537	92	8492	47	10874	3231
VB8A-chip3	2	1011	203	63405	324		219532	15537	25973	114396	17040	17676		3290	15537	85	9674	49	17284	3019



**Table 5.** Strontium isotope data for the modern oceanic epidotes and the Vetreny Belt rocks.

Sample	Description	Rb, ppm	Sr, ppm	Rb/Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr measured	<sup>87</sup> Sr/ <sup>86</sup> Sr initial		± 1se
<b>Vetreny Belt rocks</b>								
						at 2.41 Ga	at 2.43 Ga	
12106	fresh basalt	24.3	390	0.062	0.70783	0.70155		0.00069
12124	fresh basalt	15.9	224	0.071	0.70868	0.70152		0.00071
12101	fresh basalt	15.9	259	0.061	0.70705	0.70086		0.00069
<i>Altered basalt lithologies</i>								
VB16	altered pillow rind	bdl <sup>1</sup>	17	<0.059	0.70428			
VB16 duplicate	altered pillow rind				0.70423			
VB25	altered basalt	7.4	250	0.030	0.70643	0.70345		0.00029
VB9	altered pillow rind	1.6	50	0.032	0.70739	0.70416		0.00033
My1	altered basalt (hyaloclastite)	4.3	231	0.019	0.70603	0.70416		0.00020
GO25	altered basalt	15.2	297	0.051	0.70803	0.70287		0.00069
<i>Epidote separates</i>								
GO22	epidote	bdl	1053	<0.001	0.70360	0.70360		0.00003
GO4	epidote	bdl	2350	<0.001	0.70288	0.70288		0.00003
VB24	epidote	bdl	627	<0.001	0.70394	0.70394		0.00003
VB8A	epidote	bdl	2862	<0.001	0.70423	0.70422		0.00003
<i>Carbonates from underlying Kozhozero suite</i>								
02-08-04	carbonate	10.7	665	0.016	0.70625	0.70463	0.70462	0.00016
02-08-03	carbonate	1.9	342	0.006	0.70510	0.70454	0.70453	0.00004
<b>Modern oceanic epidotes from Reykjanes drilling wells (RN12 and 17B), and from Ocean Drilling Project Site 504B (Leg 83)</b>								
						at 0-6 Ma		
RN12 1070	epidote	bdl	921	<0.001	0.704691	0.70469		0.00003
RN17B 2805.5	epidote	bdl	729	<0.001	0.703859	0.70386		0.00003
RN17B 2899.75	epidote	bdl	617	<0.001	0.703953	0.70395		0.00003
83-90R_148-149	epidote	bdl	1060	<0.001	0.703834	0.70383		0.00003
83-90R_71-72	epidote	bdl	247	<0.001	0.70395	0.70395		0.00003

1 – The Rb concentrations below the detection limit (bdl) of ~1ppm result in very low Rb/Sr ratios and negligible corrections for the <sup>87</sup>Sr/<sup>86</sup>Sr<sub>initial</sub> values (within analytical uncertainty). However, for sample VB16, the low Sr concentration results in a relatively large uncertainty of <sup>87</sup>Sr/<sup>86</sup>Sr<sub>initial</sub> (not reported).

**Table 6.**  $\delta^{18}\text{O}$  values of unaltered komatiitic basalt from the lava lake and altered gabbros from Ruiga layered intrusion. Carbon and oxygen isotope values are provided for the carbonates of the underlying Kozhozero suite

Sample	Material analyzed	$\delta^{18}\text{O}$ ‰, VSMOW	$\delta^{18}\text{O}$ ‰, VPDB	$\delta^{13}\text{C}$ ‰, VPDB
12105*	unaltered basalt	5.6		
RU3	altered gabbro	1.1		
RU4	amphibole	1.0		
RU5	altered gabbro	1.9		
RU6	altered gabbro	3.0		
RU8	amphibole	1.2		
RU10	amphibole	2.1		
RU11	amphibole	-0.7		
S02-08-3	carbonate		-27.9	-0.95
S02-08-04	carbonate		-28.4	-1.38

\* - sample from (Puchtel et al., 1996);