

**Calcium carbonate veins in ocean crust record a threefold increase of seawater Mg/Ca in the past 30 Million years**

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Abstract: Chemical (Sr, Mg) and isotopic ( $\delta^{18}\text{O}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ) compositions of calcium carbonate veins (CCV) in the oceanic basement were determined to reconstruct changes in Sr/Ca and Mg/Ca of seawater in the Cenozoic. We examined CCV from ten basement drill sites in the Atlantic and Pacific, ranging in age between 165 and 2.3 Ma. Six of these sites are from cold ridge flanks in basement <46 Ma, which provide direct information about seawater composition. CCV of these young sites were dated, using the Sr isotopic evolution of seawater. For the other sites, temperature-corrections were applied to correct for seawater-basement exchange processes. The combined data show that a period of constant/low Sr/Ca (4.46 - 6.22 mmol/mol) and Mg/Ca (1.12 - 2.03 mol/mol) between 165 and 30 Ma was followed by a steady increase in Mg/Ca ratios by a factor of three to modern ocean composition. Mg/Ca - Sr/Ca relations suggest that variations in hydrothermal fluxes and riverine input are likely causes driving the seawater compositional changes. However, additional forcing may be involved in explaining the timing and magnitude of changes. A plausible scenario is intensified carbonate production due to increased alkalinity input to the oceans from silicate weathering, which in turn is a result of subduction-zone recycling of CO<sub>2</sub> from pelagic carbonate formed after the Cretaceous slow-down in ocean crust production rate.

1           **Calcium carbonate veins in ocean crust record a**  
2           **threefold increase of seawater Mg/Ca in the past 30**  
3           **Million years**  
4

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17  
18   **ABSTRACT**

19   Chemical (Sr, Mg) and isotopic ( $\delta^{18}\text{O}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ) compositions of calcium carbonate  
20   veins (CCV) in the oceanic basement were determined to reconstruct changes in Sr/Ca  
21   and Mg/Ca of seawater in the Cenozoic. We examined CCV from ten basement drill  
22   sites in the Atlantic and Pacific, ranging in age between 165 and 2.3 Ma. Six of these  
23   sites are from cold ridge flanks in basement <46 Ma, which provide direct information  
24   about seawater composition. CCV of these young sites were dated, using the Sr  
25   isotopic evolution of seawater. For the other sites, temperature-corrections were  
26   applied to correct for seawater-basement exchange processes. The combined data

27 show that a period of constant/low Sr/Ca (4.46 – 6.22 mmol/mol) and Mg/Ca (1.12 –  
28 2.03 mol/mol) between 165 and 30 Ma was followed by a steady increase in Mg/Ca  
29 ratios by a factor of three to modern ocean composition. Mg/Ca - Sr/Ca relations  
30 suggest that variations in hydrothermal fluxes and riverine input are likely causes  
31 driving the seawater compositional changes. However, additional forcing may be  
32 involved in explaining the timing and magnitude of changes. A plausible scenario is  
33 intensified carbonate production due to increased alkalinity input to the oceans from  
34 silicate weathering, which in turn is a result of subduction-zone recycling of CO<sub>2</sub> from  
35 pelagic carbonate formed after the Cretaceous slow-down in ocean crust production  
36 rate.

37

## 38 **KEYWORDS**

39 seawater evolution; mid-ocean ridges; hydrothermal circulation; carbonate veins

40

## 41 **1. INTRODUCTION**

42 Circulation of seawater through the flanks of mid-ocean ridges has profound  
43 effects on the chemistry of both seawater and crust and is a principal mechanism of  
44 cooling the lithosphere. Seawater-crust exchange budgets have been derived from the  
45 rock record (e.g., Alt and Teagle, 1999, 2003; Bach et al., 2003) and from ridge flank  
46 fluid compositions (Elderfield et al., 1999; Wheat and Mottl, 2000). Vein minerals in  
47 basaltic crust provide a stepping-stone between the two approaches, as they allow the  
48 reconstruction of element ratios in the seawater-derived fluids from which they  
49 precipitated. This approach has been validated by Coggon et al. (2004), who showed  
50 that fluid parameters (Sr isotope ratios, Mg/Ca, Sr/Ca, and temperature) can be  
51 derived from ridge-flank calcium carbonate veins (CCV) and demonstrated that trends

52 derived from the CCV compositions closely match those seen in basement fluid  
53 compositions (Elderfield et al., 1999). If the exchange between seawater and crust is  
54 faithfully recorded in CCV, they can be used to reconstruct past seawater  
55 compositions by extrapolating to past seawater temperatures. Coggon et al. (2010)  
56 were the first ones to make use of the CCV archive. They proposed that Mg/Ca and  
57 Sr/Ca were uniform throughout the period between 170 and 24 Ma and then both  
58 ratios increased by a factor of about three to present-day seawater composition. The  
59 threefold increase in Mg/Ca Coggon et al. (2010) reported is matched by similar  
60 change in the combined data from calcareous fossils (Dickson, 2002; Lear et al.,  
61 2002) and halite-hosted fluid inclusions (Horita et al., 2002; Lowenstein et al., 2003;  
62 Timofeeff et al., 2006). These records yield results that differ from reconstructions  
63 based on foraminiferal test (Creech et al., 2010; Broecker and Yu, 2011). Also, the  
64 temporal change Coggon et al. (2010) reconstructed for Sr/Ca differs from that  
65 derived from fossils (Lear et al., 2003; Steuber and Veizer, 2002). In general we see  
66 that data derived from fossils can lead to controversial results. Broecker and Yu  
67 (2011) discussed that the temperature extrapolation required for the young basement  
68 sites in the data set presented by Coggon et al. (2010) introduces considerable  
69 uncertainties in the calculation of Mg concentrations of past seawater. Another  
70 shortcoming in the existing CCV data set is that few data are available for the critical  
71 period of seawater compositional change in the Late Cenozoic.

72 Our study was specifically focused on obtaining a CCV record from cold ridge  
73 flank sites in young crust. We present Sr/Ca and Mg/Ca reconstructions for ten drill  
74 sites, of which six are in crust younger than 50 Ma and from three sites CCV had not  
75 been investigated before. The new data corroborate the earlier findings and indicate a  
76 steady increase in Mg/Ca in the past 30 Ma. The Sr/Ca increase, however, is less

77 pronounced in the CCV record, when the effect of Mg content of calcite on Sr  
78 partitioning is considered (Mucci and Morse, 1983).

79

## 80 **2. METHODS AND MATERIALS**

81 Carbonate veins from eleven drill sites in the Atlantic and Pacific were  
82 investigated (Fig. 1). Samples of carbonate veins were obtained by micro-drilling or  
83 handpicking from crushed core material. Sr/Ca and Mg/Ca ratios were analyzed by  
84 inductively coupled plasma optical emission spectrometry (ICP-OES) at IFM-  
85 GEOMAR in Kiel with a precision of 3% and 5%, respectively (2 standard deviations  
86 (sd), based on repeated measurement of standards).

87  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios were determined by thermal ionisation mass spectrometry  
88 (TIMS) with a Finnigan Triton TI at IFM-GEOMAR. The Sr isotope standard NIST  
89 SRM987, normalized to a  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of 0.11940, was measured with a  $^{87}\text{Sr}/^{86}\text{Sr}$   
90 ratio of 0.710216(14) (2sd, n = 15). The measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were corrected to a  
91 SRM987 value of 0.710248 to allow direct comparison with the Strontium Isotope  
92 Stratigraphy (McArthur and Howarth 2004). Basement ages were determined from  
93 magnetostratigraphy, using the geological time scale of Gradstein et al. (2004).

94 A subset of the samples was analyzed in-situ for Mg/Ca and Sr/Ca by laser  
95 ablation ICP-MS using a Thermo Element2 and a NewWave UP193ss at the  
96 Department of Geosciences in Bremen. Samples and standards were ablated with an  
97 irradiance of  $\sim 1 \text{ GW}/\text{cm}^2$ , a beam diameter of typically 75  $\mu\text{m}$  and a pulse rate of 5  
98 Hz. Helium was used as carrier gas and argon was added as make-up gas. For external  
99 calibration we used the glass standard reference materials (SRM) NIST610 for Mg  
100 and Sr using the composition according to Pearce et al. (1997). For data quantification  
101 we used the Cetac GeoPro™ software with Ca as internal standard (40 wt.% in

102 carbonates) and the SRM values of Pearce et al. (1997). Analytical precision and  
103 accuracy were controlled by regular analyses of the SRM BCR2-G (basaltic glass;  
104 Jochum et al. 2005) and NIES22 (otolith powder; Yoshinaga et al. 2000). Accuracy is  
105 better than 5% for Mg/Ca and 1% for Sr/Ca for NIES22, and better than 3% and 7%,  
106 respectively, for BCR2-G. Overall precision and accuracy are better than 4% for  
107 Mg/Ca and Sr/Ca.

108 O and C isotopic compositions were determined by gas-source mass spectrometry  
109 at IFM-GEOMAR in Kiel and at MARUM in Bremen with a Finnigan MAT 252 and  
110 MAT 251, respectively. The reproducibility (2sd) is  $< 0.05\text{‰}$  for  $\delta^{13}\text{C}$  and  $< 0.07\text{‰}$   
111 for  $\delta^{18}\text{O}$ . An internal standard (Solnhofener Plattenkalk) was calibrated against  
112 NBS19 for calculation of delta values relative to V-PDB.

113

### 114 **3. RESULTS**

115 Carbonate formation temperatures calculated from  $\delta^{18}\text{O}$  values (-7.53 – 4.01 for  
116 calcites and 1.86 – 4.48 for aragonites) range from 1 – 50 °C (Table S1). The data  
117 indicate that younger samples precipitated from colder water while for older samples  
118 higher formation temperatures are found. These relatively high temperatures can  
119 either be explained by warmer deep-sea water during the Cretaceous or by carbonate  
120 recrystallisation after initial formation.

121 The investigated CCV have Mg/Ca ratios of 0.3 – 67.9 mol/mol and Sr/Ca ratios  
122 of 0.01 – 0.5 mmol/mol (Table S1). Both ratios show a negative correlation with the  
123 calculated formation temperature for sites with CCV formed at elevated temperatures  
124 (Fig. 2). The negative correlation of Mg/Ca and T reflects uptake of Ca and depletion  
125 of Mg during basement-seawater interaction at elevated temperatures ( $>25^\circ\text{C}$ ; e.g.,  
126 Elderfield et al., 1999). Coggon et al. (2004) showed that carbonate veins from the

127 Juan de Fuca Ridge flank reveal a systematic trend in Mg/Ca vs. Sr/Ca plots  
128 Specifically, Mg/Ca ratios of carbonate veins correlate with formation temperature  
129 and hence the temperature-dependent intensity of exchange with basement (Coggon et  
130 al. 2004). Carbonate veins can therefore be used to reconstruct the Mg/Sr evolution of  
131 seawater, if exchange with basement can be accounted. Carbonate veins unaffected by  
132 exchange with basement (i.e., seawater-like Sr isotopic compositions, ambient deep  
133 sea temperatures of formation) provide direct information about seawater  
134 composition.

135 For retrieving past seawater Sr/Ca and Mg/Ca ratios from CCV analyses we  
136 modified the approach of Coggon et al. (2010). First, formation temperatures of the  
137 CCV were calculated from their  $\delta^{18}\text{O}$  values using the empirical calibrations from  
138 Böhm et al. (2000) for aragonite and Friedman and O'Neil (1977) for calcite, and  
139  $\delta^{18}\text{O}$  of past seawater with -0.5 ‰ for samples younger than 15 Ma, and -1 ‰ for all  
140 older samples (Muehlenbachs, 1998; Billups and Schrag, 2002). Second, the  
141 temperature-dependent Sr/Ca and Mg/Ca distribution coefficients between seawater  
142 and CCV were calculated using the calibrations by Gaetani and Cohen (2006) for  
143 aragonite

$$144 \quad K_D(\text{Sr/Ca}) = \exp(605/T - 1.89), \quad (\text{Eq. 1})$$

145 (all temperatures, as well as in the following equations are given in Kelvin)

146 and Rimstidt et al. (1998) for Mg in calcite

$$147 \quad \log K_D(\text{Mg/Ca}) = 4.436 - (1348/T) - 0.005339 T. \quad (\text{Eq. 2}).$$

148 Results from precipitation experiments with inorganic and biogenic calcite at constant  
149 temperature indicate a non-linear (power law) dependency of  $K_D(\text{Mg/Ca})$  on  
150  $(\text{Mg/Ca})_{\text{fluid}}$  (Füchtbauer and Hardie, 1976; Mucci and Morse, 1983; Ries, 2004).  
151  $K_D(\text{Mg/Ca})$  data calculated after Ries (2004) are in overall agreement with data



152 derived using the approach of Rimstidt et al. (1998); we used the latter to allow  
153 comparison with data from Coggon et al. (2010).

154 The temperature dependency of Sr partitioning into calcite is not particularly well-  
155 constrained and hence theoretical (Rimstidt et al., 1998)

$$156 \quad \text{Log } K_D(\text{Sr/Ca}) = -1.874 + (179.2/T) + 0.0006248 T \quad (\text{Eq. 3})$$

157 and empirical (Malone and Baker, 1999)

$$158 \quad K_D(\text{Sr/Ca}) = 0.0001332 (T - 273.16) + 0.04366 \quad (\text{Eq. 4})$$

159 calibrations were used to calculate partition coefficients, and the average of the two  
160 was employed in calculating Sr/Ca of fluids (cf. Coggon et al., 2010).

161 Third, we used the relation provided by Carpenter and Lohmann (1992) to  
162 determine the effect of Mg incorporation in calcite on Sr partitioning between fluid  
163 and calcite. This relation employs experimental data from Mucci and Morse (1983)

$$164 \quad K_D(\text{Sr/Ca}) = 3.5 \cdot 10^{-6} \text{ Mg (ppm)} + 0.0062 \quad (\text{Eq. 5})$$

165 demonstrating a major role of Mg incorporation in the calcite crystal lattice on the  
166 Sr/Ca exchange reactions between fluid and calcite.

167 Fully considering the effects of both temperature and Mg-content on Sr partitioning in  
168 a single dependency is not possible because of the sparse experimental data.

169 Therefore, in a fourth step, appropriate Sr partitioning coefficients for the calculations  
170 of Sr/Ca in the fluids were chosen, as is shown below. We made use of the  
171 relationships between temperature and Mg-concentrations of ridge flank fluids  
172 discovered by Mottl and Wheat (1994) who synthesized data compiled from different  
173 ridge flank systems. These authors showed that the Mg concentrations in fluids from  
174 the upper basement at ridge flanks decreases rapidly above 25°C. A similar  
175 relationship has later been documented for a ridge axis-perpendicular transect of drill  
176 holes in the eastern Juan de Fuca Ridge flank system (Elderfield et al., 1999). In order

177 to test whether the effect of Mg content on calcite Sr/Ca partitioning can be neglected  
178 at increased temperatures, we compared published calcite Sr/Ca (Coggon et al., 2004)  
179 data to calculated Sr/Ca from fluid data from the Juan de Fuca Ridge (Davis et al.,  
180 1997; Mottl et al., 2000) considering the effects of temperature and Mg separately.  
181 Figure 3 shows that considering only temperature dependencies of Sr partitioning  
182 underestimates Sr/Ca at  $T < 30^{\circ}\text{C}$ , while the match between predicted and observed  
183 Sr/Ca is satisfying for  $T > 30^{\circ}\text{C}$ . We hence use the temperature derived from O  
184 isotope compositions to decide which of the two sets of Sr partitioning data to use.  
185 Below  $30^{\circ}\text{C}$ , we consider the Mg-effect to dominate, while at  $T > 30^{\circ}\text{C}$  the Mg-effect  
186 is considered negligible and temperature-effects are assumed to dominate.

187 In a fifth step, data from all CCV from sites older than 80 Ma (417/418, 1149,  
188 and 801) with elevated temperatures were extrapolated to  $10^{\circ}\text{C}$ , using a linear  
189 regression of elemental ratios versus temperature, to account for seawater-basement  
190 exchange (see Figure 2 and Coggon et al. (2010)).  $10^{\circ}\text{C}$  corresponds to temperatures  
191 in the deep-sea reconstructed for the Early Cenozoic and Cretaceous (Zachos et al.,  
192 2001; Huber et al., 2002; Gillis and Coogan, 2011). The remaining six sites, spanning  
193 an age range from 3.5 to 46 Ma, formed at temperatures between 0 and  $7^{\circ}\text{C}$  (Fig. 2),  
194 and a temperature correction was hence not applied.

195 Last, formation ages were determined for samples that have higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios  
196 than seawater at the time the basement formed. The data compilation from McArthur  
197 and Howarth (2004) was used to constrain  $^{87}\text{Sr}/^{86}\text{Sr}$  of seawater through time. This  
198 approach is straightforward for  $\text{CCV} < 38$  Ma, as  $^{87}\text{Sr}/^{86}\text{Sr}$  of seawater has steadily  
199 increased during this period. Similar to Coggon et al. (2010), we found that  
200 extrapolated  $^{87}\text{Sr}/^{86}\text{Sr}$  for CCV from Sites 417/418 in 125 Ma basements are higher  
201 than the  $^{87}\text{Sr}/^{86}\text{Sr}$  of the Barremian Ocean. The CCV were dated at 82 Ma,

202 corresponding to the point in time at which reconstructed seawater composition  
203 (McArthur and Howard, 2004) matches the average extrapolated  $^{87}\text{Sr}/^{86}\text{Sr}$  of the CCV.  
204 Other CCV in Mesozoic basement could not be age-dated and are assumed to be 5 Ma  
205 younger than the magnetostratigraphic basement age. A 5 Ma offset was chosen  
206 because most veining and alteration takes place within the first 10 Ma of crustal  
207 evolution (e.g., Staudigel et al., 1981). Our calculated data for nine drill sites are  
208 summarized in Table 1 and displayed in Figure 4. A detailed table with analyses and  
209 calculation results for all individual samples can be downloaded from the EPSL data  
210 repository (LINK).

211 Figure 4 shows the seawater Mg/Ca and Sr/Ca and respective uncertainties  
212 derived for the different sites, as well as individual vein analyses for the sites in  
213 basement < 50 Ma, for which seawater Sr isotope dating was appropriate. The data  
214 show roughly uniform Mg/Ca (1-2 mol/mol) for seawater between 165 and 30 Ma.  
215 From about 30 Ma on, Mg/Ca strongly increased to the present-day value of 5.4  
216 mol/mol, which was reached a few million years ago. Likewise, the Sr/Ca ratio  
217 showed little variation between ~4-6 mmol/mol in the Mesozoic and Paleogene, and  
218 since 30 Ma increased to the present-day value of ~9 mmol/mol.

219

## 220 **4. DISCUSSION**

### 221 **4.1 Uncertainties in estimating Mg/Ca and Sr/Ca of past seawater**

222 Experimental and empirical studies have shown a range of environmental parameters  
223 that influence partitioning of Sr and Mg in calcite. Variable environmental conditions  
224 may introduce uncertainties to the Mg/Ca and Sr/Ca records that are discussed below,  
225 namely the influences of temperature, pH, and fluid composition. Moreover, the  
226 distribution coefficients required to calculate seawater composition are temperature-

227 dependent and the temperature estimates are sensitive to the  $\delta^{18}\text{O}$  of seawater, which  
228 changed during the transition from the ice-free greenhouse world of the Mesozoic to  
229 the icehouse world of the late Cenozoic. The exact timing of this transition is still not  
230 known. A first major increase in the Antarctic ice mass probably occurred at the  
231 Eocene-Oligocene transition, about 35 Ma ago (Pusz et al., 2011). Regional  
232 differences in seawater  $\delta^{18}\text{O}$  of up to 1‰, introduce additional uncertainties to the  
233  $\delta^{18}\text{O}$  temperature calculations. We estimate the uncertainties due to variations in  
234 seawater  $\delta^{18}\text{O}$  (ice effect and regional variability) to be on the order of  $\pm 3^\circ\text{C}$ . The  
235 Mg-content in the calcites might introduce another source of uncertainty. Tarutani et  
236 al. (1969) showed that oxygen isotope fractionation of high-Mg calcite increases by  
237 about 0.06 ‰ per mol% of  $\text{MgCO}_3$  at  $25^\circ\text{C}$ . Jimenez-Lopez et al. (2004) found a three  
238 times stronger increase of 0.17‰ per mol% of  $\text{MgCO}_3$ . As most of our calcite  
239 samples are low-Mg calcites we did not apply a correction for the  $\text{MgCO}_3$  content.  
240 This may introduce a "cold bias" to our temperature estimates of  $-1.3^\circ\text{C}$  (Tarutani et  
241 al., 1969) to  $-3.6^\circ\text{C}$  (Jimenez-Lopez et al., 2004) for calcite with 5 mol%  $\text{MgCO}_3$ .  
242 With temperature uncertainties on the order of  $\pm 4^\circ\text{C}$ , the resulting uncertainties on the  
243 partition coefficient for Mg/Ca are about  $\pm 10\%$  in equation (2). Several studies have  
244 demonstrated that the  $K_D(\text{Mg}/\text{Ca})$  of calcite also depends on the seawater Mg/Ca ratio  
245 (e.g., Füchtbauer and Hardie, 1976; Mucci and Morse, 1983; Ries, 2004; Hasiuk and  
246 Lohmann, 2010). At  $\text{Mg}/\text{Ca}_{\text{fluid}}$  ratios below about 7 mol/mol the  $K_D$  increases  
247 exponentially with decreasing  $\text{Mg}/\text{Ca}_{\text{fluid}}$ . Hence, the Mg/Ca ratios for Mg-poor  
248 Cretaceous and Jurassic seawater reconstructed with a purely temperature-dependent  
249  $K_D$  may be overestimated by as much as 50%.

250 An important factor for Sr incorporation in calcite is the precipitation rate (Lorenz  
251 1981, Tesoriero and Pankow 1996, Tang et al. 2008). Precipitation rates of calcite in

252 seawater depend predominantly on the carbonate ion concentration (Zuddas and  
253 Mucci, 1994, 1998). Carbonate ions concentration in cold deep-sea water is low, thus  
254 the precipitation rates for CCVs that formed from cold bottom water should be  
255 exceedingly low. Precipitation rates of 0.01 to 10  $\mu\text{mol}/\text{m}^2/\text{h}$  were estimated for  
256 abiogenic shallow water marine calcite cements by Carpenter and Lohmann (1992).  
257 Even higher rates, on the order of  $10^2$  to  $10^3$   $\mu\text{mol}/\text{m}^2/\text{h}$ , are common for biogenic  
258 calcite formation. For those fast precipitation rates, which prevail in trace element  
259 partitioning experiments and during biogenic carbonate precipitation, strong rate-  
260 dependencies have been documented. For instance, Tang et al. (2008) showed that an  
261 increase of the precipitation rate by a factor of 3 increases  $K_D(\text{Sr}/\text{Ca})$  by a factor of  
262 about 1.5:

$$263 \quad K_D(\text{Sr}/\text{Ca}) = 10^{-1.8} * R^{0.319} \quad (\text{Eq. 6})$$

264 (Eq. 6 is recast from equation 6 of Tang et al. (2008) and is valid for  $5^\circ\text{C}$  and for R  
265 ranging from  $10^2$  to  $10^4$   $\mu\text{mol}/\text{m}^2/\text{h}$ .)

266 Precipitation rates of calcite forming in ocean bottom waters most likely increased  
267 during the Cenozoic due to the deepening of the carbonate compensation depth  
268 (CCD), which may have contributed to the observed increase in Sr/Ca ratios of CCV  
269 calcite. Two major deepening events of the CCD occurred during the Cenozoic, the  
270 first during the Eocene-Oligocene transition (EOT) the second during the late  
271 Neogene (van Andel, 1975). Using Li/Ca ratios in benthic foraminifera, a deep ocean  
272  $[\text{CO}_3^{2-}]$  increase of about 30 to 40  $\mu\text{mol}/\text{L}$  was calculated for the EOT (34 to 33 Ma)  
273 in the South Atlantic and equatorial Pacific (Lear and Rosenthal, 2006; Peck et al.,  
274 2010). How sensitive would the Sr/Ca record of calcite be to such an increase in  
275 saturation state in the worst of circumstances?

276 We address this question by applying the dependence of calcite precipitation rates on

277 seawater  $\text{CO}_3^{2-}$  concentration from Zuddas and Mucci (1994, 1998), from which we  
278 estimate the precipitation rate increase for the EOT, using:

$$279 \quad R = 10^{6.24} * [\text{CO}_3^{2-}]^{3.34} \quad (\text{Eq. 7})$$

280 (equation for ionic strength of 0.6, with  $[\text{CO}_3^{2-}]$  in mmol/L and R in  $\mu\text{mol}/\text{m}^2/\text{h}$ ).

281 Combining Eqs. 6 and 7 results in an almost linear relationship between  $K_D(\text{Sr}/\text{Ca})$   
282 and  $[\text{CO}_3^{2-}]$  at a temperature of 5 °C:

$$283 \quad K_D(\text{Sr}/\text{Ca}) = 1.551 * [\text{CO}_3^{2-}]^{1.0655} \quad (\text{Eq. 8})$$

284 ( $[\text{CO}_3^{2-}]$  in mmol/L). Eq. 8 shows that  $K_D(\text{Sr}/\text{Ca})$  increased by about 0.05 for the  
285 estimated EOT  $[\text{CO}_3^{2-}]$  increase of 0.03 mmol/L, if CCV calcites grow at rates typical  
286 for experimental and biogenic calcite (Carpenter and Lohmann, 1992). A similar  
287 effect could be expected for the late Neogene (<10 Ma) deepening of the CCD, which  
288 was similar in magnitude to the EOT event.

289 With these maximum rate dependencies for Sr partitioning, a doubling of the  
290  $K_D(\text{Sr}/\text{Ca})$  due to changes in precipitation rates appears possible. However, the rates  
291 of abiotic precipitation in the deep-sea are likely many orders of magnitude slower  
292 than the very fast rates used in the calculation presented above. If precipitation rates  
293 are in the range relevant for marine abiotic calcite, the rate-dependency is much  
294 reduced. This was demonstrated by DePaolo (2011), who calculated that a rate  
295 increase from 1 to 100  $\mu\text{mol}/\text{m}^2/\text{h}$  would increase  $K_D(\text{Sr}/\text{Ca})$  by no more than 10%.  
296 Precipitation of carbonate in the cold deep-sea with low carbonate ion activities is  
297 most likely even slower than the lowest rate considered by DePaolo (2011). At these  
298 very slow rates, Sr/Ca partitioning occurs close to equilibrium with only minor kinetic  
299 effects.

300 In summary, at rates <1  $\mu\text{mol}/\text{m}^2/\text{h}$ , the impact of the deepening of the CCD on the  
301 Sr/Ca of CCV calcite would be a subtle increase by no more than a few percent.

302 Of other parameters affecting trace element distribution, the temperature influence on  
303 Sr partitioning in calcite is comparatively small, see eq. (3) and (4) and also depends  
304 on precipitation rates and on pH (Tang et al., 2008). This may introduce an  
305 uncertainty for  $K_D(\text{Sr}/\text{Ca})$  of up to 5% for the temperature variations observed in our  
306 CCV samples. The dependence of  $K_D(\text{Sr}/\text{Ca})$  on pH is an increase by about 30 % per  
307 pH unit. However, as pH variations in the fluids from which CCVs are precipitated  
308 are usually small (<0.5 pH units; Elderfield et al. 1999), we expect only a small pH  
309 effect (<10%) on  $K_D(\text{Sr}/\text{Ca})$  for our samples.

310 Rate dependencies for Mg partitioning are generally much smaller than those for Sr  
311 (Morse and Bender, 1990). For instance, Mucci et al. (1985) found that Mg  
312 partitioning remained unaffected in experiments, in which the precipitation rate was  
313 varied by 12 orders of magnitude.

314 We conclude that, unless calcite precipitation in rock-harbored environments is many  
315 orders of magnitude faster than what is currently believed, it is highly unlikely that  
316 any of the variations in Sr/Ca, and particularly in Mg/Ca, are related to systematic  
317 changes in the rates of calcite precipitation.

318

#### 319 **4.2 Past changes in Mg/Ca and Sr/Ca of seawater**

320 Changes in seawater composition throughout Earth history, and in particular  
321 during the Cenozoic, has been much debated in the past decades. Several  
322 reconstructions of seawater compositions were published and computational models  
323 were developed to predict variations in seawater composition primarily driven by  
324 dynamic changes in plate tectonics. Figure 5 compares the results of different  
325 reconstructions for past seawater Mg/Ca and Sr/Ca with our data.

326 For Mg/Ca, our data perfectly match those by Coggon et al. (2010) and confirm

327 the inferred increase since 30 Ma. The trend shown by the combined CCV data is  
328 qualitatively supported by the Mg/Ca variations predicted from computational models  
329 (Wallmann, 2001; Hansen and Wallmann, 2003; Spencer and Hardie, 1990) (Fig. 5a).  
330 There is also an overall excellent overlap with Mg/Ca reconstructed from halite-  
331 hosted fluid inclusions (Horita et al., 2002; Lowenstein et al., 2002; Timofeeff et al.,  
332 2006) and from biogenic carbonate (Dickson, 2002 ; Lear et al., 2002).

333 For Sr/Ca, there is an apparent difference between our data and the data from  
334 Coggon et al. (2010) (Fig. 5b), which is due to the different approach in  
335 reconstructing seawater Sr/Ca ratios: Whereas Coggon et al. (2010) considered  
336 exclusively the temperature dependency of Sr/Ca partitioning, our data include the  
337 effect of Mg content in calcite at temperatures  $< 30^{\circ}\text{C}$  as discussed above.  
338 Consequently, for the "cold" sites  $> 24$  Ma, there is a systematic offset between both  
339 data sets. The two youngest sites included in the Coggon et al (2010) study are an  
340 exception and do not show this offset, because their CCV do not consist of calcite but  
341 of aragonite, for which the Mg-effect is nonsignificant. Recalculating the Coggon et  
342 al. (2010) Sr/Ca data following the procedure outlined above yields satisfying  
343 correspondence between the two data sets (Fig. 5b). The data indicate that the Sr/Ca  
344 ratio of seawater has roughly doubled since the Paleogene, with most of the increase  
345 (from  $\sim 5$  to 9) taking place in the past 30 Ma. While the Neogene increase in Sr/Ca  
346 may be less pronounced when the effect of Mg on Sr partitioning is considered, the  
347 finding of increasing Sr/Ca is robust.

348

#### 349 **4.3 Differences in calcium carbonate vein and fossil records**

350 Our findings confirm a significant mismatch between the fossil records of Sr/Ca  
351 and the Sr/Ca evolution of seawater derived from CCVs. Data derived from biogenic



352 calcite (summarized in Steuber and Veizer, 2002) suggests that Sr/Ca of seawater  
353 increased from ~6 to ~13 mmol/mol between 170 and 70 Ma and then decreased to  
354 the present-day value. Steuber and Veizer (2002) proposed that this decrease is related  
355 to the Early Paleogene change from calcite-dominated to aragonite-dominated  
356 carbonate precipitation and reflects preferential partitioning of Sr into aragonite. A  
357 decrease of Sr/Ca from ~13 to ~8 mmol/mol between 70 and 50 Ma is also indicated  
358 by past seawater Sr/Ca reconstructed from benthic foraminifera (Lear et al., 2002). In  
359 contrast, the foraminifera results by Delaney and Boyle (1986) indicate an increase in  
360 seawater Sr/Ca from ~4 to ~8 mmol/mol between 90 and 50 Ma.

361 Creech et al. (2010) pointed out that the CCV record is inconsistent with Eocene  
362 bottom water temperatures reconstructed from Mg/Ca of foraminifera. These authors  
363 note that seawater Mg/Ca ratios must be above 2 mol/mol to be consistent with  
364 TEX86 based sea-surface temperature estimates (Schouten et al. 2007). On the other  
365 hand, the CCV record for Mg/Ca is consistent with reconstructions based on  
366 echinoderm ossicles (Dickson, 2002) and evaporite fluid inclusions (Horita et al.,  
367 2002; Lowenstein et al., 2002; Timofeeff et al., 2006) (Fig. 6), all indicating a Mg/Ca  
368 of 1.5-2.5 between 40 and 160 Ma. Creech et al. (2010) also noted strong (factor of 3)  
369 discrepancies between the CCV and foraminiferal records of seawater Sr/Ca for the  
370 Eocene. These discrepancies are reduced to a factor of 1.5 if Paleogene Sr/Ca of  
371 seawater were ~5 mmol/mol as suggested by our CCV data (Fig. 5b). Still, species-  
372 dependent Sr partitioning into biogenic carbonate is affected by physiological effects  
373 and is difficult to apprehend for past eras, thus it may be impossible to obtain  
374 consistency between the biogenic and abiogenic carbonate Sr/Ca records.

375 What are the reasons for the discrepancies between fossil-based and CCV-based  
376 reconstructions? Fossil-based Mg/Ca and Sr/Ca reconstructions for the Jurassic-

377 Neogene time period are mainly based on foraminifera (Delaney and Boyle, 1986;  
378 Lear et al., 2002, 2003; Creech et al., 2010; Broecker and Yu, 2011) (Fig. 6), with  
379 some additional data for Sr/Ca from mollusks (belemnites, bivalves, Steuber and  
380 Veizer, 2002; and gastropods, Tripathi et al., 2009) and for Mg/Ca from echinoderms  
381 (Dickson, 2002, 2004; Ries, 2004) and bivalves (Steuber and Rauch, 2005). All of the  
382 studies used planktic or benthic foraminifera of the order *Rotaliida* which build shells  
383 of low-Mg calcite. Foraminiferal Mg concentrations reported in these studies were  
384 below 1 mol-% MgCO<sub>3</sub> (i.e. Mg/Ca ratios below 10 mmol/mol). Inorganic calcite that  
385 precipitates in modern seawater has a Mg content of at least 5 mol-% in cold, or more  
386 than 10 mol-% in warm seawater (Videtich 1985). While modern echinoderms show  
387 Mg concentrations in good agreement with inorganic calcite (Dickson, 2002), the  
388 rotaliid foraminifera strongly discriminate against Mg when precipitating their shells  
389 (Erez 2003). It was suggested by Bentov and Erez (2006) that foraminifera, to build  
390 low-Mg calcite shells, actively remove Mg ions from the calcifying fluid using ion  
391 pumps and exchangers. Alternatively, they may alter the internal Mg/Ca ratio by  
392 selectively taking up calcium (de Nooijer et al., 2009). In either case foraminifera may  
393 maintain a low Mg/Ca ratio in their calcifying fluid, largely independent from the  
394 external seawater composition. Consequently, low-Mg calcite of foraminifera may be  
395 a very poor recorder of seawater Mg/Ca ratios. To our knowledge, only one study has  
396 tested the suitability of rotaliid foraminifera for recording seawater Mg/Ca ratios.  
397 Delaney et al. (1985) reported no significant correlation between the Mg/Ca ratios of  
398 the external solutions (ranging from 3 to 11 mol/mol) and shell compositions. Even if  
399 such a correlation exists, it is far from clear whether it would be linear with a constant  
400 distribution coefficient as assumed, e.g., by Lear et al. (2002) and Creech et al.  
401 (2010). Examples of non-linear Mg/Ca relationships between shells and seawater have

402 been reported by Segev and Erez (2006), Ries (2004) and Müller et al. (2011).  
403 Therefore with the current state of knowledge, Mg/Ca data from the low-Mg calcite of  
404 foraminifera can not be interpreted to reliably record seawater composition.

405 Sr/Ca uptake of foraminifera as a function of seawater Sr/Ca was investigated in  
406 two studies. The Sr/Ca experiments of Delaney and Boyle (1985) with  
407 *Globigerinoides sacculifer* and of Raitzsch et al. (2010) for *Ammonia tepida* at  
408 different solution Sr/Ca ratios (4.4 to 8.7 mmol/mol and 4.6 to 15.5 mmol/mol,  
409 respectively) show a linear correlation between shell and water chemistry with a  
410 constant distribution coefficient. However, several studies (e.g. Elderfield et al., 2000,  
411 Lear et al., 2003, Kısakürek et al., 2011) found significant offsets in Sr/Ca ratios  
412 between different species of planktic and benthic foraminifera. So far, it is not clear  
413 what controls these offsets (see e.g. Elderfield et al. 1996, Kısakürek et al., 2011).  
414 Therefore, Sr/Ca records from foraminifera may provide information on the evolution  
415 of seawater chemistry, but should be interpreted with caution.

416 This is further pointed out by the discrepancies between the different  
417 foraminiferal Sr/Ca records (Delaney and Boyle, 1986; Lear et al., 2003) and the  
418 Sr/Ca records based on molluscs (Steuber and Veizer, 2002; Tripathi et al., 2009) as  
419 discussed by Coggon et al. (2010). For molluscs Lorens and Bender (1980) found a  
420 linear correlation between culture solution Sr/Ca (1.2 to 12.4 mmol/mol) and shell  
421 Sr/Ca for the calcitic shells of *Mytilus edulis*. On the other hand, Sr incorporation in  
422 mollusc shells is known to be strongly controlled by physiological processes (e.g.  
423 Elliot et al., 2009; Heinemann et al., 2011). We conclude that much more research is  
424 necessary to resolve the discrepancies between reconstructions of seawater chemistry  
425 derived from different fossil shells and from CCVs.

426 Broecker and Yu (2011) criticized the results of Coggon et al. (2010) in particular

427 for the scarcity of data within the critical interval of Mg/Ca increase and the  
428 uncertainties introduced by extrapolating data from warm ridge flanks to deep-sea  
429 temperatures. Our data set is not ridden by these shortcomings, yet confirms the  
430 threefold increase in Mg/Ca in the past 30 Ma. So the discrepancy between the  
431 foraminiferal record, suggesting a 1.7-fold increase, and the other records can not be  
432 explained by the coarse time resolution of the CCV records or by artefacts of the data  
433 processing. But what caused the Cenozoic changes in seawater composition?

434

#### 435 **4.4 Causes of seawater compositional changes**

436 The computational "hydrothermal model" by Spencer and Hardie (1990), later  
437 adjusted by Hardie (1996), considers the Mg/Ca<sub>sw</sub> variations due to waxing and  
438 waning hydrothermal fluxes and matches the reconstructed compositions of past  
439 seawater quite well. In their model, the global high-temperature hydrothermal flux is  
440 scaled to seafloor production rates derived from sealevel records by Gaffin (1987).  
441 Demicco et al. (2005) were able to improve on the Spencer and Hardie (1990) model  
442 by incorporating low-temperature hydrothermal processes in ridge flanks in their  
443 model calculations. Wallmann (2001) and Hansen and Wallmann (2003) developed a  
444 "comprehensive model" that takes into account Cretaceous and Cenozoic variations in  
445 hydrothermal and weathering fluxes, ocean floor alteration, sedimentation,  
446 subduction, volcanism, metamorphism, as well as carbonate accumulation. The  
447 quality of the fit between the predicted Mg/Ca evolution of seawater from the  
448 "hydrothermal model" and the observed changes suggest that diminishing  
449 hydrothermal fluxes likely played a dominant role in causing increased Mg/Ca of  
450 seawater. Because the predicted Mg/Ca trends of the "comprehensive model"  
451 (Wallmann, 2001; Hansen and Wallmann, 2003) and the "hydrothermal model"

452 (Spencer and Hardie, 1990, Hardie 1996) are principally similar, one may conclude  
453 that changes in hydrothermal fluxes are important in controlling first-order seawater  
454 compositional changes since the Cretaceous. A pronounced difference between the  
455 results of both models is the increase in Mg/Ca beginning at ca. 80 Ma in the  
456 "hydrothermal model" and at ca. 30 Ma in the "comprehensive model". Also, the  
457 magnitude of change is greater in the "comprehensive model" (Mg/Ca increase by a  
458 factor of  $> 5$ ; Fig. 5a). We argue below that feedbacks implemented in the  
459 comprehensive model may cause the accelerated increase in Mg/Ca and Sr/Ca at 30  
460 Ma. The slight Neogene increase in seawater Sr/Ca reconstructed from CCV  
461 compositions is also in line with results of the comprehensive model calculation  
462 results (Fig. 5b).

463 Despite the model predictions of a three- to five-fold change in Mg/Ca, Broecker  
464 and Yu (2011) argued that an increase of Mg/Ca<sub>sw</sub> during the Cenozoic by more than a  
465 factor of 2 would be difficult to apprehend. One critical issue is the actual change in  
466 seafloor spreading rates, which is the main driver of seawater compositional change in  
467 the models. The models implement a decrease in ocean crust production rate (and  
468 hence hydrothermal flux) by 50 to 60 per cent from Early to Late Cretaceous times  
469 (Spencer and Hardie, 1990; Demicco et al., 2005; Wallmann, 2001), but a new  
470 assessment of spreading rate changes in the Cretaceous and Cenozoic indicates that  
471 the actual decrease was merely about 33 per cent (Seton et al., 2009), so the decrease  
472 in hydrothermal flux may be less than previously estimated. Broecker and Yu (2011)  
473 argued that this small change in spreading rate is insufficient in explaining a threefold  
474 increase in Mg/Ca of seawater.

475 However, the new seafloor spreading reconstructions by Seton et al. (2009) also  
476 suggest that the average age of seafloor has steadily increased between 64 Ma and 42

477 Ma. Coggon et al. (2010) proposed that this increase caused a decrease in ridge flank  
478 hydrothermal activity that drove seawater composition from low Mg/Ca and Sr/Ca in  
479 the Cretaceous and Paleogene to high present-day values, because hydrothermal fluids  
480 (axial black-smoker vent fluids and ridge flank fluids) have Sr/Ca of around 3  
481 mmol/mol and Mg/Ca near zero (Von Damm, 1990; Wheat and Mottl, 2000) (Fig. 7).  
482 The Sr/Ca ratios we propose are higher than those advised by Coggon et al. (2010),  
483 and are actually more in line with the concept of a hydrothermal driver of variations in  
484 seawater composition (Fig. 7).

485 Figure 7 also illustrates that both decrease in hydrothermal flux and diminishing  
486 continental runoff can qualitatively explain an increase in seawater Mg/Ca and Sr/Ca  
487 in the past 30 Myrs. The decrease in continental runoff during the Cenozoic, however,  
488 is only on the order of 30 % (Berner, 1991), which is probably insufficient in causing  
489 the large compositional changes of seawater. Moreover, a late Cretaceous decrease in  
490 spreading rate by mere 33 % (Seton et al., 2009) cannot explain the Cenozoic increase  
491 in Sr/Ca by about 100% and Mg/Ca by 300% solely by reduced hydrothermal  
492 exchange. A question also is why the pronounced increases in Mg/Ca and Sr/Ca  
493 began tens of millions of years after the drop of spreading rates.

494 An increased sedimentary sink flux of Ca during the past 30 Myrs, rather than a  
495 mere increase of seawater Mg and Sr, is the most efficient way to cause correlated  
496 increases of Mg/Ca and Sr/Ca. Submarine magmatic/hydrothermal systems act as sink  
497 of alkalinity (Spivack and Staudigel, 1994), but are also a source of Ca (Wheat and  
498 Mottl, 2000) and therefore cannot drive preferential Ca removal by oceanic carbonate  
499 production. In contrast, enhanced rates of erosion and chemical weathering by the  
500 reaction of silicate rocks with atmospheric CO<sub>2</sub> would boost carbonate alkalinity of  
501 seawater and facilitate marine calcium carbonate sedimentation. A possible feedback

502 between sea-level change, subduction and recycling of carbonate sediments, and  
503 alkalinity increase in the oceans was proposed by Wallmann (2001) to provide a  
504 plausible explanation for both the delayed response in ocean chemistry to waning  
505 hydrothermal flux and the high amplitude of change. In Wallmann's model, a Late  
506 Cenozoic trigger of change was the decrease in ocean crust production rates, which  
507 caused a sea level drop and shifted carbonate deposition from the shelves to the  
508 pelagic oceans. Subduction and metamorphism of these pelagic carbonates millions of  
509 years later caused an increase in arc-related CO<sub>2</sub> flux, which in turn increased global  
510 weathering rates (Caldeira, 1992). The alkalinity is balanced by a concomitant flux  
511 increase of not only dissolved Ca but also Mg, both released during rock weathering.  
512 The net result of this mechanism is that the alkalinity flux is greater than the Ca-flux,  
513 which causes enhanced calcium carbonate sediment formation, thus depleting Ca from  
514 seawater (Wallmann, 2001). This model requires an increase in weatherability, which  
515 is not linked to increased CO<sub>2</sub> levels in the atmosphere (pCO<sub>2</sub> has decreased in the  
516 Cenozoic). The source of the increased weatherability is uncertain, in particular since  
517 the notion of increased late-Cenozoic continental run-off has recently been challenged  
518 (Willenbring and von Blanckenburg, 2010). Still, a Cenozoic acceleration of erosion  
519 due to increased mountain building activity has already been invoked to explain the  
520 drastic Neogene changes in the Sr isotope record (Raymo et al., 1988). The timing of  
521 the increases in <sup>87</sup>Sr/<sup>86</sup>Sr, Mg/Ca and Sr/Ca is similar, and it hence appears likely that  
522 they are related to a common process.

523

## 524 **5. CONCLUSIONS**

525 Our investigation of calcium carbonate veins from six sites in young ridge flank  
526 crust leads to better constraints of the increasing Mg/Ca and Sr/Ca ratio in seawater

527 during the Late Cenozoic. Consistent with previously published records from CCV,  
528 fossil echinoderms, and fluid inclusions, our data indicate nearly constant Mg/Ca ( $1.5$   
529  $\pm 0.5$  mol/mol) and Sr/Ca ( $5 \pm 1$  mmol/mol) of seawater between 165 and 30 Ma.  
530 Both ratios increased to present-day values within the past 30 Myrs. The increases of  
531 Mg/Ca and Sr/Ca are correlated, thus diminished hydrothermal activity and ridge  
532 flank circulation are likely driving forces of the observed changes. The magnitude and  
533 timing of changes requires additional processes, however. Increased input of  
534 carbonate alkalinity without an equivalent increase of the Ca flux can have increased  
535 marine carbonate sedimentation and hence decreased seawater Ca in the past 30 Myrs.  
536 The source of carbonate alkalinity can be enhanced silicate weathering related to an  
537 increased CO<sub>2</sub> flux from recycling of deep-sea carbonate in subduction zones  
538 (Wallmann, 2001). This hypothesis can account for the delay between Late  
539 Cretaceous slowdown in seafloor production and the compositional changes of  
540 seawater in the past 30 Myrs. We expect that the magnitude of change in Mg/Ca  
541 predicted in the model would decrease from  $\geq 5$  to the observed value of  $\sim 3$  if a more  
542 recent estimate for spreading rates (Seton et al. 2009) is used as input parameter.  
543 Future modelling studies will have to address the sensitivity of changes in Mg/Ca  
544 ratio to spreading rate and hydrothermal flux. In addition, better constraints on the  
545 actual relations between spreading rate, average crustal age, and hydrothermal flux are  
546 needed to test whether the assumed linear relationships hold.

547

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557

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852

853

854 **FIGURE CAPTIONS**

855

856 **Figure 1:** Location map of drill sites from which carbonate veins were investigated.

857

858 **Figure 2:** Calculated Mg/Ca fluid composition from calcite vein compositions plotted  
859 against calculated temperature. The symbols represent mean values for one single  
860 vein, vesicle or breccias within the different cores. Progressive fluid-rock interaction  
861 is represented by increasing temperature and decreasing Mg/Ca ratios. The  
862 composition of contemporaneous seawater is estimated by extrapolating this trend to  
863 the temperature of bottom seawater during calcite carbonate vein precipitation (also  
864 see Coggon et al. (2010) supplementary data).

865

866 **Figure 3:** Calculated and measured Sr/Ca in calcites versus formation temperature  
867 from the Juan de Fuca ridge (Davis et al., 1997). Fluid data were used to calculate  
868 calcite composition either with temperature dependent distribution coefficient  
869 (Rimstidt et al., 1998 and Malone and Baker, 1999) (open circles) or with Mg-content  
870 dependent distribution coefficient (Carpenter and Lohmann, 1992)(open diamonds).  
871 Ca-carbonate analyses (Coggon et al. 2004) are included for comparison (dots). Stars  
872 indicate which distribution coefficient (T-dependent vs. Mg-dependent) yields the  
873 best match between model and observation.

874

875 **Figure 4:** Reconstructed Mg/Ca (a) and Sr/Ca (b) of past seawater based on calcium  
876 carbonate veins from the ocean crust. The triangles with error bars are averages for  
877 different drill sites (see Table 1). Error bars are 2 times standard deviation of the mean  
878 reconstructed ratio. For Sr/Ca, the values were obtained by combining different  
879 methods as is described in the text; the uncertainties were propagated to determine the

880 sizes of the error bars. Gray circles are data for individual veins for which Sr isotope  
881 seawater dating was possible. For sites in basement > 38 Myrs, dating of the  
882 carbonate veins was not possible and no individual analyses are depicted. These ages  
883 are assumed to be 5 Ma younger than basement (see text). See Table 1 and S1 for  
884 further details.

885

886 **Figure 5:** Comparison of Mg/Ca and Sr/Ca in past seawater reconstructed by different  
887 methods. Scaling of the plots is similar to Fig. 4. Triangles: CCV data of this study  
888 (see Table 1); large open circles: CCV data from Coggon et al. (2010); solid line:  
889 reconstructed Mg/Ca based on biogenic carbonate (Dickson, 2002; 2004); hexagons:  
890 Mg/Ca from halite-hosted fluid inclusions (Horita et al., 2002; Lowenstein et al.,  
891 2001; Timofeeff et al., 2006); large open circles: data from Coggon et al. 2010 small  
892 filled circles: data from Coggon et al. 2010 re-calculated by including the Mg effect  
893 (see text). Note that the re-calculated Sr/Ca ratios shift to significantly higher values.  
894 Also shown are computational model trends from Wallmann (2001) and Hansen and  
895 Wallmann (2003) (continuous line) and Hardie (1996) (dashed line).

896

897 **Figure 6:** Proxy and model reconstructions of seawater Mg/Ca ratios for the past 200  
898 Ma. Wallmann coupled global Ca/Mg/C cycle model (Wallmann, 2004; Farkas et al.,  
899 2007) calculates dolomite formation rates as a function of Mg/Ca<sub>sw</sub> based on the data  
900 from halite fluid inclusions, echinoderms and rudists. Seafloor production and  
901 subduction rates are calculated from the marine <sup>87</sup>Sr/<sup>86</sup>Sr record (Veizer et al., 1999).  
902 In contrast, the model of Stanley and Hardie (1998) is scaled to first-order sealevel  
903 variations as a proxy for ocean crust production rates (Gaffin 1987), which are used to  
904 calculate mid ocean ridge/riverine ion flux ratios with the mixing model of Spencer

905 and Hardie (1990). The porefluid reconstruction of Fantle and DePaolo (2006)  
906 calculates seawater Mg concentrations from porefluid data of deep-sea sediments  
907 which are combined with Ca concentrations modelled with a bulk sediment calcium  
908 isotope record. The model version using a variable isotopic composition of the  
909 weathering flux is shown. Fluid inclusion data of halite are from Lowenstein et al.  
910 (2001), Horita et al. (2002) and Timofeeff et al. (2006) as listed in Table 1 of Coggon  
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913 reflects different temperature calibrations. Planktic foraminifera: "Cr" from Creech et  
914 al. (2010) (*Morozovella crater*, *Acarinina primitiva*, values for section top and  
915 bottom) error bars defined by different SST reconstructions; "B&Y" from Broecker  
916 and Yu (2011) (*Morozovella velascoensis*, *Acarinina soldadoensis* average value from  
917 Zachos et al., 2003). Rudists from Steuber and Rauch (2005). Error bars reflect  
918 different temperature reconstructions. Echinoderms from Dickson (2002, 2004),  
919  $Mg/Ca_{sw}$  calculated with power functions for echinoid plates from Ries (2004) for  
920 variable and constant (25°C) temperature. Error bars reflect differences between the  
921 two equation results

922

923 **Figure 7:** Plot of reconstructed seawater Sr/Ca versus Mg/Ca for the CCV of this  
924 study with compositions of modern seawater, river waters (e.g. Vance et al. 2009,  
925 Gaillardet et al. 1999) and hydrothermal fluids (Von Damm et al. 1990, Wheat and  
926 Mottl 2000) as reference. Also shown is the data field for calcite veins of the  
927 Paleocene-Cretaceous seawater reconstructions from Coggon et al (2010). Most CCV  
928 data of this study show a trend of seawater composition away from the composition of  
929 hydrothermal fluids, consistent with variable hydrothermal fluxes causing most of the

930 observed variations.

Figure 1  
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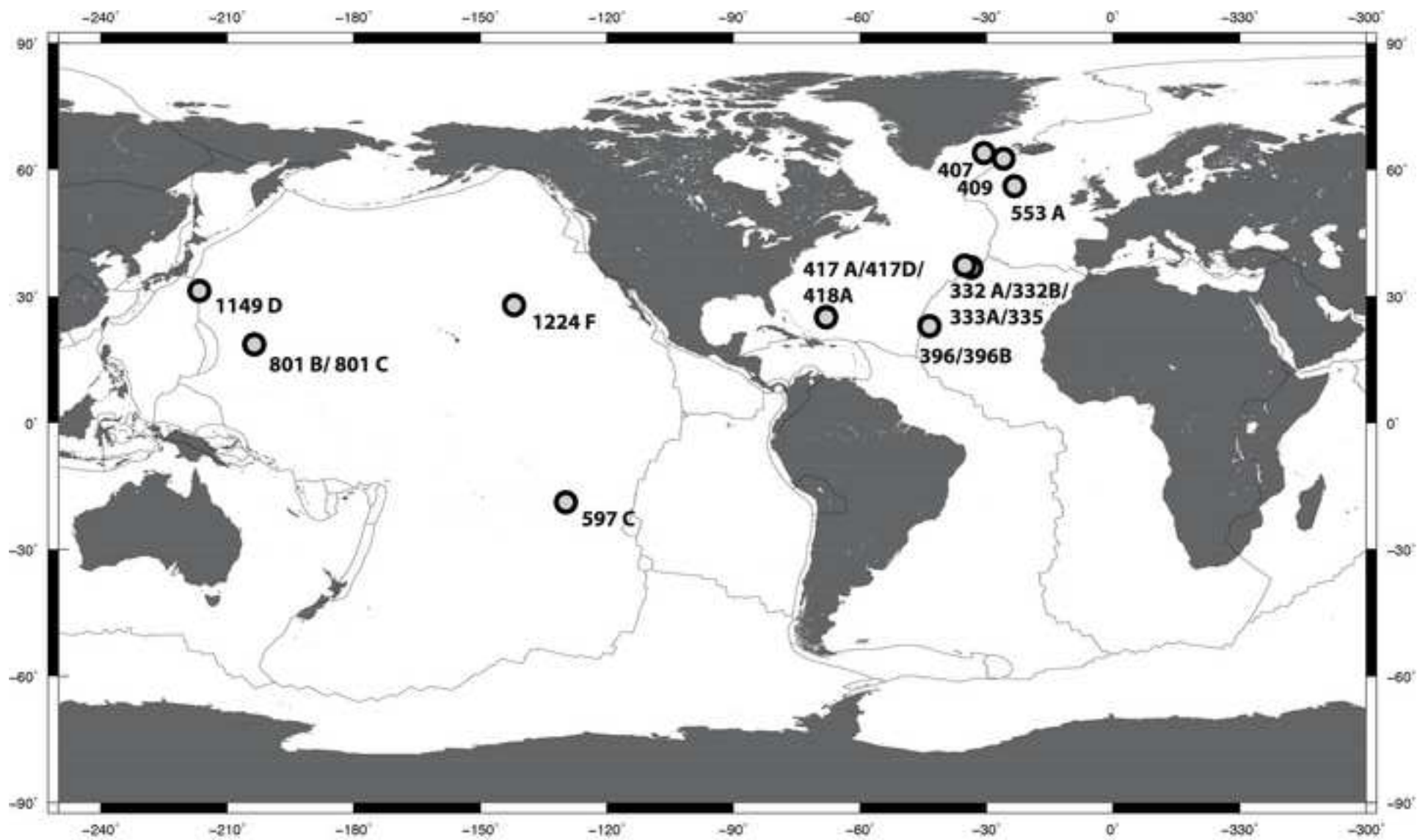


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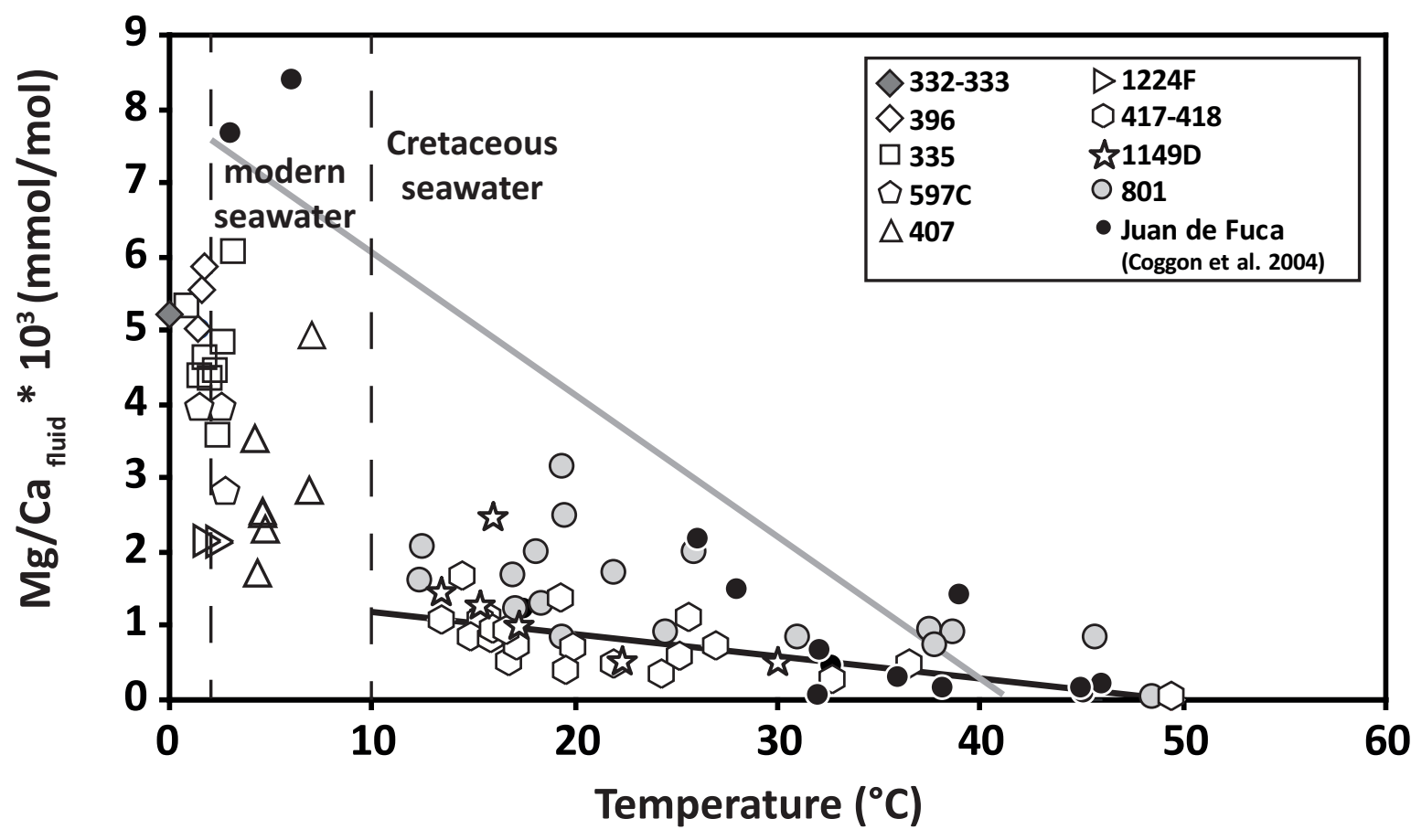




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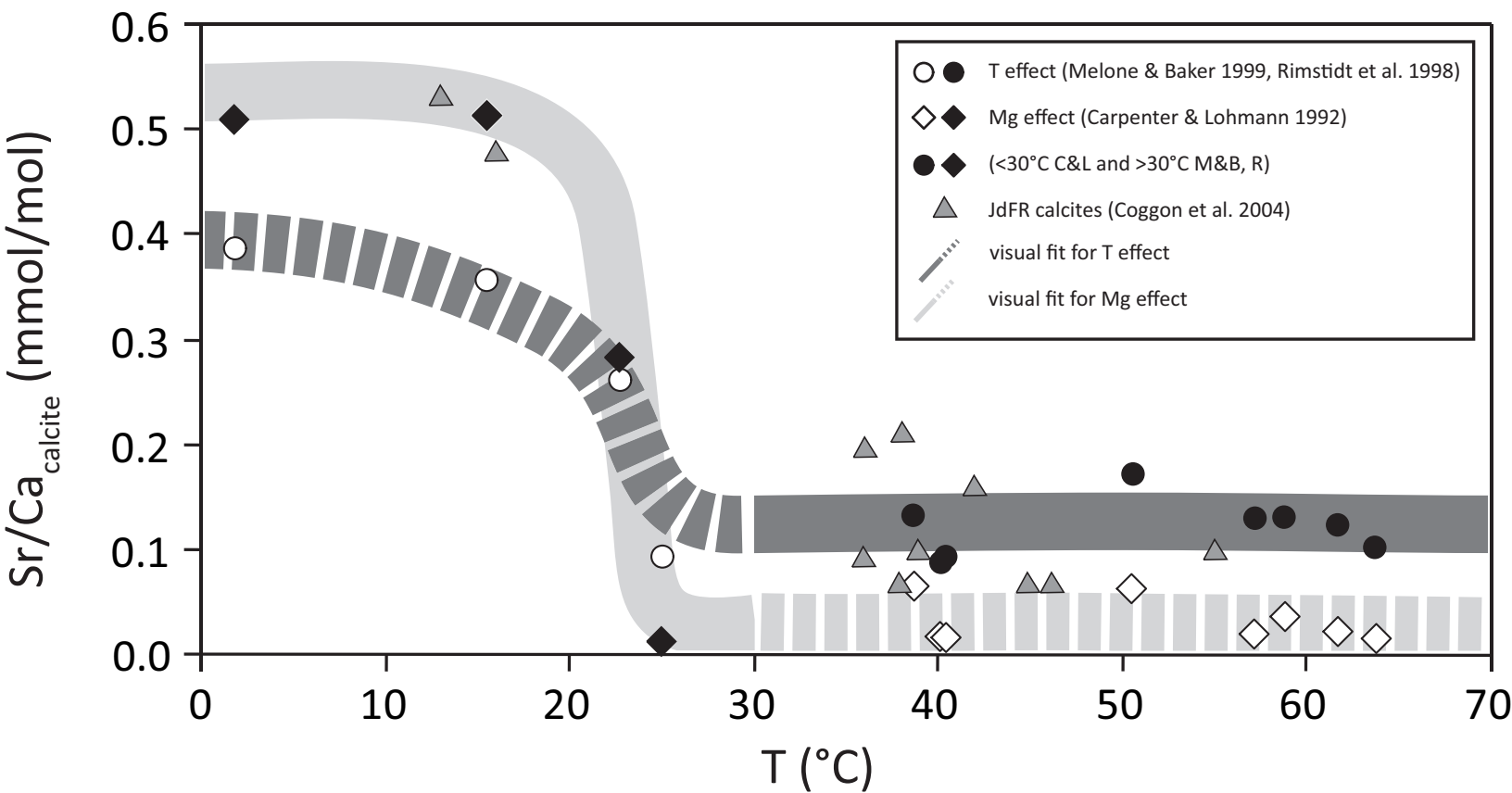


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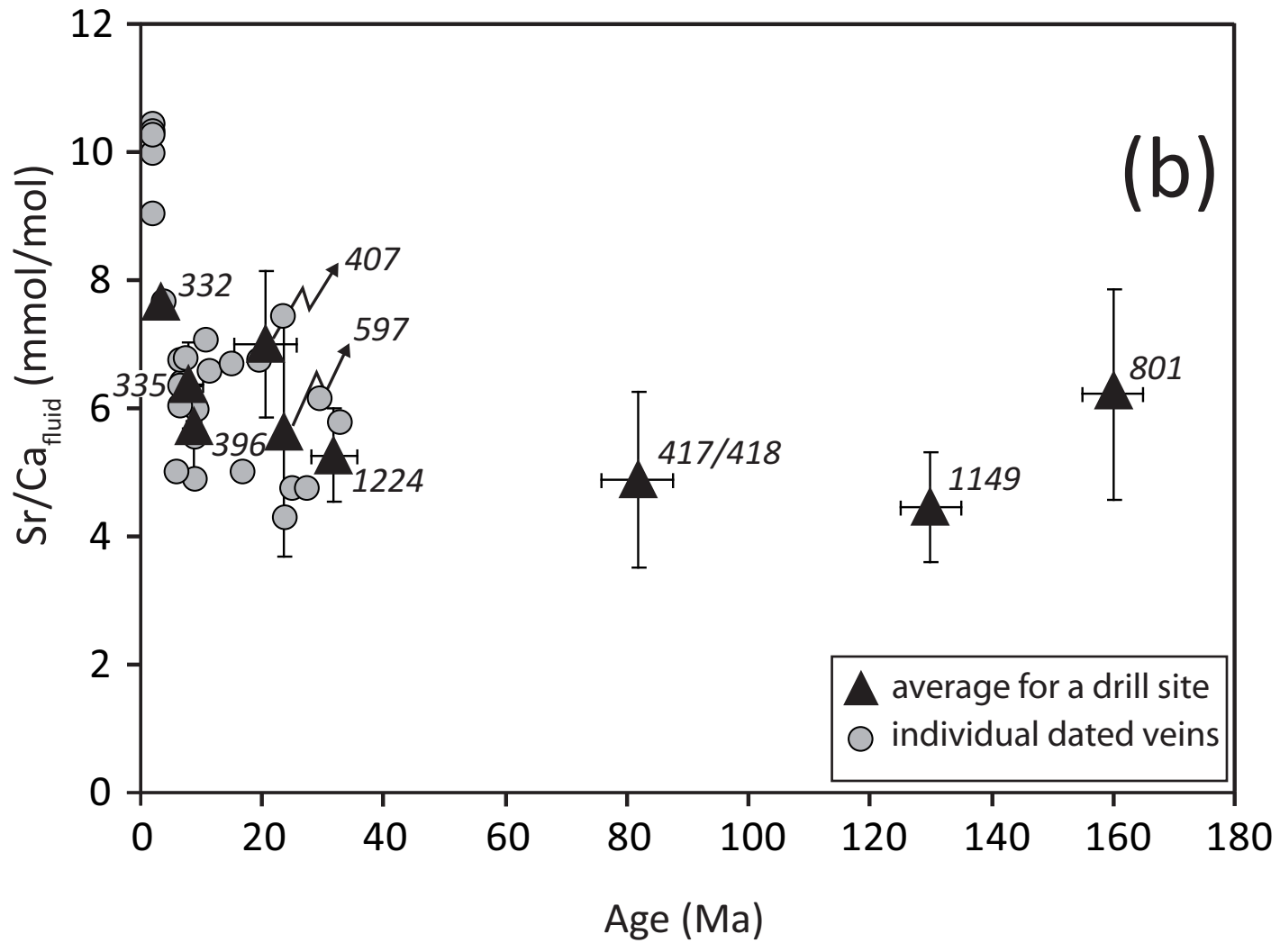
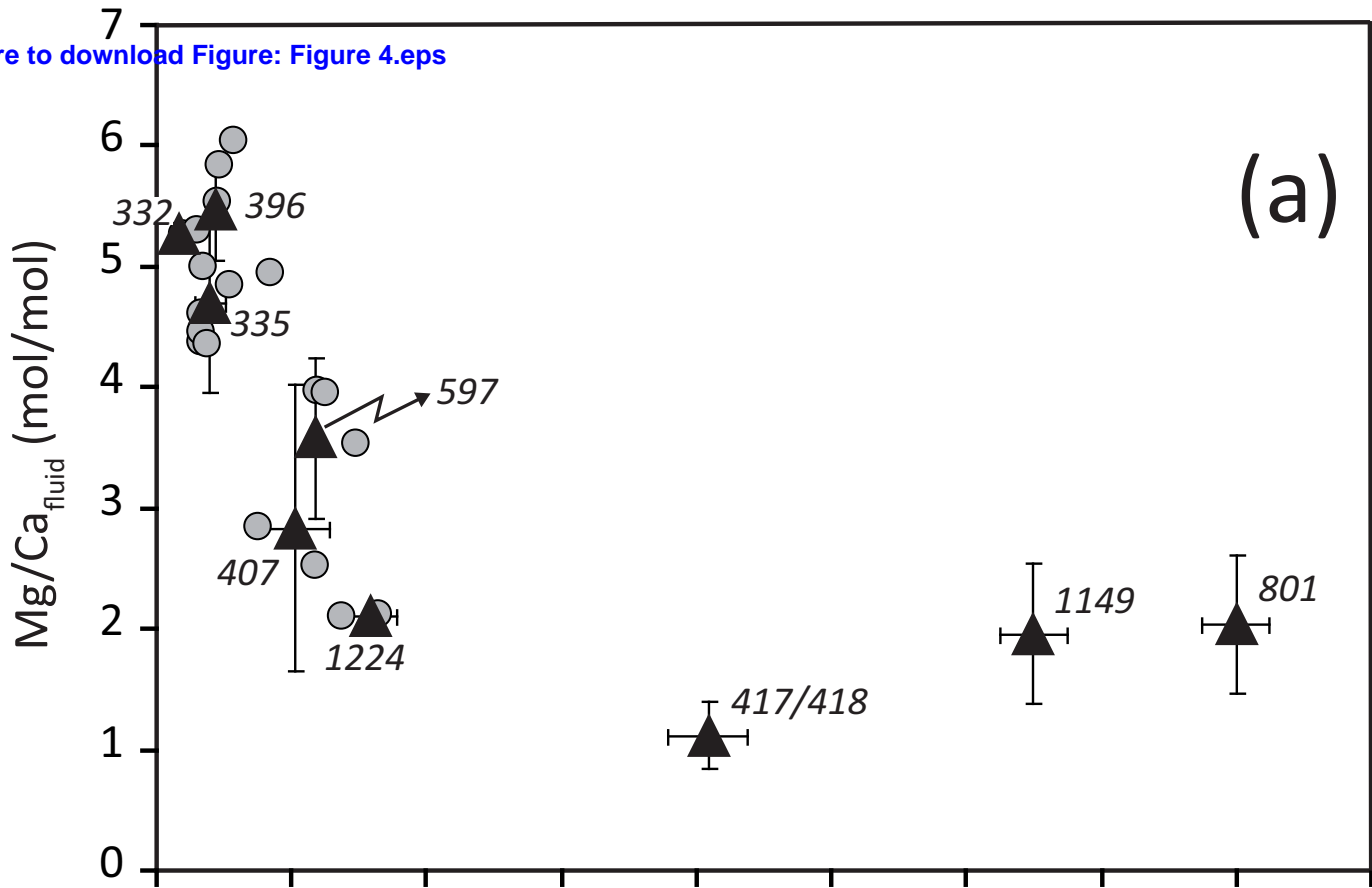


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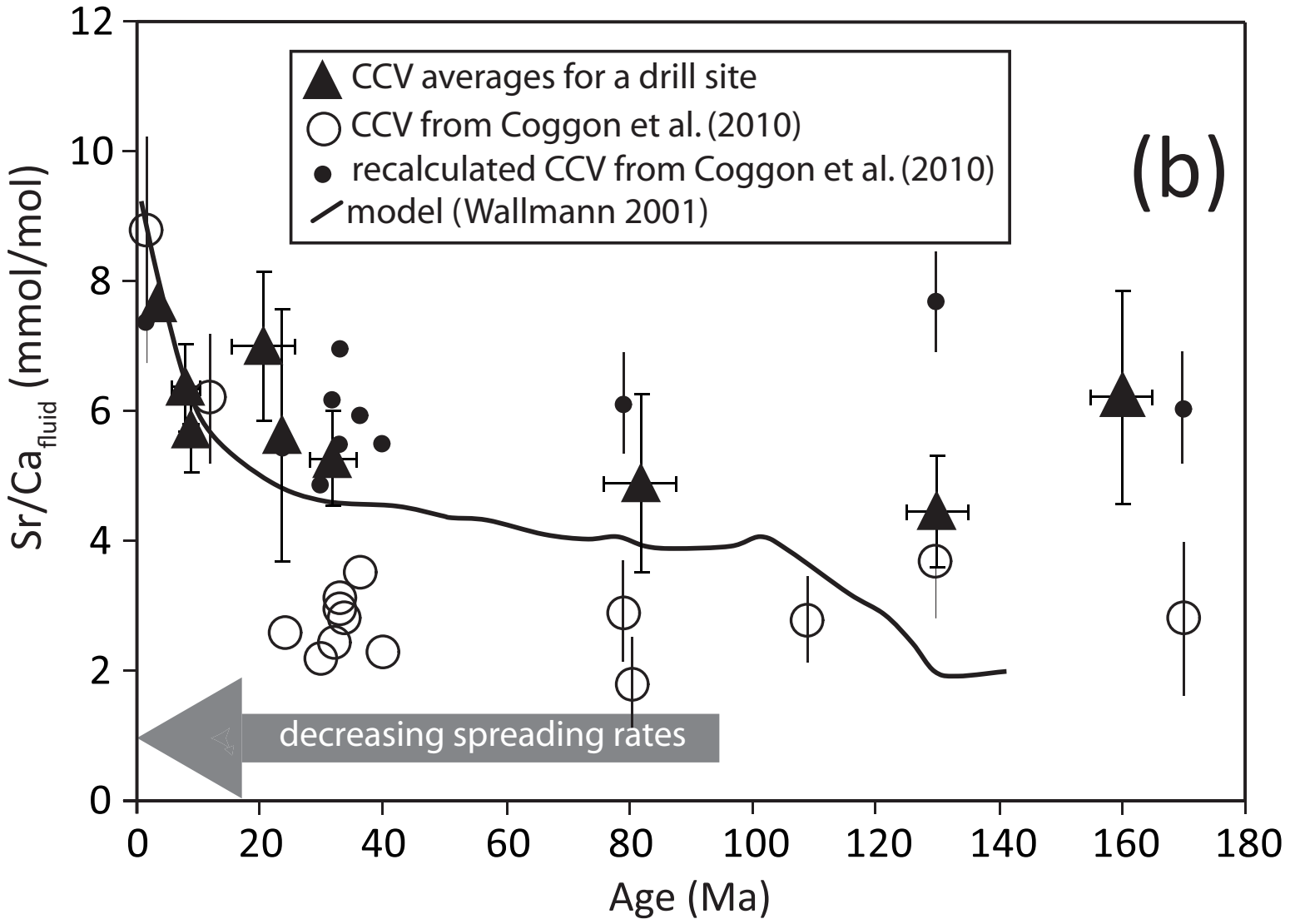
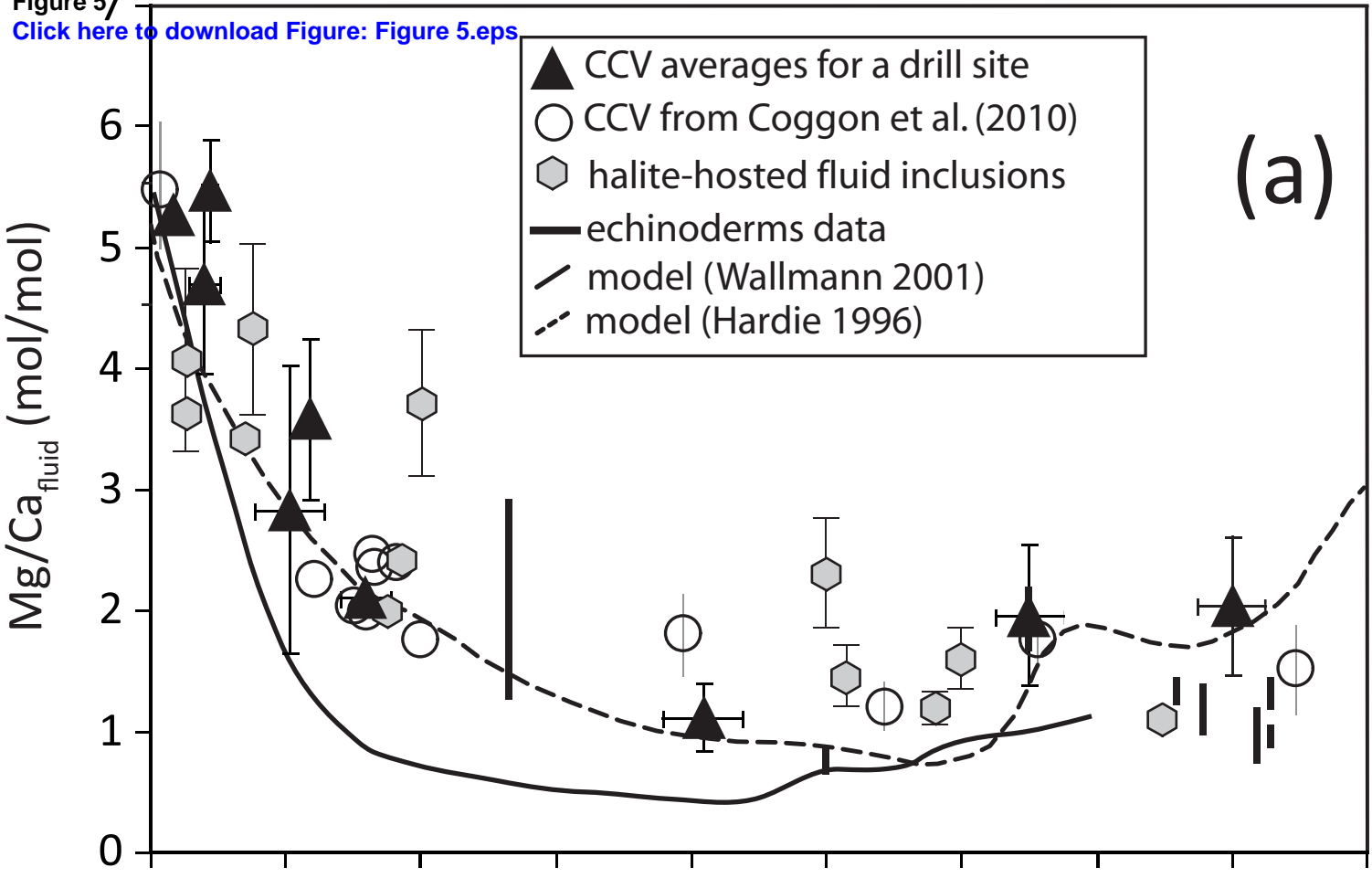


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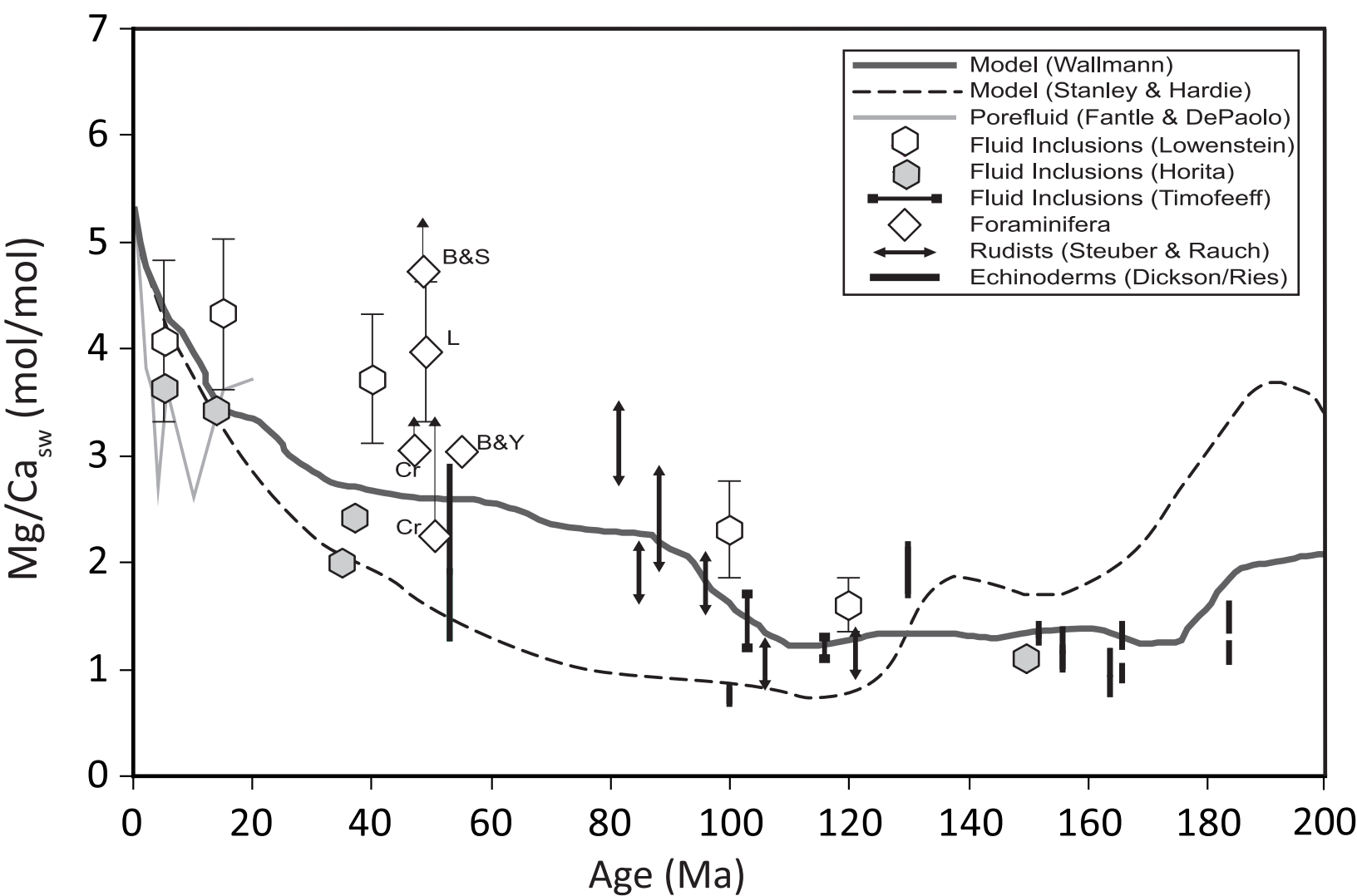
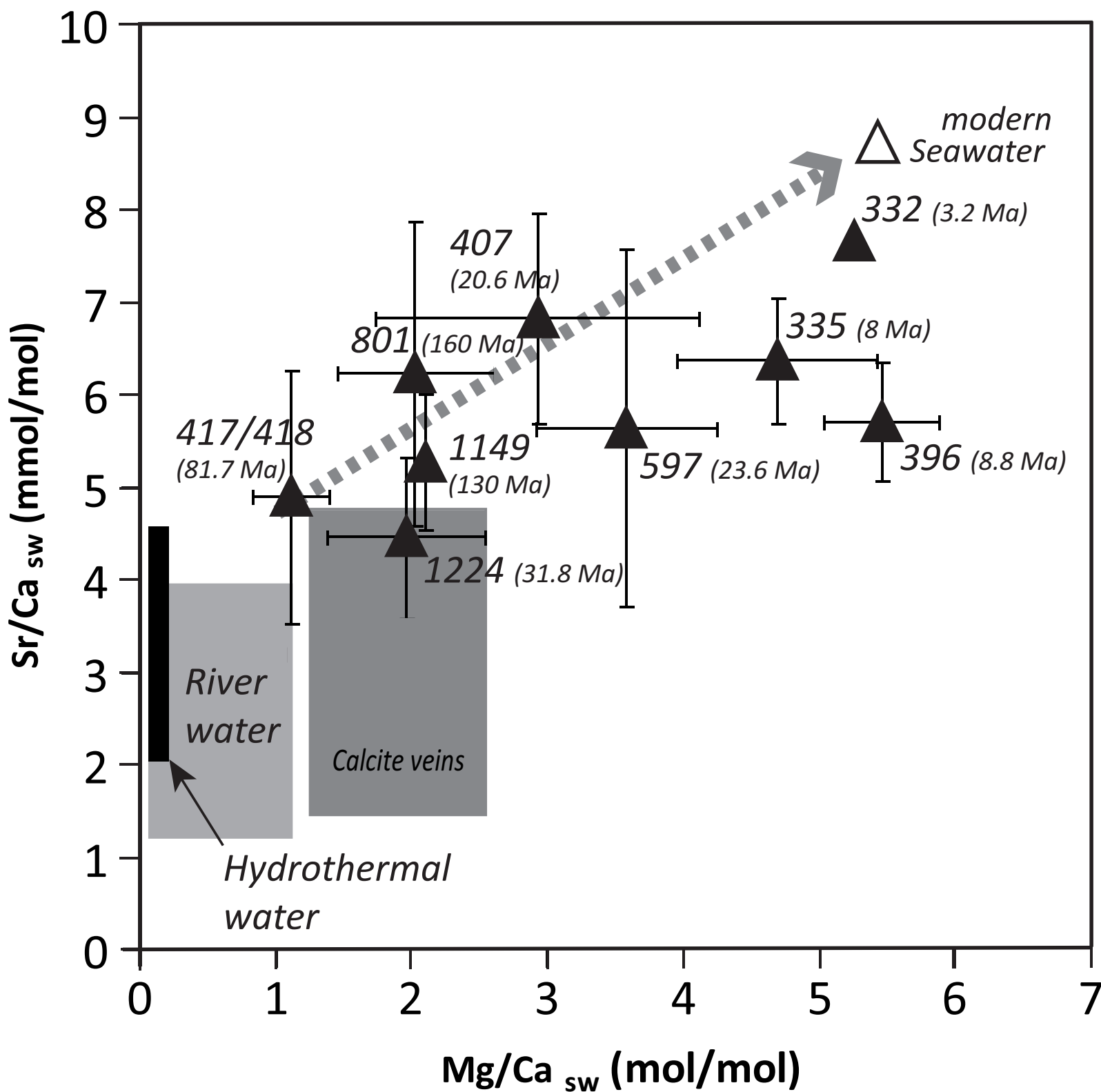


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**Table 1**  
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Table 1: Summary of reconstructed seawater composition from Ca carbonate vein (CCV) analyses

Site	Crustal age	CCV age	sd	Sr/Ca (R)	sd	Sr/Ca (M&B)	sd	Sr/Ca (avg)	sd	Sr/Ca (C&L)	sd	Sr/Ca (C&L, avg)	sd	Mg/Ca	sd
	(Ma)	(Ma)		(mmol/mol)		(mmol/mol)		(mmol/mol)		(mmol/mol)		(mmol/mol)		(mol/mol)	
409	2.8	2.1	0.2	10.00*	0.57										
332	3.9	3.2	0.5	4.82	0.03	9.29	0.82	7.06	0.82	7.66		7.66		5.26	
396	10.3	8.6	1.1	4.48	0.84	9.09	1.70	6.79	1.90	5.70	0.65	5.70	0.65	5.46	0.42
335	15	7.9	2.3	3.95	0.66	7.99	1.29	5.97	1.14	5.97	0.69	6.36	0.69	4.71	0.71
597	24.5	23.6	0.7	2.64	0.51	5.32	1.02	3.98	2.14	5.64	1.93	5.64	1.95	3.61	0.62
407	35	20.6	5.1	3.20	1.45	5.03	1.64	4.12	2.19	5.62	2.42	6.74	1.02	2.93	1.04
1224	46	31.8	3.9	1.63	0.25	3.29	0.49	2.46	0.55	5.27	0.73	5.27	0.73	2.11	0.02
417/418	120	81.7	6	1.38	0.57	2.55	1.01	1.96	0.79	4.63	1.42	4.83	1.38	1.14	0.27
1149	130	130	5	1.70	0.22	3.17	0.40	2.44	0.31	4.44	0.84	4.44	0.86	1.96	0.58
801	170	170	5	2.81	0.88	5.19	1.58	4.00	1.24	5.99	1.66	6.26	1.65	2.06	0.57

Sr/Ca (R), Mg/Ca (R): calculated after Rimstidt et al. (1998), T-dependent

Sr/Ca (M&B): calculated after Malone and Baker (1999), T-dependent

Sr/Ca (avg): average of both methods (M&B and R)

Sr/Ca (C&L): calculated after Carpenter and Lohmann (1992), Mg-dependent

\*: Aragonite veins only; calculation after Gaetani and Cohen (2006)

sd: standard deviation

# Table S1

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Table S1: Ca carbonate vein compositions

Leg	Site	Core	Section	Top cm Section	Bot cm Section	Type	Crustal age (Ma)	Sediment thickness (m)	Curated depth (mbsf)	$\delta^{18}\text{O}$ (PDB)	$\delta^{13}\text{C}$	T [K]	$^{87}\text{Sr}/^{86}\text{Sr}$	Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ at crustal age	Age CCV (Ma)
49	409	9	2	35	39	vesicles	2.8	80	92.9	4.23	3.70	272.2	0.709085	0.709080	2
Duplicate										4.48	3.83	271.2	0.709094	0.709080	2
49	409	9	3	68	70	vesicles	2.8	80	94.7	4.43	2.94	271.2	0.709089	0.709080	2
Duplicate										4.29	2.70	272.2	0.709085	0.709080	2
49	409	25	4	82	86	vug	2.8	80	248.3	4.37	3.88	274.2	0.709088	0.709080	2
37	332A	23	1	71	75	breccia	3.9	104	264.2	3.85	1.83	274.2	0.709050	0.709060	3.9
37	332B	8	2	38	40	vein	3.9	148.5	324.4	3.89	2.64	273.2	0.709031	0.709060	3.9
37	332B	33	2	136	142	vein	3.9	148.5	572.4	1.92	0.78	279.2	0.708928	0.709060	3.9
37	332B	36	1	32	39	vein	3.9	148.5	598.3	1.08	2.87	293.2	0.708962	0.709060	3.9
37	332B	36	2	53	61	vein	3.9	148.5	600.0	0.97	-7.22	293.5	0.708804	0.709060	3.9
37	333A	9	4	38	42	vein	3.5	218	438.9	2.72	2.71	279.2	0.708951	0.709060	3.9
45	396	15	2	50	56	vug	10.3	96	128.7	4.01	2.22	274.7	0.708947	0.708860	7
45	396	15	3	80	89	vein	10.3	96	130.5	3.90	2.47	275.0	0.708898	0.708860	9.5
46	396B	13	1	45	55	vein	10.3	150.5	216.5	3.85	2.79	275.2	0.708911	0.708860	9
46	396B	23	1	3	6	vug	10.3	150.5	315.0	3.94	2.67	274.9	0.708907	0.708860	9
37	335	6	2	4	12	vein	15	454	459.0	3.05	2.54	275.5			
37	335	7	3	26	32	breccia	15	454	470.3	2.77	2.50	276.4	0.708834	0.708840	12
37	335	7	3	105	114	vein	15	454	471.1	3.22	2.50	274.9	0.708953	0.708840	7
37	335	8	3	125	130	vein	15	454	479.3	3.20	2.39	275.0			
37	335	9	1	50	57	breccia	15	454	486.5	2.94	2.45	275.8	0.708865	0.708840	11
Duplicate										3.30	2.36	274.7	0.708962	0.708840	7
37	335	9	4	46	52	vein	15	454	491.0	3.06	2.53	275.4	0.708959	0.708840	7
37	335	10	3	130	135	breccia	15	454	499.8	3.12	2.50	275.2	0.708937	0.708840	8
37	335	16	1	1	5	vein	15	454	552.5	3.48	2.33	274.1	0.708971	0.708840	6
92	597C	3	2	133	135	vein	29	52	58.3	2.41	2.35	276.0			
92	597C	4	6	125	126	vein	29	52	73.3	2.79	2.12	274.7	0.708239	0.708200	24
92	597C	6	5	105	107	vein	29	52	89.6	2.48	2.30	275.8	0.708206	0.708200	25
49	407	36	2	90	110	vug, carb a	35	304	331.4	1.82	-3.81	278.0	0.708293	0.707810	24
49	407	36	2	90	110	vug, carb b	35	304	331.4	1.60	0.92	278.7	0.708493	0.707810	20
49	407	45	1	116	118	vug	35	304	434.7	1.02	0.45	280.8	0.708712	0.707810	17
49	407	45	1	130	138	vein	35	304	434.8	1.94	0.70	277.5			
49	407	46	2	102	104	vein	35	304	445.5	2.00	1.22	277.3	0.708008	0.707810	30
49	407	46	4	34	35	vein	35	304	447.8	1.45	2.38	279.3			





Table S1: Ca carbonate vein compositions

Leg	Site	Core	Section	Top cm Section	Bot cm Section	Type	Crustal age (Ma)	Sediment thickness (m)	Curated depth (mbsf)	$\delta^{18}\text{O}$ (PDB)	$\delta^{13}\text{C}$	T [K]	$^{87}\text{Sr}/^{86}\text{Sr}$	Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ at crustal age	Age CCV (Ma)
49	407	46	4	120	130	vein	35	304	448.7	1.23	2.39	280.1	0.708787	0.707810	15
49	407	46	4	132	135	breccia, vein	35	304	448.8	1.20	2.52	280.2	0.708675	0.707810	17
49	407	47	1	126	128	vein	35	304	453.8	1.89	2.09	277.7			
Duplicate										1.84	2.06	277.9			
49	407	47	2	114	115	vein	35	304	455.1	1.87	2.16	277.8	0.708284	0.707810	24
200	1224F	1	3	104	105	vein	46	28	31.7	1.89	1.36	277.7	0.707782	0.707760	35
200	1224F	6	1	32	34	breccia	46	28	75.3	2.67	2.11	275.1	0.708086	0.707760	28
200	1224F	13	1	120	121	vein	46	28	134.7	2.59	2.32	275.4	0.707913	0.707760	33
81	553A	43	3	54	56	vug	53	499	553.5	-8.71	-6.68	329.9	0.707558	0.707700	
81	553A	54	1	74	75	vug	53	499	556.7	-9.53	-6.64	335.2	0.707543	0.707700	
51	417A	24	1	59	60	vein	120	208	218.1	-0.76	3.47	287.8			
51	417A	24	5	37	39	vein	120	208	223.9	-0.16	3.49	284.2			
51	417A	26	5	90	92	vein	120	208	243.4	-1.02	2.78	288.9	0.707395	0.707420	
Duplicate										-0.99	2.74	288.8	0.707339	0.707420	
51	417A	27	1	88	90	vein	120	208	246.9	-0.95	2.42	288.6			
Duplicate										-1.06	2.69	289.1			
51	417A	29	2	107	109	vein	120	208	267.6	-1.27	2.63	290.0	0.707332	0.707420	
Duplicate										-1.34	2.58	290.3			
51	417A	32	3	70	76	vein	120	208	297.2	-2.41	2.26	295.1			
Duplicate										-1.98	1.86	293.1	0.707323	0.707420	
51	417A	39	3	116	118	vein	120	208	363.1	-3.10	3.17	298.3			
51	417A	46	2	129	130	vein	120	208	410.3	-0.96	1.90	288.7	0.707275	0.707420	
51	417D	22	1	12	16	breccia	120	343	344.1	-5.30	-3.61	309.7			
51	417D	22	2	22	25	vein	120	343	345.7	-0.45	1.94	286.5			
51	417D	27	4	58	60	breccia	120	343	367.2	-0.84	1.90	288.2			
51	417D	28	1	112	115	vein	120	343	376.8	-0.84	1.96	288.1	0.707413	0.707360	
51	417D	31	4	140	143	vein	120	343	408.9	-2.91	0.83	297.4			
Duplicate										-2.83	0.96				
51	417D	39	5	12	14	vein	120	343	470.8	-0.71	2.93	287.6			
52	417D	48	6	80	84	vein	120	343	540.3	-1.88	3.18	292.7			
Duplicate										-3.47	3.24	300.1			
52	417D	64	3	115	118	vein	120	343	664.2	-1.26	1.66	289.9			
52	418A	30	1	44	45	breccia	120	324	414.9	-4.57	2.76	305.8			
52	418A	35	2	77	80	vein	120	324	460.3	-3.17	3.11	298.7	0.707299	0.707430	
53	418A	54	1	22	24	breccia	120	324	611.2	-7.53	1.22	322.5	0.706661	0.707430	
53	418A	77	2	67	74	vesicles	120	324	795.3	-1.83	1.40	292.4	0.707397	0.707430	

Table S1: Ca carbonate vein compositions

Leg	Site	Core	Section	Top cm Section	Bot cm Section	Sr/Ca [mmol/mol]	K (Sr-Ca) (Rimstidt, Geatani)	K (Sr-Ca) (M&B)	K (Sr-Ca) (C&L)	(Sr/Ca) fluid (Rimstidt)	(Sr/Ca) fluid (M&B)	(Sr/Ca) fluid (C&L)	(Sr/Ca) fluid (avg: Rimstidt and M&B)	(Sr/Ca) fluid (<30°C C&L and >30°C avg)	Mg/Ca [mmol/mol]	K (Mg-Ca) (Rimstidt)	(Mg/Ca) fluid	Comments
49	407	46	4	120	130	0.26	0.087	0.045	0.039	2.98	5.84	6.69	4.41	6.69	38.1	0.013	2.84	
49	407	46	4	132	135	0.32	0.087	0.045	0.064	3.65	7.14	5.01	5.39	5.01	66.4	0.013	4.94	
49	407	47	1	126	128	0.25	0.088	0.044	0.035	2.84	5.65	7.23	4.25	7.23	33.1	0.013	2.63	
Duplicate						0.26	0.088	0.044	0.031	3.00	5.95	8.44	4.47	8.44	29.1	0.013	2.31	
49	407	47	2	114	115	0.25	0.088	0.044	0.034	2.83	5.63	7.44	4.23	7.44	31.8	0.013	2.53	
200	1224F	1	3	104	105	0.43	0.088	0.044							82.0	0.013		Aragonite-MgCc mix?
200	1224F	6	1	32	34	0.13	0.089	0.044	0.027	1.45	2.94	4.75	2.20	4.75	24.5	0.012	2.10	
200	1224F	13	1	120	121	0.16	0.089	0.044	0.028	1.80	3.64	5.79	2.72	5.79	25.0	0.012	2.12	
81	553A	43	3	54	56	0.19	0.075	0.051	0.041	2.53	3.71	4.60	3.12	3.12	25.0	0.039	0.64	
81	553A	54	1	74	75	0.20	0.074	0.052	0.039	2.70	3.85	5.11	3.27	3.27	21.0	0.042	0.50	
51	417A	24	1	59	60													
51	417A	24	5	37	39													
51	417A	26	5	90	92	0.11	0.084	0.046	0.023	1.36	2.50	5.01	1.93	5.01	15.0	0.017	0.89	
Duplicate						0.12	0.085	0.046	0.025	1.43	2.63	4.73	2.03	4.73	18.1	0.017	1.07	
51	417A	27	1	88	90	0.07	0.085	0.046	0.024	0.82	1.52	2.95	1.17	2.95	15.9	0.017	0.95	
Duplicate						0.08	0.084	0.046	0.024	0.97	1.79	3.41	1.38	3.41	16.3	0.017	0.96	
51	417A	29	2	107	109	0.06	0.084	0.046	0.024	0.74	1.36	2.63	1.05	2.63	15.7	0.017	0.90	
Duplicate						0.05	0.084	0.046	0.022	0.62	1.14	2.43	0.88	2.43	13.1	0.017	0.75	
51	417A	32	3	70	76	0.05	0.083	0.047	0.020	0.65	1.15	2.68	0.90	2.68	9.9	0.020	0.50	
Duplicate						0.06	0.083	0.046	0.023	0.75	1.35	2.71	1.05	2.71	14.0	0.019	0.75	
51	417A	39	3	116	118	0.06	0.082	0.047	0.023	0.76	1.33	2.74	1.05	2.74	12.3	0.021	0.58	
51	417A	46	2	129	130	0.13	0.085	0.046	0.026	1.57	2.91	5.19	2.24	5.19	18.3	0.017	1.09	
51	417D	22	1	12	16	0.12	0.079	0.049	0.027	1.50	2.45	4.47	1.98	1.98	13.5	0.027	0.50	
51	417D	22	2	22	25	0.11	0.085	0.045	0.024	1.25	2.35	4.39	1.80	4.39	17.4	0.016	1.09	
51	417D	27	4	58	60	0.11	0.085	0.046	0.024	1.25	2.32	4.46	1.78	4.46	16.2	0.017	0.97	
51	417D	28	1	112	115	0.09	0.085	0.046	0.022	1.06	1.96	4.01	1.51	4.01	14.5	0.017	0.88	
51	417D	31	4	140	143	0.12	0.082	0.047	0.018	1.45	2.54	6.54	2.00	6.54	7.2	0.021	0.35	
Duplicate																		
51	417D	39	5	12	14	0.19	0.085	0.046	0.034	2.27	4.22	5.70	3.25	5.70	28.0	0.016	1.71	
52	417D	48	6	80	84	0.05	0.083	0.046	0.018	0.55	0.98	2.57	0.76	2.57	7.9	0.019	0.43	
Duplicate						0.11	0.081	0.047	0.027	1.37	2.36	4.17	1.86	4.17	16.3	0.022	0.74	
52	417D	64	3	115	118	0.08	0.084	0.046	0.023	0.89	1.64	3.31	1.27	3.31	14.5	0.017	0.84	
52	418A	30	1	44	45	0.02	0.080	0.048	0.020	0.22	0.36	0.87	0.29	0.29	6.7	0.025	0.27	
52	418A	35	2	77	80	0.15	0.082	0.047	0.033	1.89	3.28	4.70	2.58	4.70	23.9	0.021	1.12	
53	418A	54	1	22	24	0.01	0.076	0.050	0.018	0.10	0.16	0.43	0.13	0.13	0.3	0.034	0.01	
53	418A	77	2	67	74	0.21	0.083	0.046	0.033	2.47	4.47	6.35	3.47	6.35	25.2	0.018	1.37	

Table S1: Ca carbonate vein compositions

Leg	Site	Core	Section	Top cm Section	Bot cm Section	Type	Crustal age (Ma)	Sediment thickness (m)	Curated depth (mbsf)	$\delta^{18}\text{O}$ (PDB)	$\delta^{13}\text{C}$	T [K]	$^{87}\text{Sr}/^{86}\text{Sr}$	Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ at crustal age	Age CCV (Ma)
185	1149D	7	1	136	140	vein	130	307	321.1	-1.07	1.49	289.1	0.707353	0.707390	
185	1149D	8	2	116	119	vein	130	307	332.0	-1.35	1.36	290.3			
185	1149D	9	3	58	61	vein	130	307	342.4	-0.95	2.17	288.6			
185	1149D	10	1	53	57	vein	130	307	348.9	-0.67	2.70	287.4			
185	1149D	11	1	130	131	vug	130	307	359.2	-4.03	-1.49	303.0	0.707197	0.707390	
185	1149D	11	2	82	85		130	307	360.2	-0.55	2.65	286.9			
Duplicate										-3.83	-0.26	301.9			
185	1149D	11	3	32	34		130	307	361.2	-0.45	2.63	286.5	0.707376	0.707390	
Duplicate										-2.48	1.35	295.4	0.707360	0.707390	
185	1149D	17	1	124	125	vein	130	307	416.7	-2.97	2.12	297.7			
129	801B	40	1	97	100	vein	170	461.6	477.9	-1.87	-3.73	292.6	0.706958	0.707160	
129	801B	42	1	82	84	vein	170	461.6	488.4	-2.90	-6.15	297.4	0.707018	0.707160	
129	801B	43	2	105	107	vein	170	461.6	494.8	-2.96	1.45	297.7	0.707132	0.707160	
Duplicate										-2.01	0.98	293.3	0.707048	0.707160	
129	801B	43	3	51	53	vein	170	461.6	495.7	-5.83	-1.05				
129	801B	44	1	87	89	vein	170	461.6	502.6	-3.23	-1.48	299.0	0.706959	0.707160	
Duplicate										-1.86	2.46	292.6	0.706931	0.707160	
129	801C	1	4	82	83	vein	157	426	499.0	-1.20	-0.29	289.7			
129	801C	5	4	130	134	vein	170	426	537.0	-1.32	-0.83	290.2			
129	801C	6	3	31	32	vein	170	426	543.8	-1.43	1.45	290.7			
129	801C	6	4	89	90	vein	170	426	545.9	-1.61	1.49	291.5			
Duplicate										-1.55	0.74	291.2			
129	801C	8	2	26	28	vein	170	426	561.3	-1.87	1.08	292.6			
129	801C	10	6	45	46	vein	170	426	577.0	-0.21	1.70	285.5			
185	801C	14	3	135	136	vein	170	426	608.4	-1.32	1.80	290.2			
185	801C	16	5	61	62	breccia	170	426	629.9	-4.58	-8.31	305.8			
Duplicate										-5.69	-9.03	311.8			
185	801C	17	2	27	29	vein	170	426	634.6	-5.49	-2.60	310.7			
185	801C	21	3	36	37	vein	170	426	673.4	-4.27	1.36	304.2			
185	801C	27	1	114	117	vug	170	426	720.8	-6.51	1.91	316.5			
Duplicate										-6.94	1.42	319.0			
185	801C	28	1	12	14	vein	170	426	728.8	-0.24	2.13	285.7			
185	801C	30	5	63	66	vesicles	170	426	753.9	-7.39	2.08	321.7			
185	801C	37	2	88	90	vein/vesicles	170	426	816.2	-5.52	1.59	310.9			
185	801C	38	1	67	69	vein	170	426	823.5	-6.93	1.65	318.9			
185	801C	38	2	121	123	vein	170	426	825.5	-2.41	1.89	295.1			

Table S1: Ca carbonate vein compositions

Leg	Site	Core	Section	Top cm Section	Bot cm Section	Sr/Ca [mmol/mol]	K (Sr-Ca) (Rimstidt, Geatani)	K (Sr-Ca) (M&B)	K (Sr-Ca) (C&L)	(Sr/Ca) fluid (Rimstidt)	(Sr/Ca) fluid (M&B)	(Sr/Ca) fluid (C&L)	(Sr/Ca) fluid (avg: Rimstidt and M&B)	(Sr/Ca) fluid (<30°C C&L and >30°C avg)	Mg/Ca [mmol/mol]	K (Mg-Ca) (Rimstidt)	(Mg/Ca) fluid	Comments
185	1149D	7	1	136	140	0.13	0.084	0.046	0.046	1.54	2.84	2.81	2.19	2.81	42.0	0.017	2.47	
185	1149D	8	2	116	119	0.12	0.084	0.046	0.027	1.43	2.61	4.45	2.02	4.45	19.3	0.017	1.10	
185	1149D	9	3	58	61	0.12	0.085	0.046	0.029	1.45	2.69	4.17	2.07	4.17	22.7	0.017	1.35	
185	1149D	10	1	53	57													
185	1149D	11	1	130	131	0.03	0.081	0.048	0.024	0.37	0.63	1.26	0.50	1.26	12.1	0.023	0.52	
185	1149D	11	2	82	85													
Duplicate																		
185	1149D	11	3	32	34	0.10	0.085	0.045	0.030	1.17	2.20	3.36	1.69	3.36	23.6	0.016	1.48	
Duplicate																		
185	1149D	17	1	124	125	0.07	0.083	0.047	0.021	0.85	1.50	3.35	1.17	3.35	10.9	0.020	0.55	
129	801B	40	1	97	100	0.16	0.083	0.046	0.051	1.92	3.46	3.16	2.69	3.16	46.1	0.018	2.49	
129	801B	42	1	82	84	0.20	0.082	0.047		2.44	4.27		3.35		229			Cc-Dolomite?
129	801B	43	2	105	107	2.43	0.082	0.047	0.029						19.3			Cc-Aragonite?
Duplicate						0.94	0.083	0.046							939			Dolomite?
129	801B	43	3	51	53													
129	801B	44	1	87	89	0.26	0.082	0.047	0.049	3.18	5.52	5.30	4.35	5.30	42.5	0.021	1.98	
Duplicate						0.09	0.083	0.046	0.061	1.08	1.95	1.47	1.51	1.47	58.4	0.018	3.16	
129	801C	1	4	82	83	0.37	0.084	0.046		4.39	8.06		6.22					Cc-Dolomite?
129	801C	5	4	130	134	0.35	0.084	0.046	0.036	4.17	7.64	9.74	5.91	9.74	29.9	0.017	1.72	
129	801C	6	3	31	32	0.17	0.084	0.046	0.029	2.02	3.68	5.75	2.85	5.75	22.2	0.018	1.26	
129	801C	6	4	89	90	0.13	0.084	0.046	0.031	1.61	2.93	4.32	2.27	4.32	24.0	0.018	1.33	
Duplicate						0.22	0.084	0.046	0.042	2.63	4.78	5.21	3.70	5.21	36.8	0.018	2.06	
129	801C	8	2	26	28	0.10	0.083	0.046	0.025	1.19	2.14	4.03	1.67	4.03	16.0	0.018	0.86	
129	801C	10	6	45	46	0.22	0.086	0.045	0.031	2.57	4.86	7.05	3.71	7.05	25.6	0.016	1.65	
185	801C	14	3	135	136	0.13	0.084	0.046	0.029	1.60	2.93	4.60	2.26	4.60	22.1	0.017	1.27	
185	801C	16	5	61	62	0.06	0.080	0.048	0.024	0.77	1.29	2.58	1.03	1.03	11.5	0.025	0.46	
Duplicate						0.18	0.079	0.049	0.038	2.23	3.59	4.63	2.91	2.91	25.9	0.028	0.92	
185	801C	17	2	27	29	0.13	0.079	0.049	0.038	1.66	2.70	3.47	2.18	2.18	26.3	0.027	0.96	
185	801C	21	3	36	37	0.12	0.080	0.048	0.032	1.45	2.44	3.67	1.95	1.95	21.0	0.024	0.88	
185	801C	27	1	114	117													
Duplicate																		
185	801C	28	1	12	14	0.21	0.085	0.045	0.038	2.46	4.63	5.59	3.54	5.59	33.0	0.016	2.12	
185	801C	30	5	63	66	0.04	0.077	0.050	0.019	0.46	0.71	1.84	0.59	0.59	1.6	0.034	0.05	
185	801C	37	2	88	90	0.13	0.079	0.049	0.034	1.69	2.74	3.96	2.21	2.21	21.4	0.028	0.78	
185	801C	38	1	67	69	0.06	0.077	0.050	0.042	0.74	1.14	1.37	0.94	0.94	28.5	0.032	0.89	
185	801C	38	2	121	123	0.22	0.083	0.047	0.041	2.65	4.70	5.34	3.67	5.34	34.3	0.020	1.75	