Biogeosciences
Discussions

1   **Impact of ambient conditions on the Si isotope fractionation in marine pore**

2   **fluids during early diagenesis**

3

4   Sonja Geilert[1], Patricia Grasse[1], Kristin Doering[1,2], Klaus Wallmann[1], Claudia Ehlert[3], Florian Scholz[1],

5   Martin Frank[1], Mark Schmidt[1], Christian Hensen[1]

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7   [1]GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstr. 1-3, 24148 Kiel, Germany

8   [2]Department of Oceanography, Dalhousie University, Halifax, Canada

9   [3]Marine Isotope Geochemistry, ICBM, University of Oldenburg, Germany

10

11   ABSTRACT

12

13   Benthic fluxes of dissolved silica (Si) from sediments into the water column are driven by the

14   dissolution of biogenic silica ($bSiO_2$) and terrigenous Si minerals and modulated by the precipitation

15   of authigenic Si phases. Each of these processes has a specific effect on the isotopic composition of

16   silica dissolved in sediment pore waters such that the determination of pore water $\delta^{30}Si$ values can

17   help to decipher the complex Si cycle in surface sediments. In this study, the $\delta^{30}Si$ signatures of pore

18   fluids and $bSiO_2$ in the Guaymas Basin (Gulf of California) were analyzed, which is characterized by

19   high $bSiO_2$ accumulation and hydrothermal activity. The $\delta^{30}Si$ signatures were investigated in the

20   deep basin, in the vicinity of a hydrothermal vent field, and at an anoxic site located within the

21   pronounced oxygen minimum zone (OMZ). The pore fluid $\delta^{30}Si_{pf}$ signatures differ significantly

22   depending on the ambient conditions. Within the basin, $\delta^{30}Si_{pf}$ is essentially uniform averaging

23   +1.2±0.1‰ (1SD). Pore fluid $\delta^{30}Si_{pf}$ values from within the OMZ are significantly lower (0.0±0.5‰,

24   1SD), while pore fluids close to the hydrothermal vent field are higher (+2.0±0.2‰, 1SD).

25   Reactive transport modelling results show that the $\delta^{30}Si_{pf}$ is mainly controlled by silica dissolution

26   ($bSiO_2$ and terrigenous phases) and Si precipitation (authigenic aluminosilicates). Precipitation

27   processes cause a shift to high pore fluid $\delta^{30}Si_{pf}$ signatures, most pronounced at the hydrothermal

28   site. Within the OMZ however, additional dissolution of isotopically depleted Si minerals (e.g. clays)

29   facilitated by high mass accumulation rates of terrigenous material (MAR_{terr}) is required to promote

30   the low $\delta^{30}Si_{pf}$ signatures while precipitation of authigenic aluminosilicates seems to be hampered by

31   high water/rock ratios. Guaymas OMZ $\delta^{30}Si_{pf}$ values are markedly different from those of the

32   Peruvian OMZ, the only other marine setting where Si isotopes have been investigated to constrain

33   early diagenetic processes. These differences highlight the fact that $\delta^{30}Si_{pf}$ signals in OMZs worldwide

34   are not alike and each setting can result in a range of $\delta^{30}Si_{pf}$ values as a function of the environmental

35   conditions. We conclude that the benthic silica cycle is more complex than previously thought and

36   that additional Si isotope studies are needed to decipher the controls on Si turnover in marine

37   sediment and the role of sediments in the marine silica cycle.

38

39   KEYWORDS: Si isotopes, reverse weathering, hydrothermal system, oxygen minimum zone,

40   environmental conditions

41

42   1.   INTRODUCTION

43

44   Silicon (Si) is one of the key macronutrients in the ocean mainly utilized by siliceous organisms such

45   as diatoms, radiolarians or sponges (see recent review by Sutton et al., 2018). The marine Si cycle is

46   closely linked to the carbon (C) cycle by marine siliceous organisms, which transport C to the

47   sediment and thus exert a strong control on C export from the atmosphere impacting present and

48   past climate (e.g. Lewin, 1961; Tréguer and Pondaven, 2000; Tréguer and De La Rocha, 2013; and

49   recent reviews by Frings et al., 2016 and Sutton et al., 2018). Studies of Si isotopes (δ^{30}Si) have

50   revealed complex uptake and dissolution processes of siliceous organisms, which have a dominant

51   control on the δ^{30}Si distribution in ocean waters (e.g. de la Rocha et al., 1997; Varela, 2004; Cardinal

52   et al., 2005; Beucher et al., 2008; Fripiat et al., 2011; Ehlert et al., 2012; Grasse et al., 2013; Sutton et

53   al., 2013; de Souza et al., 2014, 2015). Diatoms constitute the largest part of the Si cycling fluxes in

54   the ocean (Ragueneau et al., 2000) and discriminate between its isotopes during Si uptake, whereby

55   the light isotopes are preferentially incorporated into the diatom frustules (e.g. de la Rocha et al.,

56   1997). Si isotope fractionation during silica uptake is dependent on e.g. the diatom species, the

57   availability of Fe, and the degree of silica utilization. Fractionation factors between -0.5 and -2.1‰

58   have been derived from regional water mass mixing and laboratory studies (de la Rocha et al., 1997;

59   Varela, 2004; Cardinal et al., 2005; Beucher et al., 2008; Sutton et al., 2013; Meyerink et al., 2017).

60   After a planktonic bloom whereupon the nutrients are exhausted, biogenic silica (bSiO$_2$, mainly

61   diatoms) sinks through the ocean, partially dissolves and accumulates on the seafloor, where its

62   preservation and recycling is controlled by dissolution and Si re-precipitation processes. The

63   dissolution of bSiO$_2$ mainly controls the accumulation of silicic acid (Si(OH)$_4$) in pore fluids, although

64   the in-situ concentration remains below the equilibrium concentration of dissolved bSiO$_2$, which has

65   been explained by simultaneous formation of authigenic silicates (e.g. McManus et al., 1995; Van

66   Cappellen and Qiu, 1997a, b; Rickert et al., 2002). This process is termed reverse weathering given

67   that the authigenic precipitates are rich in seawater-derived cations, like Na, K or Mg (Mackenzie et

68   al., 1981; Michalopoulos and Aller, 1995). Experimental studies of bSiO$_2$ dissolution kinetics revealed

69   a dependence of the bSiO$_2$ reactivity on sediment depth as well as the ratio between terrigenous

70   material and $bSiO_2$ (Michalopoulos and Aller, 1995; Van Cappellen and Qiu, 1997a, b; Dixit et al.,

71   2001; Rickert et al., 2002). Marine weathering of terrigenous material (primary silicates like feldspars

72   and secondary silicates like clays), was found to release cations such as aluminum (Al) or iron (Fe),

73   which reduce the solubility and dissolution rate of $bSiO_2$ and induce aluminosilicate precipitation

74   (Michalopoulos and Aller, 1995; Van Cappellen and Qiu, 1997a, b; Michalopoulos et al., 2000; Dixit et

75   al., 2001; Rickert et al., 2002; Loucaides et al., 2010). The accumulation of Si in pore fluids and the Si

76   reflux into bottom waters are controlled by three interdependent processes, namely: opal

77   dissolution, dissolution of terrigenous solids, precipitation of authigenic minerals.

78   Early silica diagenesis has been shown to fractionate Si isotopes as a function of the crystallization

79   state, seawater Si concentration, sedimentation rate, and terrigenous mineral content (Tatzel et al.,

80   2015; Geilert et al., 2016). Since the light ^{28}Si isotope is more reactive compared to the heavier

81   isotopes (^{29}Si, ^{30}Si) , processes such as reverse weathering, adsorption, and direct silica precipitation

82   from saturated solutions show low $\delta^{30}Si$ values in the reaction product and high $\delta^{30}Si$ values in its

83   substrate (i. e. fluids) (e.g. Georg et al., 2006a, 2009; Delstanche et al., 2009; Opfergelt et al., 2013;

84   Geilert et al., 2014; Roerdink et al., 2015; Ehlert et al., 2016). The few modelling and experimental

85   studies, addressing Si isotope fractionation during formation of secondary phases, report isotope

86   fractionation factors between -1.6 and -2‰ (Ziegler et al., 2005; Méheut et al., 2007; Dupuis et al.,

87   2015; Ehlert et al., 2016).

88   The $\delta^{30}Si$ data for marine pore waters from the Peruvian margin upwelling region, which is

89   characterized by very high diatom productivity and $bSiO_2$-rich sediments (Abrantes et al., 2007;

90   Bruland et al., 2005), agree with these findings and clearly indicate Si isotope fractionation as a

91   consequence of authigenic aluminosilicate precipitation accompanied by a Si isotope fractionation

92   factor of -2.0‰ (Ehlert et al., 2016). Also pore fluids from the Greenland margin and Labrador Sea

93   reflect early diagenetic reactions detected by pore fluid $\delta^{30}Si$ values (between +0.76 and +2.08‰)

94   and the $\delta^{30}Si$ values were interpreted as the product of reverse weathering reactions (Ng et al.,

95   2020). In this study, the Guaymas Basin in the Gulf of California was chosen as study area, as it is

96   characterized by a relatively high diatom productivity and sediments that are predominantly

97   composed of diatomaceous muds (up to 50% diatoms; Kastner and Siever, 1983). Moreover, the

98   Guaymas Basin in the Gulf of California is influenced by hydrothermal activity (e.g. Von Damm, 1990).

99   These $bSiO_2$-rich sediments are thus ideal for dedicated studies of early diagenesis under the

100   influence of different thermal and redox conditions. We investigated the processes controlling Si

101   isotope fractionation during early diagenesis based on pore fluid and $bSiO_2$ data from three

102   fundamentally different environmental settings within the Guaymas Basin including the deep basin, a

103   hydrothermal site, and a site within the Oxygen Minimum Zone (OMZ) on the slope of the Guaymas

104   Basin (Fig. 1). In addition, the Si isotope composition of the water column, bottom waters, and

105 hydrothermal fluids was determined. A numerical transport-reaction model was applied to the OMZ

106 setting to constrain marine weathering processes and to compare the results to the Peruvian margin.

107 The aim of this study was to constrain the factors controlling Si isotope fractionation during early

108 diagenesis and to identify processes influencing $bSiO_2$ dissolution and authigenic silicate

109 precipitation.

110

111   2. GEOLOGICAL SETTING, SAMPLING, AND METHODS

112

113   2.1 Geological setting

114

115 The Guaymas Basin in the Gulf of California is a currently opening continental rifting environment

116 with two graben systems (northern and southern trough), which are offset by a transform fault and

117 reaches spreading rates of up to 6 cm yr^{-1} (Calvert, 1966). High biological productivity and

118 terrigenous matter input result in high sediment accumulation rates and have produced thick

119 sequences of organic-rich sediments (DeMaster, 1981; Curray and Moore, 1982). Siliceous sediments

120 at the Guaymas Slope show fine laminations within the OMZ (dissolved oxygen <10 µM at ca. 500 –

121 900 m water depth; Campbell and Gieskes, 1984) due to the absence of burrowing organisms

122 (Calvert, 1964). The Guaymas Basin is characterized by vigorous hydrothermal activity represented

123 by Black Smoker type vents discovered in both the northern and southern troughs (Berndt et al.,

124 2016; Von Damm et al., 1985). Hydrothermal plumes spread horizontally and mix with deep basin

125 water up to 300 m above the seafloor resulting in a fraction of hydrothermal fluids of ~0.1% in the

126 deep waters of the Guaymas Basin (Campbell and Gieskes, 1984). Hydrothermal sills and dikes

127 intruding into the sediments were found to accelerate early diagenetic reactions (due to the released

128 heat) and change pore fluid geochemistry significantly (Gieskes et al., 1982; Kastner and Siever, 1983;

129 Von Damm et al., 1985; Von Damm, 1990). At present, pore fluids in surface sediments show a

130 seawater composition (Geilert et al., 2018) and the absence of diagenetic high-temperature

131 processes render these pore fluids suitable for studying recent early diagenetic processes.

132

133   2.2 Sampling

134

135 Sediments were sampled via multicorer (MUC) deployment during RV SONNE cruise SO241 in

136 summer 2015 as described in detail in Geilert et al. (2018). In total, 6 stations have been investigated;

137 4 within the basin (termed basin sites: MUC33-11, MUC22-04, MUC23-05, MUC15-02), one in the

138 vicinity of a hydrothermal vent field (termed hydrothermal site: MUC66-16), and one within the OMZ

139 (termed OMZ site: MUC29-09) (Fig. 1, Table 1). The coring locations within the basin were sampled in

140   water depths between 1726 and 1855 m below sea level (mbsl). The hydrothermal site (MUC66-16)

141   was sampled in 1842 mbsl and was located at a distance of ~500 m from the active hydrothermal

142   mound described by Berndt et al. (2016). The OMZ site (MUC29-09) was sampled on the Guaymas

143   Basin slope of the Mexican mainland in 665 mbsl.

144   After core retrieval, bottom water above the sediment was sampled and filtered immediately using

145   0.2 µm cellulose acetate membrane filters. Bottom water from MUC22-04 may have been

146   contaminated with surface waters during core retrieval as indicated by Si and Mn concentrations

147   (53.8 µM and 0.05 µM, respectively) lower than at the remaining sites within the deep basin, which

148   show distinct anomalies caused by mixing with hydrothermal plume fluids (e.g. MUC15-02: Si = 177.8

149   µM and Mn = 0.34 µM). Processing of sediments was conducted in a cool laboratory in an argon-

150   flushed glove bag immediately after core retrieval. Sampling intervals were 1-5 cm with the highest

151   resolution close to the sediment surface and increasing distance downcore. Pore fluids were

152   separated from sediments by centrifugation (20 min at 4500 rpm) and subsequently filtered (0.2µm

153   cellulose acetate membrane filters) for further analyses.

154

155   Water column samples were taken using a video-guided Niskin Water sampler CTD-Rosette System.

156   Water samples were taken in the basin above MUC15-02 at 1844 mbsl (VCTD02), within the

157   hydrothermal plume between 1781 and 1800 mbsl (VCTD06 and 09) above the Black Smoker mound

158   as described in Berndt et al. (2016), and above the OMZ site (MUC29-09) at 586 mbsl (Fig. 1).

159

160   2.3 bSiO$_2$ separation and digestion

161

162   The bSiO$_2$ mass fractions of sediment samples were determined using an automated leaching

163   method following Müller and Schneider (1993) at GEOMAR Helmholtz-Centre for Ocean Research

164   Kiel. The sample material was treated with 1M NaOH at 85°C to extract the opal fraction. The

165   increase in dissolved silica was monitored and evaluated using a method described by DeMaster

166   (1981). The precision of the mass fraction determination was 5 to 10% (1SD). The bSiO$_2$ was

167   separated from the sediment for Si isotope analyses following the method of Morley et al. (2004).

168   About 500 mg of a freeze-dried sediment sample was transferred into a centrifuge tube. Organic

169   matter and carbonate material was removed by adding H$_2$O$_2$ (Suprapur) and HCl, respectively. Clay

170   particles (grain size <2µm) were separated from the remaining sediment by the Atterberg method

171   following Stoke's law (Müller, 1967). The remaining sediment (bSiO$_2$ and heavy minerals) was sieved

172   using a 5 µm-sieve and subsequently separated from the remaining detritus using heavy liquid

173   separation (sodium-polytungstate solution). The heavy liquid purification method was repeated until

174   clean, examined via light microscopy, bSiO$_2$ samples (>95%) were obtained. Light microscopy

175   revealed that the $bSiO_2$ fraction essentially consisted of diatoms and only traces of radiolarians and

176   sponges were present (<5%). The $bSiO_2$ samples were stored in Milli-Q water (MQ water). The $bSiO_2$

177   sample of the OMZ site stems from a nearby gravity core (GC07), which is described in detail in

178   Geilert et al. (2018). Aliquots of the cleaned $bSiO_2$ samples were transferred into Teflon vials and

179   dried on a hot plate. Subsequently, 1 ml of 0.1 M NaOH was added and the samples were placed on a

180   hot plate at 130°C for 24 hours. After sample digestion, the supernatant and residue (undissolved

181   traces of radiolarians and sponges) were separated via centrifugation. The supernatant was treated

182   with 200 µl H_2O_2 (Suprapur) in order to remove remaining organic matter and then dried and re-

183   dissolved in 1 ml 0.1 M NaOH at 130°C for 24 hours. After the digestion procedure, the samples were

184   diluted with MQ water and neutralized with 1 M HCl.

185

186   2.4 XRD measurements

187

188   X-ray diffraction analyses of the dried clay samples were performed at the Central Laboratory for

189   Crystallography and Applied Material Science, ZEKAM, dept. of Geosciences, University Bremen,

190   using a Philips X'Pert Pro multipurpose diffractometer. The diffractometer was equipped with a Cu-

191   tube, a fixed divergent slit of $\frac{1}{4}°$, a secondary Ni filter, and a X'Celerator detector system. A

192   continuous scan from 3 to 85° 2θ was applied for the measurements with a calculated step size of

193   0.016° 2θ (calculated time per step was 50 seconds). Quantification of mineral phases were based on

194   the Philips software X'Pert High Score[TM], the freely available X-ray diffraction software MacDiff 4.25

195   (Petschick et al., 1996), and the QUAX full-pattern method after Vogt et al. (2002). The standard

196   deviation is ±1-3% for well crystallized minerals (see also Vogt et al., 2002) and ±5% for the remaining

197   mineral phases.

198

199   2.5 Geochemical analyses of fluid and solid phases

200

201   Analyses of major and trace element concentrations of pore fluids from the basin sites and the

202   hydrothermal site as well as the water column are described in Geilert et al. (2018). OMZ site pore

203   fluids were treated in the same way. In brief, the pore fluids were analysed onboard by photometry

204   (NH_4) and on shore for dissolved anions (Cl) and cations (Si, K, Na, Mg) using ion chromatography (IC,

205   METROHM 761 Compact, conductivity mode) and inductively coupled plasma optical emission

206   spectrometry (ICP-OES, VARIAN 720-ES), respectively. Analytical precision was constrained using the

207   IAPSO seawater standard for all chemical analyses (Gieskes et al., 1991) and was found to be <1% for

208   Cl, <2% for K, Na, Mg, and <5% for Si.

209

210 Freeze dried and ground sediment samples were digested in HF (40% Suprapur), HNO_3 (Suprapur),

211 and $HClO_4$ (60% p.a.) for major element analyses. The accuracy of the method was tested by method

212 blanks and the reference standards SDO-1 (Devonian Ohio Shale, USGS) and MESS-3 (Marine

213 Sediment Reference Material, Canadian Research Council). The digested samples were measured for

214 their K and Al contents by ICP-OES (VARIAN 720-ES) and reproducibility was ≤5%. Total carbon (TC)

215 and total organic carbon (TOC) were measured in freeze-dried and ground sediment samples by flash

216 combustion using the Carlo Erba Element Analyzer (NA-1500). Carbonate carbon ($CaCO_3$) was

217 calculated by subtracting TOC from TC.

218

219 The digested $bSiO_2$ samples were analyzed for their Al and Si contents using the Agilent 7500 series

220 quadrupole ICPMS at GEOMAR to provide information about potential clay contamination of the

221 separated $bSiO_2$ fraction (Shemesh et al., 1988), whereby Al/Si ratios below 50 mM/M are considered

222 as negligible clay contamination (van Bennekom et al., 1988; Hurd, 1973). Al/Si ratios in the studied

223 $bSiO_2$ ranged between 15 and 39 mM/M, with three exceptions in MUC22-04, MUC15-02, and

224 MUC66-16 yielding Al/Si ratios of 71 mM/M, 57 mM/M, 50 mM/M, respectively. However, all

225 $\delta^{30}Si_{bSiO2}$ values agreed well with surrounding $\delta^{30}Si_{bSiO2}$ values and clay contamination is thus

226 considered insignificant. All other $bSiO_2$ samples are considered clay-free.

227

228   2.6 Sample purification and Si isotope measurements

229

230 Fluid and digested $bSiO_2$ samples were prepared for Si isotope measurements following the

231 purification method of Georg et al. (2006b). The concentration of the samples was adjusted and

232 loaded (1 ml with ~64 µM Si) onto 1 ml pre-cleaned cation-exchange resin (Biorad AG50 W-X8) and

233 subsequently eluted with 2 ml MQ water. Matrix effects originating from dissolved organic

234 compounds and anions, which cannot be separated by this purification method, have previously

235 been found to potentially influence Si isotope measurements (van den Boorn et al., 2009; Hughes et

236 al., 2011). However, no influence of the matrix effects on pore fluid Si isotope measurements has

237 been found during our measurements following several tests described in Ehlert et al. (2016). Briefly,

238 Ehlert et al. (2016) removed organic compounds by H_2O_2 and and SO_4 by Ba addition yielding $\delta^{30}Si$

239 values identical to untreated samples, within error. Therefore, our samples were not treated with

240 H_2O_2 or Ba before sample purification and Si isotope measurements.

241 Si isotope samples were measured in medium resolution on a NuPlasma MC-ICPMS (Nu

242 InstrumentsTM, Wrexham, UK) at GEOMAR using the Cetac Aridus II desolvator. Sample Si

243 concentrations of about 21 µM resulted in a ^{28}Si intensity of 3 to 4 V. The MQ blank was ≤ 3mV,

244 resulting in a blank to signal ratio <0.1 %. The measurements were performed using the standard-

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245   sample bracketing method to account for mass bias drifts of the instrument (Albarède et al., 2004). Si

246   isotopes are reported in the δ^{30}Si notation, representing the deviation of the sample ^{30}Si/^{28}Si from

247   that of the international Si standard NBS28 in permil (‰). Long-term δ^{30}Si values of the reference

248   materials Big Batch (-10.6±0.2‰; 2SD; n=49), IRMM018 (-1.5±0.2‰; 2SD; n=48), Diatomite

249   (+1.3±0.2‰; 2SD; n=44), and BHVO-2 (-0.3±0.2‰; 2SD; n=13) are in good agreement with δ^{30}Si

250   values in the literature (e.g. Reynolds et al., 2007; Zambardi and Poitrasson, 2011). The seawater

251   inter-calibration standard Aloha (1000 m) resulted in +1.3±0.2‰ (2SD; n=8) in very good agreement

252   to Grasse et al. (2017). Additionally, two in-house matrix standards have been measured. The pore

253   fluid matrix standard yielded an average δ^{30}Si value of +1.3±0.2‰ (2SD; n=17) and the diatom matrix

254   standard (E. rex) -1.0±0.2‰ (2SD; n=22), which agrees well with earlier reported values (Ehlert et al.,

255   2016). All samples were measured 2-4 times on different days and the resulting δ^{30}Si values have

256   uncertainties between 0.1 and 0.4‰ (2SD, Table 1). The δ^{30}Si values of pore fluids, bSiO$_2$, and bottom

257   water are given as δ^{30}Si$_{pf}$, δ^{30}Si$_{bSiO2}$, and δ^{30}Si$_{bw}$, respectively. Error bars in the figures indicate the

258   uncertainty of the individual sample measurements (two standard deviation, 2SD).

259

260   2.7 Numerical model

261

262   A numerical reactive-transport model was applied to simulate Si turnover within OMZ site sediments.

263   The model was based on a previously published Si isotope model (Ehlert et al., 2016) and was

264   extended to consider the dissolution of additional phases. A detailed description of the model can be

265   found in the supplementary information.

266

267   2.8 Calculation of the amount of terrigenous material and mass accumulation rate

268

269   The amount of terrigenous material (%) for the Guaymas Basin was calculated as the total mass

270   subtracted by the carbonate content (CaCO$_3$), the organic matter content (OC), and the bSiO$_2$ content

271   (Sayles et al., 2001):

272

273   Terrigenous material = 100 – (CaCO$_3$ + OC + bSiO$_2$)   (1)

274

275   The mass accumulation rate (MAR) was calculated as

276

277             $MAR = S*d*(1-\Phi)$ (2)

278

279   with S the sedimentation rate as 0.18 cm yr^{-1} (Thunell et al., 1994) and d the bulk dry density as 2.5 g

280   cm^{-3}. The porosity (Φ) was taken at the deepest part of the core with 0.925.

281

282   3. RESULTS

283

284   3.1 Water chemistry and sediment composition

285

286   All water column, pore fluid, and hydrothermal Si concentration data, bSiO$_2$ weight fractions as well

287   as Si isotope values are reported in Tables 1 and 2. A detailed description of the water column

288   properties, pore fluids, and hydrothermal fluid chemistry can be found in Berndt et al. (2016) and

289   Geilert et al. (2018). Pore fluids predominantly show a seawater composition at all sampling sites and

290   are not influenced by high temperature processes related to sill intrusions or mixing with

291   hydrothermal fluids. Pore fluid geochemistry of major elements in the OMZ resembles that of the

292   remaining sampling sites with the exception of a strong enrichment in NH$_4$ (Table 1S and Geilert et

293   al., 2018) as well as high Fe and low Mn concentrations (Scholz et al., 2019). The porosity corrected K

294   (see supplement) and Al contents in the sediments ranged between 0.9 and 21.2 wt% and 2.9 and

295   66.6 wt%, respectively (Table 1). The TOC contents ranged between 0.3 and 7.8 % and are shown in

296   Table 1S.

297

298   3.2 Bottom water, water column, and hydrothermal fluid Si concentrations and δ^{30}Si values

299

300   The bottom water Si concentration ranged between 173 and 254 µM for all basin sites and the

301   hydrothermal site (between 1726 and 1855 mbsl) with the exception of MUC22-04, where Si

302   concentrations were as low as 54 µM (possible surface water contamination, see section 2.2 and

303   Table 1). The bottom water δ^{30}Si$_{bw}$ signatures ranged between +1.5‰ and +2.0‰ for all basin sites

304   and the hydrothermal site and overlap within error (average δ^{30}Si$_{bw}$: +1.8±0.2‰, 1SD; highest δ^{30}Si$_{bw}$

305   for surface contaminated sample (MUC22-04)). Bottom water Si concentration for the OMZ site was

306   31 µM (665m water depth). The bottom water within the OMZ site had a distinctly lower δ^{30}Si$_{bw}$

307   value of +0.8‰. Here, a potential contamination with surface waters can be excluded given that they

308   are characterized by high δ^{30}Si values (from 1.7 to 4.4‰; Ehlert et al., 2012; Grasse et al., 2013), due

309   to the preferential biological uptake of ^{28}Si (de la Rocha et al., 1997).

310

311   The basin water (VCTD02), which was sampled about 1 m above the seafloor, had a Si concentration

312   of 163 µM and a δ^{30}Si$_{deepBasin}$ value of +1.5‰. Hydrothermal plume Si concentrations ranged between

313   253 and 690 µM and δ^{30}Si values ranged from +0.7‰ (VCTD09-06) to +1.4‰ (VCTD06-06). The water

314 column within the OMZ (586 mbsl) had a Si concentration of 78 µM and a $\delta^{30}Si_{OMZ}$ value of +1.5‰

315 (Table 2).

316

317   3.3 Pore fluid Si concentration and $\delta^{30}Si_{pf}$ values

318

319 Pore fluid Si concentrations generally increased asymptotically with depth from bottom water values

320 until reaching maximum average concentrations between 605 and 864 µM Si (Table 1, Fig. 2). For the

321 basin sites MUC33-11 and MUC15-02 as well as the OMZ site the Si concentrations asymptotically

322 increased until average values of 742 (≥8 cm below seafloor (cmbsf)), 729 (≥9 cmbsf), and 765 (≥9

323 cmbsf) µM were reached, respectively. Hydrothermal site Si concentrations were higher and

324 increased to 864 µM (≥4.5 cmbsf). MUC22-04 and MUC23-05 Si concentrations initially increased to

325 values of on average 605 µM (5.5 - 11 cmbsf) and 735 µM (3.5 - 9 cmbsf) and then decreased again to

326 364 µM (26 cmbsf) and 640 µM (22 cmbsf), respectively.

327

328 Pore fluid $\delta^{30}Si_{pf}$ values for all basin sites ranged from +0.9‰ to +1.5‰ (Table 1, Fig. 2), which is

329 lower than the respective bottom water $\delta^{30}Si_{BW}$ values ($\delta^{30}Si_{BW}$ from +1.6‰ to +2.0‰). The decrease

330 in Si concentration at MUC22-04 and MUC23-05 below 13 cmbsf and 11 cm cmbsf, respectively, is

331 not reflected in a significant change in $\delta^{30}Si_{pf}$. The hydrothermal site showed the highest $\delta^{30}Si_{pf}$ values

332 ranging from +1.8‰ and +2.2‰, which is higher than the bottom water $\delta^{30}Si_{BW}$ (+1.5‰). In contrast,

333 the OMZ site had the lowest $\delta^{30}Si_{pf}$ values between -0.5‰ and +0.8‰, which was also characterized

334 by very low $\delta^{30}Si_{bw}$ (+0.8‰; Table 1).

335

336   3.4 $bSiO_2$ content and $\delta^{30}Si_{bSiO2}$ values

337

338 The $bSiO_2$ content of the sediments (Table 1, Fig. 2) varied between 4.7 wt% and 47.6 wt%. Lowest

339 contents were present at the basin site MUC22-04 (7.6 -13.1 wt%) and the hydrothermal site (4.7 -

340 14.6 wt%). The remaining sampling sites showed higher $bSiO_2$ contents of on average 23±7 wt%

341 (1SD). The $\delta^{30}Si_{bSiO2}$ signatures ranged between +0.4‰ and +1.0‰ and did not vary systematically

342 with depth or sampling site within error. The small variability in $\delta^{30}Si_{bSiO2}$ signatures most likely stems

343 from natural variability within the Guaymas Basin.

344

345   3.5 XRD results of the clay fraction

346

347 The main silicate mineral phases of all samples were phyllosilicates (16-59 wt%), primary silicates

348 (quartz, plagioclase, potassium feldspar; 15-38 wt%), and amorphous SiO_2 (4-43 wt% including

349   abiogenic and biogenic opal) (Table 2S). The phyllosilicates were mainly composed of variable

350   fractions of smectite, illite, montmorillonite, and kaolinite. Apart from silicate minerals, minor

351   amounts of Fe-(hydr-)oxides (≤10 wt%, most between 2 and 3 wt%), pyroxenes (≤8 wt%), and

352   carbonates (≤6 wt%) were present. Biogenic opal fragments were identified via light microscopy to

353   be the dominating amorphous silicate phase at all sites besides the hydrothermal site and MUC23-05

354   in the basin basin. At the hydrothermal site, the abiogenic amorphous silica fraction was the

355   dominating silica phase in the uppermost and lowermost core sections with only minor occurrences

356   of biogenic opal fragments. Abiogenic amorphous silica was also found in the uppermost and

357   lowermost core sections of MUC23-05.

358

359   4.   DISCUSSION

360

361   Pore fluid Si concentration and $\delta^{30}Si_{pf}$ signatures vary significantly between sampling sites and appear

362   to depend strongly on ambient conditions. The Si concentration and isotope compositions are

363   proposed to be affected by dissolution of $bSiO_2$, the dissolution of terrigenous phases, and the

364   formation of authigenic aluminosilicates; the latter process is defined as reverse weathering.

365   Dissolution of $bSiO_2$ is most effective in the reactive surface layer (≤ 10 cmbsf) where the degree of

366   silica undersaturation is highest. As soon as Si is released into solution via $bSiO_2$ dissolution, Si re-

367   precipitates as authigenic aluminosilicates as a function of the availability of reactive metals, made

368   available by dissolution of terrigenous material (e.g. Michalopoulos and Aller, 1995; Van Cappellen

369   and Qiu, 1997a,b; Loucaides et al., 2010). In the course of this process authigenic silicate

370   precipitation induces $\delta^{30}Si$ fractionation, whereby the [28]Si is preferentially incorporated into the solid

371   phase, enriching the remaining fluid in [30]Si (e.g. Georg et al., 2006a; Opfergelt et al., 2013; Ehlert et

372   al., 2016). In the following sections, the processes during early diagenesis influencing pore fluid

373    $\delta^{30}Si_{pf}$ signatures under different ambient conditions are discussed. For the OMZ site, we quantify

374   these processes using a reactive transport model and compare the results to the only other OMZ site

375   where pore fluid $\delta^{30}Si_{pf}$ data is available, the Peruvian margin.

376

377   4.1. Influences on $\delta^{30}Si_{pf}$ due to source mixing

378

379   In the open ocean, a strong correlation between the inverse Si concentration (1/Si) and Si isotope

380   composition in intermediate and deep waters exists, showing low $\delta^{30}Si$ values with high Si

381   concentrations and can be used to identify water mass mixing between two endmembers with

382   distinct Si characteristics (e.g. de Souza et al., 2012). Here, we use the two endmember mixing Eq. (3)

383   to calculate the mixing between the deep water column and fluids originating from $bSiO_2$ dissolution

384   according to

385

$$\delta^{30}Si_{mix} = \frac{(\delta^{30}Si_{\text{water column}} * [Si]_{\text{water column}} * f) + (\delta^{30}Si_{bSiO2} * [Si]_{bSiO2} * (1-f))}{([Si]_{\text{water column}} * f) + ([Si]_{bSiO2} * (1-f))}$$

386   (3)

387   with $\delta^{30}Si_{\text{water column}}$ and $[Si]$ $_{\text{water column}}$ as the respective water column Si isotope composition and

388   concentration (Table 2) and $\delta^{30}Si_{bSiO2}$ as the average $bSiO_2$ value (+0.8‰) of all sites. The equilibrium

389   concentration in respect to $bSiO_2$ dissolution was derived from an experimental study by Van

390   Cappellen and Qiu (1997a) with $[Si]_{bSiO2}$ = 900μM. Mixing fractions are represented by f, varied over

391   100% water column and 0% fluids affected by $bSiO_2$ dissolution and vice versa.

392   Pore fluid $\delta^{30}Si_{pf}$ values of all sites deviate from mixing curves between the deep water column and

393   fluids originating from $bSiO_2$ dissolution and are obviously affected by additional processes (Fig. 3).

394   The $\delta^{30}Si_{pf}$ values of the basin sites and hydrothermal site are higher (+0.9‰ to +2.2‰) compared to

395   the respective mixing curves, while $\delta^{30}Si_{pf}$ values of the OMZ site are lower (-0.5‰ to +0.8‰). While

396   a shift to lower $\delta^{30}Si_{pf}$ values compared to fluid mixing point to dissolution of an isotopically light

397   phase, show higher $\delta^{30}Si_{pf}$ values that precipitation processes are important, given that the light Si

398   isotope is preferentially incorporated in authigenic secondary phases (Georg et al., 2009). This

399   indicates that processes governing the pore fluid Si isotope composition differ significantly between

400   the individual sites.

401

402   4.2. Influences on $\delta^{30}Si_{pf}$ from terrigenous and biogenic material

403

404   The terrigenous/$bSiO_2$ ratio was found to be the main mechanism controlling asymptotic pore fluid Si

405   concentration and the benthic Si flux (Van Cappellen and Qiu, 1997a, b). Maximum Si concentrations

406   were reached asymptotically at four out of six sampling sites (Fig. 2). Two sites within the basin

407   (MUC22-04 and MUC23-05) show lower Si concentrations in the deep core sections (Fig. 2), which

408   are most likely related to the decrease of reactive silica with depth, caused by the formation of less

409   soluble silica phases (Van Cappellen and Qiu, 1997a). At these sites, the asymptotic Si concentration

410   is defined as the maximum concentration values in the center of the core. The amount of terrigenous

411   material for the Guaymas Basin was calculated according to Eq. (1) and accounts for 75%.

412

413   Asymptotic Si concentrations plotted against the terrigenous/$bSiO_2$ ratio fall on the global trend

414   except for the hydrothermal site (Fig. 4a). Here, high geothermal gradients are likely responsible for

415   the higher Si concentrations with respect to the global trend (see also section 4.3.2). In contrast to

416   the asymptotic Si concentration, no strong correlation of the pore fluid $\delta^{30}Si_{pf}$ values with the

417   terrigenous/bSiO$_2$ ratio exists (Fig. 4b). In order to identify processes responsible for the different

418   pore fluid $\delta^{30}Si_{pf}$ values and to facilitate comparison between the three settings within the Guaymas

419   Basin, only average $\delta^{30}Si_{pf}$ values will be discussed in the following.

420

421   Average $\delta^{30}Si_{pf}$ values show distinct variations between the individual settings. The $\delta^{30}Si_{pf}$ values of

422   the OMZ site are lower (0.0±0.5‰, 1SD, n = 6) than those of the basin sites (+1.2±0.1‰, 1SD, n = 17)

423   and the hydrothermal site, which shows the highest $\delta^{30}Si_{pf}$ values (+2.0±0.2‰, 1SD, n = 3).

424

425   4.3 Influence of the ambient environmental conditions on the $\delta^{30}Si_{pf}$ values

426

427   4.3.1 Basin sites

428

429   Pore fluid $\delta^{30}Si_{pf}$ values of the basin sites deviate from the mixing curve between the deep water

430   column and fluids originating from bSiO$_2$ dissolution and are shifted to higher values (+1.2±0.1‰; Fig.

431   3). This shift to higher $\delta^{30}Si_{pf}$ values can be explained by Si re-precipitation as authigenic

432   aluminosilicates, which preferentially incorporate the light ^{28}Si isotope (Fig. 5a). Alteration of

433   terrigenous material leads to mobilization and re-precipitation of Al and the uptake of K from

434   seawater in the authigenic phase (Michalopoulos and Aller, 2004). The sedimentary K/Al ratio can

435   thus be used to detect these early diagenetic reactions in addition to pore fluid $\delta^{30}Si_{pf}$ values.

436   Authigenic aluminosilicates formed during alteration of terrigenous material were found to have K/Al

437   ratios of 0.32 (Michalopoulos and Aller, 2004), which is higher than the pristine K/Al ratio of

438   terrigenous material carried by rivers (K/Al = 0.19; Viers et al., 2009). The average K/Al ratio of the

439   basin sites is 0.34±0.01 (1SD), which is in the same range as K/Al ratios indicative of authigenic

440   aluminosilicate formation (Michalopoulos and Aller, 2004). Thus, bSiO$_2$ dissolution and re-

441   precipitation of Si in authigenic aluminosilicates control the pore fluid $\delta^{30}Si_{pf}$ values in the basin sites.

442

443   4.3.2 Hydrothermal site

444

445   The $\delta^{30}Si_{pf}$ values from the hydrothermal site are higher (+2.0±0.2‰) than the mixing curve between

446   the deep water column and fluids originating from bSiO$_2$ dissolution and also much higher than pore

447   fluid $\delta^{30}Si_{pf}$ values from the basin (Fig. 3, 5a). The high $\delta^{30}Si_{pf}$ values indicate that precipitation plays a

448   significant role at this site. Sedimentary K/Al ratios are equivalent to basin values (K/Al = 0.34) and

449   thus show the formation of authigenic aluminosilicates. Consequently, the higher pore fluid $\delta^{30}Si_{pf}$

450   values compared to the basin sites can either be explained by a different Si isotope fractionation

451 factor or by the precipitation of additional silica phases. The hydrothermal site is located in close

452 proximity to a hydrothermal vent field and hydrothermal deposits are mainly composed of Fe-

453 sulfides (Berndt et al., 2016), while nearby sediments are dominated by amorphous silica, quartz, and

454 Fe-Si silicates (e.g. ferrosilite, fayalite) (Kastner, 1982; Von Damm et al., 1985). Si adsorption to iron

455 (oxyhydr)oxide and incorporation into Fe-Si gels can create substantial Si isotope fractionation

456 (Delstanche et al., 2009; Zheng et al., 2016). Pore fluids show high Fe^{2+} concentrations (up to 190 µM;

457 Scholz et al., 2019) and Si concentrations lower than amorphous Si and quartz solubilities at various

458 depths (this study; Von Damm et al., 1985; Gieskes et al., 1988), indicating precipitation of the

459 respective mineral phase during pore fluid ascent. Gieskes et al. (1988) reported on amorphous silica

460 cement in the hydrothermally-influenced sediments of the Guaymas Basin, which is supported by

461 findings of this study and likely explains the high amorphous SiO_2 contents identified by XRD (~35

462 wt%; see Sect. 3.5; Table 2S). In the Guaymas Basin, high thermal gradients (up to 11 K m^{-1}; Geilert et

463 al., 2018) caused by igneous sill intrusions near the active spreading center significantly influence

464 diagenetic reactions at depth and accelerate Si dissolution and precipitation (Fig. 5a) (e.g. Kastner

465 and Siever, 1983). This can also explain the high pore fluid $\delta^{30}Si_{pf}$ values, given that deep Si saturated

466 fluids ascent and Si precipitates, likely along with Fe, over a large temperature range, whereby lower

467 temperatures are associated with larger Si isotope fractionation shifting pore fluid $\delta^{30}Si_{pf}$ to the

468 observed high values (Geilert et al., 2014; Zheng et al., 2016).

469

470   4.3.3 OMZ site

471

472 At the OMZ site, the $\delta^{30}Si_{pf}$ values are significantly lower (on average 0.0±0.5‰) than the water

473 column $\delta^{30}Si_{water\ column}$ value (+1.5±0.2‰) and also lower than the $\delta^{30}Si_{bSiO2}$ value (+0.8‰) (Fig. 2, 3).

474 Interestingly, the only other $\delta^{30}Si_{pf}$ values from an OMZ were obtained at the Peruvian margin (Ehlert

475 et al., 2016), where the $\delta^{30}Si_{pf}$ values are slightly higher than the water column $\delta^{30}Si_{bw}$ values (+1.6‰

476 and +1.5‰, respectively). As Ehlert et al. (2016) concluded, the Peruvian $\delta^{30}Si_{pf}$ values are influenced

477 by $bSiO_2$ dissolution and precipitation of authigenic aluminosilicates, the latter process shifting pore

478 fluid $\delta^{30}Si_{pf}$ to values higher than those of the water column. Consequently, in order to explain the

479 extremely low $\delta^{30}Si_{pf}$ values at the Guaymas Basin OMZ, an additional process must occur. We

480 hypothesize that a phase enriched in ^{28}Si needs to dissolve in order to shift the pore fluid $\delta^{30}Si_{pf}$

481 values and this phase might be 1) iron (oxyhydr)oxides with adsorbed ^{28}Si or 2) terrestrial clays.

482

483 Silicon exhibits a strong affinity to iron (oxyhydr)oxides (see also section 4.3.2; Davis et al., 2002) and

484 Si isotopes fractionate significantly during Si adsorption and co-precipitation (Delstanche et al., 2009;

485 Zheng et al., 2016). Dissolved Fe^{2+} in pore fluids can be transferred across the sediment-water

486 interface via diffusion and re-precipitates as iron (oxyhydr)oxides, where it subsequently dissolves

487 again in the reducing sediment. This process can repeat, resulting in multiple cycles of Fe dissolution

488 and re-precipitation on the Guaymas Basin slope (Scholz et al., 2019). We hypothesize that the light

489 ^{28}Si adsorbs to iron (oxyhydr)oxides in the water column and that upon reductive dissolution of Fe

490 minerals in the surface sediment, the light ^{28}Si isotope is re-released into the pore fluids, adding to

491 the observed low $\delta^{30}Si_{pf}$ values. However, the quantification of this Fe-Si shuttle and the contribution

492 to the low $\delta^{30}Si_{pf}$ values to the OMZ pore fluids remains difficult given that Fe undergoes multiple

493 cycles of dissolution and re-precipitation. Furthermore, the exact process of complexation, Si isotope

494 fractionation, and co-precipitation is unknown and requires further investigations. We can only

495 speculate that the transport of ^{28}Si via the Fe-Si shuttle is only of minor importance given that the

496 MAR of $bSiO_2$ and terrigenous material are dominating the Si supply to Guaymas OMZ sediments

497 (Calvert, 1966; DeMaster, 1981a).

498

499 The low $\delta^{30}Si_{pf}$ values can also be explained by dissolution of terrigenous clay particles, which are

500 generally enriched in ^{28}Si, showing a large range in $\delta^{30}Si$ with the majority between -3‰ to 0‰

501 (Frings et al., 2016 and references therein). Clays are usually considered to be the stable end product

502 of silicate weathering. However, fine clay particles and highly reactive surface sites of clays such as

503 montmorillonite, smectite and illite may dissolve in natural waters (Cappelli et al., 2018; Golubev et

504 al., 2006; Köhler et al., 2005). The dissolution is promoted by organic ligands and the reduction of

505 structural iron of clay minerals under reducing conditions (Anderson and Raiswell, 2004). Humic

506 substances that are abundant in OMZ sediments enriched in organic matter may catalyze the

507 microbial reduction of structural iron in clays (Lovley et al., 1998) and their dissolution (Liu et al.,

508 2017). Clays are abundant in OMZ sediments, given that fine-grained terrigenous material is

509 transported downslope from the shelf to the basin (Scholz et al., 2019). Furthermore, the microbial

510 oxidation of ferrous Fe in these fine-grained silicate minerals and its subsequent conversion to

511 reactive iron minerals was also found to contribute to the Fe cycling at the Guaymas Basin slope

512 (Scholz et al., 2019).

513

514 In order to constrain the possibility of terrigenous clay dissolution and the related shift to low $\delta^{30}Si_{pf}$

515 values in the Guaymas OMZ a reactive transport model was applied, based on our previously

516 published $\delta^{30}Si$ model (Ehlert et al., 2016). The data obtained at the Guaymas OMZ were used to

517 model the turnover of Si in these sediments and the previously published model extended to

518 consider additional processes (Fig. 6). A full description of the model is presented in the

519 supplementary information. The model was fit to dissolved silica concentrations and $\delta^{30}Si$ values

520 measured in pore fluids and biogenic opal and K/Al ratios determined in the solid phase (Fig. 6). High

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521   rates of terrigenous clay dissolution were applied at the sediment surface to reproduce the observed

522   minima in $\delta^{30}Si_{pf}$ pore fluid values and K/Al ratios in a model run best fitting our data set (Fig. 6, best

523   fit). Since the terrigenous phases deposited at the sediment surface contain potassium (K_{terr} = 1.7

524   wt%, K/Al = 0.19; Viers et al., 2009) and are depleted in ^{30}Si (clay $\delta^{30}Si \approx$ -2‰; Frings et al., 2016 and

525   references therein), the dissolution of these phases induces a decline in pore fluid $\delta^{30}Si$ and solid

526   phase K/Al (supplementary information). The precipitation of authigenic phases that are depleted in

527   ^{30}Si (Si isotoppe fractionation: $\Delta^{30}Si_{au}$ = -2‰; Ehlert et al., 2016) and characterized by high K contents

528   (K/Al = 0.32; Michalopoulos and Aller, 2004) induces a down-core increase in pore fluid $\delta^{30}Si_{pf}$ and

529   solid phase K/Al below the surface minimum. Consequently, terrigenous clay dissolution under the

530   reducing conditions of the OMZ and subsequent authigenic aluminosilicate precipitation can explain

531   the low $\delta^{30}Si_{pf}$ values detected in Guaymas OMZ pore fluids (Fig. 5).

532

533   Additional simulations were conducted to investigate how the solid phase and pore fluid composition

534   is affected by the dissolution of terrigenous clay phases and the precipitation of authigenic phases

535   (Fig. 6). The surface minima in pore fluid $\delta^{30}Si_{pf}$ and solid phase K/Al disappear when the dissolution

536   rate is set to zero (R_{terr} = 0) while the ongoing precipitation of authigenic phases leads to a strong

537   down-core increase and high values at depth that are not consistent with the data. Pore fluid $\delta^{30}Si_{pf}$

538   and solid phase K/Al values strongly decrease with depth when the rate of authigenic phase

539   precipitation is set to zero (R_{au} = 0) such that the model yields values that are significantly lower than

540   the measured values. Dissolved silica concentrations cannot be used to further constrain R_{terr} and R_{au}

541   because they are largely controlled by the dissolution of biogenic opal (R_{opal}). Dissolved K

542   concentrations show a much lower sensitivity to R_{terr} and R_{au} than solid phase K/Al ratios due to the

543   high porosity of the OMZ sediments. Changes in dissolved K are largely eliminated by molecular

544   diffusion that is favored by the high porosity while the effect of the solid phase reactions R_{terr} and R_{au}

545   on the pore fluid composition is diminished by the low solid phase contents and the high background

546   concentration of dissolved K in ambient bottom waters. However, the model runs show that the

547   more sensitive pore fluid $\delta^{30}Si_{pf}$ and solid phase K/Al can be used to constrain the balance between

548   the dissolution of terrigenous phases and the precipitation of authigenic phases and that both

549   reactions are required to model the low $\delta^{30}Si_{pf}$ values measured in the Guaymas OMZ.

550

551   The modelled Si isotope composition of the benthic flux is -0.97‰, which is lower than the $\delta^{30}Si$

552   value of the bottom water (+0.8‰). The higher bottom water $\delta^{30}Si$ value along with the low Si

553   concentration (~30µM), which is lower than the ambient water column Si concentration (~80µM),

554   indicates that a certain amount of Si must directly re-precipitate at the sediment water interface. Still

555   the $\delta^{30}Si$ of the bottom water is lower compared to the ambient water column, showing a benthic Si

556   flux with low δ^{30}Si values at continental margin settings, which is also in excellent agreement with

557   previously modelled and calculated δ^{30}Si values (Ehlert et al., 2016; Grasse et al., 2016). These

558   findings show that benthic Si fluxes at continental margins are a source of low δ^{30}Si values to the

559   ocean and need to be taken into account in future marine Si budget models.

560

561   4.4 Controlling processes and the impact on the global marine Si cycle

562

563   Stable and radioactive Si isotope data revealed significant sedimentary import and export processes

564   influencing the marine silica cycle (Ehlert et al., 2013, 2016; Tréguer and De La Rocha, 2013; Grasse

565   et al., 2016; Rahman et al., 2017; Sutton et al., 2018). Diatom burial removes about 9.9 Tmol yr^{-1} Si

566   from the ocean to the sediments, however, effects of terrigenous silicate dissolution and reverse

567   silicate weathering on $bSiO_2$ burial, preservation, and the benthic Si flux (and its Si isotope

568   composition) are not well constrained (Sutton et al., 2018). It has previously been shown that silicate

569   minerals dissolve in deep methanogenic sediments where the dissolution process is favored by high

570   CO_2 and organic ligand concentrations in ambient pore fluids (Wallmann et al., 2008). Similar to

571   chemical weathering on land, the dissolution of terrigenous silicate phases in marine sediments leads

572   to a release of cations and the conversion of CO_2 into HCO_3^-. Moreover, this marine weathering

573   process provides the dissolved Al that is needed for reverse weathering reactions. Our OMZ data

574   show for the first time that marine silicate weathering (dissolution of terrigenous silicates) also

575   occurs in OMZ surface sediments where it can outpace reverse weathering (precipitation of

576   authigenic silicates). Our study indicates that ambient environmental conditions appear to

577   significantly influence the balance between marine weathering and reverse weathering and thereby

578   the Si flux back to the ocean. Pore fluid δ^{30}Si$_{pf}$ values depend on a complex interplay between $bSiO_2$,

579   terrigenous silicate dissolution, and authigenic aluminosilicate precipitation, however, the controlling

580   factors that determine which process dominates are difficult to constrain (Fig. 5). In view of the OMZ

581   settings (Guaymas Basin versus Peruvian margin), the most pronounced difference is the MAR$_{terr}$

582   which is significantly higher in the Guaymas Basin (252 g m^{-2} yr^{-1}; calculated by multiplying the

583   terrigenous content derived in Eq. (1) with the MAR from Eq. (2)) than at the Peruvian margin (100 g

584   m^{-2} yr^{-1}; MAR from Ehlert et al., 2016; terrigenous content calculated after Eq. (1) with 6 wt% $bSiO_2$,

585   15 wt% OC, 8 wt% $CaCO_3$) (Fig. 5a, b). The high terrigenous detritus content is supplied via rivers in

586   the Guaymas Basin (Calvert, 1966; DeMaster, 1981). In combination with the high MAR$_{terr}$ in the

587   Guaymas OMZ, high water/rock ratios (high porosity) additionally promote dissolution processes (Fig.

588   5). Lower MAR$_{terr}$ and water/rock ratios found in the Peruvian upwelling margin appear to limit the

589   dissolution rate of terrigenous phases and promote authigenic aluminosilicate precipitation (Fig. 5b,

590   c), shifting pore fluid δ^{30}Si$_{pf}$ to higher values compared to the corresponding δ^{30}Si$_{bSiO2}$ and δ^{30}Si$_{bw}$

591   values. This illustrates that the pore fluid $\delta^{30}Si_{pf}$ values of apparently similar settings (e.g. OMZ sites)

592   highly depend on the ambient environmental conditions and are not easily transferable.

593

594   4.5 Hydrothermal impact on the marine Si cycle

595

596   Findings of this study show that additional Si sources like hydrothermal input appear to affect the

597   oceanic $\delta^{30}Si$ values only in close vicinity to the hydrothermal fields. The $\delta^{30}Si$ values of the

598   hydrothermal plume (+0.7 to +1.4‰) are highly diluted by seawater (≥ 94%, Table 2) and thus

599   deviate from hydrothermal fluid $\delta^{30}Si$ values (-0.3‰; De La Rocha et al., 2000). However, the

600   currently available data set regarding $\delta^{30}Si$ values of hydrothermal fluids is limited (two data points;

601   De La Rocha et al., 2000), even though they are in excellent agreement with oceanic crust $\delta^{30}Si$

602   values (-0.29±; Savage et al., 2010), the rock through which hydrothermal fluids circulate and gain

603   their Si isotopic signature. In our data set, no correlation exists between the $\delta^{30}Si$ values and the Si

604   concentration of the hydrothermal plume (Fig. 1S) and instead the $\delta^{30}Si$ values are predominantly

605   controlled by Si precipitation, likely in the hydrothermal conduit during ascent or after discharge in

606   contact with colder seawater. Temperature variations and interlinked precipitation rates were found

607   in addition to co-precipitation with Al or Fe to cause large Si fractionation such that precipitates are

608   enriched in ^{28}Si (Geilert et al., 2014, 2015; Oelze et al., 2015; Roerdink et al., 2015; Zheng et al.,

609   2016). The varying impacts of these factors can also explain why the diluted hydrothermal plume

610   $\delta^{30}Si$ values with the highest hydrothermal share (Table 2) does not show the lowest $\delta^{30}Si$ values,

611   indicative of hydrothermal fluids, given that Si is more reactive compared to Mg, the element on

612   which the hydrothermal share calculations are based (see supplement from Berndt et al., 2016). The

613   large range in hydrothermal plume $\delta^{30}Si$ values, which clearly show high degrees of seawater

614   dilution, illustrates the complexity of precipitation processes when hydrothermal fluids get in contact

615   with cold seawater and which requires further investigations especially with respect to the impact on

616   the global marine Si cycle.

617

618   5.   CONCLUSIONS

619

620   Marine silicate weathering and reverse weathering impact the pore fluid isotopic composition of

621   sediments and are key processes of the marine silica cycle. In the Guaymas Basin, these processes

622   have been studied under markedly differing thermal and redox conditions. Si isotope compositions of

623   pore fluids combined with those of biogenic silica and ambient bottom waters helped to decipher

624   marine weathering and reverse weathering reactions, which would have remained undetected by

625   elemental concentrations alone and highlight the importance of Si isotope studies to constrain early

626   diagenetic reactions. Si concentrations and $\delta^{30}Si_{pf}$ signatures are the result of the interplay between

627   silica dissolution and Si precipitation, however, the involved phases differ significantly between the

628   study sites. Large differences in $\delta^{30}Si_{pf}$ values in a regionally constrained basin show that oxic/anoxic

629   conditions, hydrothermal fluids, water/rock ratios and the input of terrigenous material strongly

630   affect the pathways and turnover rates of Si in marine sediments. The light $\delta^{30}Si_{pf}$ and $\delta^{30}Si_{BW}$ values

631   from the Guaymas OMZ confirm earlier studies suggesting a light Si isotope value of the benthic Si

632   flux (Ehlert et al., 2016; Grasse et al., 2016), which need to be taken into account in future oceanic

633   mass balances of Si and in modelling studies concerning the isotopic Si cycle. Environmental settings,

634   in particular the MARs of terrigenous material, water/rock ratios, and redox conditions appear to be

635   the major factors controlling the balance between marine silicate weathering and reverse

636   weathering and the Si isotope fractionation in pore fluids of marine sedimentary settings and need to

637   be considered particularly in marine Si isotope studies.

638

639   AUTHOR CONTRIBUTION

640

641   SG, CH, MS, and FS helped sampling and processing of the samples onboard. SG, PG, and KD

642   conducted the Si isotope measurements. SG, CE, PG, KD, FS, and MF helped interpreting the data.

643   KW designed the reactive transport model. SG prepared the manuscript with the contribution of all

644   authors.

645

646   COMPETING INTEREST

647

648   The authors declare that they have no conflict of interest.

649

650   ACKNOWLEDGEMENTS

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942 **Tables**

943

944 Table 1: Pore fluid Si concentration (µM), $\delta^{30}Si_{pf}$ values (‰) as well as biogenic silica weight fraction

945 (bSiO$_2$ in wt%), Al/Si ratio (mM/M), $\delta^{30}Si_{bSiO2}$ values (‰), porosity (Ø), Al and K contents (wt%) for the

946 basin sites, hydrothermal site, and OMZ site.

947

948 Table 2: Water column and hydrothermal plume Si concentration (µM) and Si isotope values (‰).

949 Additionally, the share of hydrothermal fluids within the hydrothermal plume is given based on the

950 calculation provided by Berndt et al. (2016) in their supplementary materials.

951

952 **Figures**

953

954 Fig. 1. A) Location map of the sampling stations in the Guaymas Basin, Gulf of California. Black square

955 in the overview map indicates the sampling area. B) Sedimentary bSiO$_2$ content at each sampling

956 station. Water column stations were above MUC15-02 (VCTD02) in the basin, the hydrothermal site

957 (VCTD06, 09), and at the OMZ site (VCTD07).

958

959 Fig 2: Depth (cmbsf) profiles for all stations for pore fluid Si concentration (Si(OH)$_4$) in µM (grey

960 symbols) and $\delta^{30}Si_{pf}$ values (colored symbols) and biogenic opal weight fraction (bSiO$_2$) in wt% (grey

961 symbols) and $\delta^{30}Si_{bSiO2}$ values (colored symbols). The dashed line is the $\delta^{30}Si$ value of the deep basin

962 (VCTD02) and the dotted line represents the $\delta^{30}Si$ value of the water column in the OMZ (VCTD07).

963 The uppermost Si isotope data point in the pore fluid diagrams refers to the bottom water (labelled

964 BW). Note the different depth scale for the OMZ site. The brackets around the MUC22-04 bottom

965 water Si concentration value indicate possible surface water contamination. Error bars not indicated

966 are within symbol size. The long-term error (2SD) of international standards is indicated in the upper

967 right $\delta^{30}Si_{pf}$-depth profile.

968

969 Fig. 3. Pore fluid $\delta^{30}Si$ values are displayed versus the inverse Si concentration (1/Si) for the basin

970 sites, the hydrothermal site, and the OMZ site. Error bars not indicated are within symbol size. Mixing

971 curves are calculated after Eq. (3) between the respective water column and the average bSiO$_2$ $\delta^{30}Si$

972 value for all sites (see text for details).

973

974 Fig. 4. Asymptotic Si concentration (a) and the pore fluid $\delta^{30}Si_{pf}$ values (b) as a function of the

975 terrigenous/bSiO$_2$ ratio for the basin sites, the hydrothermal site, and the OMZ site in the Guaymas

976   Basin. An exponential increase in silicate concentrations with decreasing terrigenous/bSiO$_2$ ratio is

977   observed, which is not reflected by corresponding systematic changes in δ^{30}Si$_{pf}$. The values for the

978   terrigenous/bSiO$_2$ ratio defining the global trend (grey dots) are from the Southern Ocean, Scotia

979   Sea, Norwegian Sea, NE Atlantic, Juan de Fuca Ridge, Arabian Sea, and the Peru Basin (Van Cappellen

980   and Qiu, 1997a; Rabouille et al., 1997; Rickert, 2000).

981

982   Fig. 5. Conceptual model of the processes influencing pore fluid δ^{30}Si$_{pf}$ values in the Guaymas Basin

983   (a) and the Peruvian margin (b). Bold values in the sediment show the average pore fluid δ^{30}Si$_{pf}$

984   values. Arrow length indicates the dominating process (dissolution versus precipitation). The δ^{30}Si

985   values in the hydrothermal plume indicate dilution with seawater (see section 4.5). (c) The average

986   pore fluid δ^{30}Si$_{pf}$ values are shown, indicating the dominance of precipitation or dissolution processes

987   for the three settings in the Guaymas Basin and the Peruvian OMZ.

988

989   Fig. 6. Data and model results for OMZ core. a: Porosity. b: Biogenic opal concentration in solid

990   phase. c: K/Al ratio in solid phase. d: Dissolved silica concentration in pore fluids. e: Dissolved

991   potassium in pore fluids. f: Isotopic composition of dissolved silica. g: rate of biogenic opal

992   dissolution. h: Rate of authigenic phase precipitation. i: Rate of terrigenous phase dissolution.

Table 1

Station/MUC# Station name	Latitude (N) / Longitude (W)	Water depth (m)	Depth (cmbsf)	Pore fluid			Sediment						
				Si (µM)	$\delta^{30}Si$ pf (‰)	2SD (‰)	bSiO$_2$ (wt%)	(Al/Si) bSiO2 (mM/M)	$\delta^{30}Si$ bSiO2 (‰)	2SD (‰)	Φ	Al (mg g^{-1})	K* (mg g^{-1})
SO241-33/11/ Basin site	27° 33.301' 111° 32.883'	1855	BW	173	1.9	0.2	-	-	-	-	-	-	-
			0.5	381	1.3	0.2	22.6	39	0.8	0.1	0.932	44.4	13.7
			1.5	455	-	-	23.1	-	-	-	0.920	45.2	13.9
			2.5	563	1.2	0.1	24.2	-	-	-	0.905	46.3	14.1
			3.5	635	-	-	22.4	-	-	-	0.894	-	-
			4.5	685	-	-	-	-	-	-	0.892	49.1	14.7
			6	686	-	-	25.2	-	-	-	0.875	39.2	12.4
			8	745	-	-	-	-	-	-	0.857	-	-
			10	726	-	-	21.9	-	-	-	0.852	-	-
			12.5	737	0.9	0.2	18.5	-	-	-	0.826	53.2	16.0
			15.5	750	-	-	14.4	-	-	-	0.800	61.4	17.9
			18.5	751	-	-	14.8	-	-	-	0.787	-	-
			22	712	1.2	0.2	19.6	26	0.8	0.2	0.801	59.5	17.5
SO241-22/04/ Basin site	27° 28.165' 111° 28.347'	1839	BW	54	2.0	0.2	-	-	-	-	-	-	-
			0.5	349	1.0	0.2	11.6	37	0.9	0.2	0.910	57.8	17.0
			1.5	377	-	-	-	-	-	-	0.907	-	-
			2.5	394	-	-	-	-	-	-	0.890	53.6	16.4
			3.5	421	-	-	-	-	-	-	0.897	-	-
			4.5	474	-	-	-	-	-	-	0.895	-	-
			5.5	558	1.1	0.1	10.9	-	-	-	0.893	58.7	17.3
			7	590	-	-	-	-	-	-	0.895	-	-
			9	637	1.2	0.2	13.1	-	-	-	0.890	58.6	17.2
			11	636	-	-	-	-	-	-	0.891	-	-
			13	597	-	-	-	-	-	-	0.895	-	-
			15.5	545	-	-	-	-	-	-	0.896	-	-
			18.5	440	1.5	0.2	7.6	-	-	-	0.895	57.9	17.3
			22	404	-	-	-	-	-	-	0.876	-	-
			26	364	1.3	0.2	9.8	71	0.5	0.2	0.842	66.6	19.4

Station	Lat	Long		Depth										
SO241-23/05/ Basin site	27° 30.282'	111° 40.770'	1726	BW	216	1.8	0.3	-	-	-	-	-	-	-
				0.5	485	1.4	0.2	28.2	23	0.9	0.2	0.934	30.3	9.2
				1.5	610	-	-	-	-	-	-	0.921	-	-
				2.5	713	-	-	-	-	-	-	0.921	-	-
				3.5	753	1.3	0.1	30.1	-	-	-	0.923	31.8	9.8
				4.5	751	-	-	-	-	-	-	0.918	-	-
				5.5	726	-	-	-	-	-	-	0.908	33.1	9.8
				7	713	-	-	-	-	-	-	0.904	-	-
				9	731	1.1	0.2	28.3	-	-	-	0.894	35.3	10.6
				11	690	-	-	-	-	-	-	0.879	-	-
				13	651	-	-	-	-	-	-	0.829	-	-
				15.5	663	-	-	-	-	-	-	0.829	27.6	8.0
				18.5	664	-	-	-	-	-	-	0.825	-	-
				22	640	1.3	0.4	21.4	15	0.4	0.1	0.807	27.7	8.1
SO241-15/02/ Basin site	27°26.925'	111°29.926'	1845	BW	178	1.6	0.2	-	-	-	-	-	-	-
				0.5	474	1.2	0.3	26.7	19	0.9	0.3	0.958	31.5	10.7
				1.5	569	-	-	24.7	-	-	-	0.943	33.9	10.8
				2.5	590	-	-	27.3	-	-	-	0.935	35.7	11.1
				3.5	610	-	-	27.7	-	-	-	0.918	35.9	11.0
				4.5	605	-	-	-	-	-	-	0.927	30.4	9.2
				5.5	607	1.2	0.2	30.4	-	-	-	0.924	37.2	11.3
				7	635	-	-	-	-	-	-	0.908	37.2	11.4
				9	711	-	-	25.2	-	-	-	0.913	34.5	10.6
				11	746	-	-	30.1	-	-	-	0.918	32.0	9.9
				13	673	-	-	-	-	-	-	0.920	32.2	10.2
				15.5	707	1.2	0.2	47.6	-	-	-	0.927	23.9	7.7
				18.5	727	-	-	-	-	-	-	0.929	21.3	6.6
				22	753	-	-	-	-	-	-	0.919	29.4	9.1
				26	737	-	-	-	-	-	-	0.882	46.4	13.9
				30	781	1.2	0.2	23.6	57	1.0	0.2	0.864	51.8	15.4
SO241-66/16/ Hydrothermal site	27° 24.577'	111° 23.265'	1842	BW	254	1.5	0.2	-	-	-	-	-	-	-
				0.5	427	2.0	0.2	13.3	52	0.8	0.2	0.911	17.4	4.8
				1.5	554	-	-	-	-	-	-	0.900	18.9	5.2

31

Site	Depth								Φ		
	2.5	702	-	-	-	-	-	-	0.855	17.4	4.4
	3.5	752	-	-	-	-	-	-	0.820	16.7	4.1
	4.5	781	-	-	-	-	-	-	0.808	16.0	3.8
	5.5	781	2.2	0.1	11.0	-	-	-	0.793	15.4	3.5
	6.5	875	-	-	-	-	-	-	0.775	14.8	3.3
	9	877	-	-	-	-	-	-	0.770	13.4	2.7
	11	892	-	-	7.0	-	-	-	0.742	9.4	1.3
	13	914	-	-	4.7	-	-	-	0.810	17.8	3.9
	15.5	903	-	-	14.6	-	-	-	0.802	21.9	5.4
	18.5	888	1.8	0.1	8.2	35	0.9	0.1	0.620	2.9	-
SO241-29/09/ OMZ site 27°42.410' 111°13.656' 665	BW	31	0.8	0.2	-	-	-	-			
	0.5	247	-0.5	0.3	15.3	-	-	-	0.970	35.1	12.67
	1.5	425	-	-	-	-	-	-	0.954	46.6	14.0
	2.5	458	-0.3	0.1	16.9	-	-	-	0.945	48.9	14.9
	3.5	492	-	-	-	-	-	-	0.947	47.2	14.7
	4.5	569	-	-	-	-	-	-	0.939	48.6	15.0
	5.5	618	0.3	0.2	15.3	-	-	-	0.935	51.1	15.3
	6.5	655	-	-	-	-	-	-	0.928	50.4	15.4
	7.5	735	-	-	-	-	-	-	0.923	53.4	16.2
	9	763	0.0	0.2	13.5	-	-	-	0.926	51.8	15.8
	11	754	-	-	-	-	-	-	0.926	39.5	10.1
	13	753	-	-	-	-	-	-	0.929	48.6	14.2
	15	767	-	-	16.23	26	0.8	0.1	0.909	53.3	15.9
	18.5	772	-	-	-	-	-	-	0.913	53.8	15.9
	20.5	781	-0.2	0.2	18.1	-	-	-	0.911	53.3	15.7
	23.5	763	-	-	-	-	-	-	0.906	56.1	16.8
	26.5	765	-	-	-	-	-	-	0.919	47.8	14.5
	29	763	-	-	-	-	-	-	0.929	41.5	12.6
	30	768	-	-	-	-	-	-	0.925	45.9	13.9
	38	760	0.8	0.2	21.9	-	-	-	0.925	45.8	13.5

Φ = porosity
* porosity corrected

Table 2

Cruise-Station/VCTD#/ bottle#/Station name	Latitude (N) / Longitude (W)	Depth	Si	δ^{30}Si	2SD	hydrothermal fluid share*
		(mbsl)	(µM)	(‰)	(‰)	(%)
Water column						
SO241-12/02/	27° 26.133	1844	163	1.5	0.1	0.1
Basin site	111° 30.268					
SO241-42/07/	27° 42.411	586	78	1.5	0.2	0
OMZ site	111° 13.663					
Hydrothermal plume						
SO241-67/09/06/	27° 24.750	1800	253	0.7	0.1	2.1
Hydrothermal site	111° 23.240					
SO241-67/09/09/	27° 24.750	1800	206	1.4	0.2	0.2
Hydrothermal site	111° 23.240					
SO241-67/09/12/	27° 24.750	1800	690	1.0	0.2	5.7
Hydrothermal site	111° 23.240					

* calculation in Berndt et al. (2016)

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6