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1   Chromium isotopes in marine hydrothermal sediments
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26 **Abstract-** Hydrothermal chromium (Cr) cycling contributes to marine Cr inventories and their
27 Cr isotopic composition, yet Cr isotope effects associated with this cycling remain poorly
28 documented. Here we determine the distribution, isotopic composition, and diagenetic mobility
29 of Cr in hydrothermal sediments from the distal flank of the South East Pacific Rise (SEPR,
30 DSDP-site 598). We find that Cr is primarily associated with the metalliferous iron
31 (oxyhydr)oxide and detrital components of the sediment (0.4 – 3.6 mg kg^{-1}), whereas Cr
32 concentrations are much lower in the dominant carbonate phase ($<0.03 \pm 0.2$ mg kg^{-1}). The Cr:Fe
33 ratio of the metalliferous component, however, decreases with increasing depth below the
34 sediment water interface, with an apparent loss of $>80\%$ Cr from the sediment relative to Fe. We
35 propose this loss is tied to oxidation of authigenic Cr(III) to Cr(VI) followed by diagenetic
36 remobilization and efflux from the sediment pile. The bulk δ^{53}Cr composition of the SEPR
37 sediments is isotopically light (-0.24 to -0.57 $\pm$ 0.05‰) and the authigenic δ^{53}Cr is as light as -
38 1.2 $\pm$ 0.2‰, and we argue that this light Cr isotopic composition results from the partial
39 reduction of oxic seawater-bearing Cr(VI) by reduced hydrothermal vent fluids enriched in
40 Fe(II)$_{aq}$. Diagenetic oxidation of the reactive Cr pool by Mn-oxides and loss of Cr(VI) from the
41 sediment may further deplete the sediment in ^{53}Cr during diagenesis. The δ^{53}Cr composition of
42 the detrital Cr fraction of the sediment (average δ^{53}Cr composition = -0.05 $\pm$ 0.04‰) falls within
43 the igneous silicate earth (ISE) range, revealing that detrital Cr delivered to this region of the
44 Pacific ocean is unfractionated, and has carried a relatively constant δ^{53}Cr composition over the
45 last 5.7 million years. Together our results show that light δ^{53}Cr compositions in hydrothermal
46 sediments are imparted through a combination of processes previously overlooked in the marine
47 Cr biogeochemical cycle, and that the δ^{53}Cr composition of such sediments may provide a rich
48 source of information on paleo-marine redox conditions.
49
50

51 1.0 Introduction

52   Chromium (Cr) isotope ratios are emerging as proxy that can track the evolving redox

53 state of the ocean-atmosphere system over geologic time-scales (Cole et al., 2016; Crowe et al.,

54 2013; Frei et al., 2011; Gueguen et al., 2016; Holmden et al., 2016; Planavsky et al., 2014). The

55 simplest application of the Cr isotope system uses large amplitude shifts in the Cr isotopic

56 composition of sedimentary rocks, like banded iron formations (BIF) and ironstones, together

57 with shales and limestones to record the onset of Cr redox cycling, which is indicative of the

58 presence of oxygen in Earth's surface environments (Bonnand et al., 2013; Cole et al., 2016;

59 Crowe et al., 2013; Frei et al., 2009; Gilleaudeau et al., 2016; Planavsky et al., 2014). However,

60 more detailed insight into Cr isotope systematics could enable more nuanced applications of the

61 proxy. For example, improved knowledge of the distribution of Cr isotopes in a wider range of

62 sedimentary reservoirs that serve as Cr repositories and archives of past Earth surface chemistry

63 is essential for the development of a global isotope mass balance. Further knowledge of the

64 modern Cr cycle also provides a means to test many of the assumptions built into the current

65 interpretation of the Cr isotope record.

66   Our emerging picture of the global Cr cycle is illustrated schematically in Figure 1.

67 Chromium resides in the continental crust bound in its relatively low solubility trivalent redox

68 state Cr(III), and is hosted in silicate and oxide minerals (Fendorf, 1995; Oze et al., 2004). In the

69 modern Earth system, with O_2 comprising 21% of the atmosphere, this Cr is liberated to runoff

70 predominantly through oxidative weathering at Earth's surface, which produces Cr(VI) from

71 Cr(III) through heterogenous solid-state catalysis by Mn-oxides. (Rai et al., 1989; Schroeder and

72 Lee, 1975). It has also been suggested that Cr(III) may also be oxidized by H_2O_2 in the local

73 absence of O_2 in serpentinizing systems (Oze et al., 2016), however a strong oxidant like O_2 is

74 likely required to generate this peroxide or other oxidants of Cr at the outset. Riverine transport

75 of Cr(VI) produced during oxidative weathering sustains the largest Cr flux to the modern oceans

76 (Jeandel and Minster, 1984; McClain and Maher, 2016; Reinhard et al., 2013). Once in the

77 oceans, this Cr(VI) is likely removed from seawater via reduction, by an as yet unknown

78 diversity of electron donors, to Cr(III), which in turn is scavenged by settling particles and

79 ultimately deposited in sea-floor sediments (Dossing et al., 2011; Ellis et al., 2002; Gueguen et

80 al., 2016; Kitchen et al., 2012; Reinhard et al., 2014). A fraction of Cr may also be delivered to

81 the oceans via rivers as Cr(III), partly stabilized as Cr(III)-organic complexes, or dissolved in

82 low pH systems (Fendorf, 1995; Rai et al., 1989; Yusof et al., 2007).

83   The contribution of hydrothermal systems to the marine Cr inventory remains poorly

84 constrained, and may represent a net source or sink of Cr in the global marine Cr mass balance.

85 Previous work suggests that Cr from hydrothermal vents represents ~0.02% of the Cr riverine

86 flux, or 12×10^6 mol yr^{-1}, implying that the contribution of Cr to seawater from hydrothermal

87 fluids is likely very small (Reinhard et al., 2013). While vent fluids emit Cr(III) derived from

88 acid dissolution of basaltic ocean crust, much of this Cr(III) is scavenged by Fe (oxyhydr)oxide

89 particles formed during the mixing of Fe(II)-laden vent fluids with ambient oxygenated seawater

90 (Dymond and Roth, 1988; Feely et al., 1996; Rudnicki and Elderfield, 1993; Sander and

91 Koschinsky, 2000). Deposition of these Fe (oxyhydr)oxides may thus quantitatively capture the

92 vent flux of Cr, which is then largely deposited in proximal and distal hydrothermal sediments

93 (Trocine and Trefry, 1988). However, given the typically strong vent flux of ferrous Fe – a

94 potent reductant of Cr(VI) – precipitation of hydrothermal Fe (oxyhydr)oxides particles may also

95 capture a fraction of seawater Cr(VI), rendering vent systems a net sink for seawater Cr (Trocine

96 and Trefry, 1988). While the fate of Cr in these particles remains unknown, long distance

97 transport of hydrothermal Fe and associated elements may distribute hydrothermal Cr over long

98 distances in the oceans. Cr(III) associated with Fe (oxyhydr)oxides generally has a low solubility

99 (e.g., Oze et al. (2004)) and, therefore, deposition of Cr in hydrothermal sediments may lead to

100 effective and quantitative burial of hydrothermal Cr with such phases. It has also been suggested,

101 however, that there is extensive Cr remobilization in surficial continental-margin Mn-oxide

102 bearing sediments (Shaw et al., 1990), which implies the potential for Cr remobilization from

103 Mn-oxide bearing hydrothermal sediments. Additional information on the fate of Cr deposited in

104 hydrothermal sediments is thus needed to better constrain the role of vent systems in the marine

105 Cr cycle.

106   Chromium isotopes are fractionated during redox reactions. During oxidative weathering,

107 the resulting Cr(VI) is enriched in the ^{53}Cr (heavy) isotope through a possible combination of

108 Cr(III) oxidation to Cr(VI) and partial re-reduction of Cr(VI) (Crowe et al., 2013; Zink et al.,

109 2010). Despite current uncertainty around the precise mechanism for this fractionation, heavy

110 δ^{53}Cr(VI) is exported from the weathering environment in runoff, leaving Cr(III) in the residual

111 soil isotopically light (^{53}Cr depleted) (Crowe et al., 2013; D'Arcy et al., 2016; Frei et al., 2011;

112 Frei et al., 2009). Oxidative weathering thus sets the heavy $\delta^{53}Cr$ composition observed in some

113 rivers (e.g. D'Arcy et al. (2016); Frei et al. (2009); Wu et al. (2017)), and contributes to the

114 heavy isotopic composition of seawater (modern values lie between ~ 0.5 and 1.5‰, Bonnand et

115 al. (2013); Scheiderich et al. (2015). On the other hand, dissolution of Cr(III), unless mediated by

116 strongly complexing organic acids (see Saad et al. (2017)), is unlikely to be associated with large

117 isotope fractionation (Crowe et al., 2013; Konhauser et al., 2011). Given that acid dissolution of

118 basalt provides Cr to vent fluids, the efflux of Cr(III) from hydrothermal vent waters is expected

119 to carry an isotopic signature no different from the igneous silicate earth (ISE), -0.12 ± 0.10‰

120 (Schoenberg et al., 2008). As a result, Cr(III) escaping removal via Fe (oxyhydr)oxide particle

121 scavenging in the vicinity of vents, would likely contribute a Cr isotope flux indistinguishable

122 from ISE to the marine Cr inventory, with potential to partly offset heavy signals imparted

123 through the riverine influx of Cr(VI) (Crowe et al., 2013; Schoenberg et al., 2008). Hydrothermal

124 Cr(III) precipitates, however, might also be expected to carry a lighter but variable Cr isotopic

125 composition, if diagenetic reactions remobilized Cr as result of partial oxidation or, if

126 hydrothermal particles captured seawater Cr(VI) through partial reduction.

127   To assess Cr deposition and cycling in hydrothermal settings we have determined the

128 abundances and distribution of Cr, Mn and Fe, together with Cr isotope ratios, from the western

129 distal flank of the South East Pacific Rise (SEPR), one of the fastest spreading centres on the

130 ridge crest system with rates of up to 14.5 cm yr^{-1} (Lyle, 1986). Three sediment cores from the

131 SEPR at DSDP sites 598, 599 and 600 were examined, with a focus on the more distal site 598,

132 which is currently ~1130 km west of the ridge crest. These sites have collected particulate

133 hydrothermal materials derived from the crest of the SEPR spreading center and transported by

134 westward-flowing deep-ocean circulation. Sequential extraction techniques were employed to

135 target Cr in different mineral phases of the sediment, and we used the molar ratios of Cr, Fe and

136 Mn to evaluate post-depositional alteration. We then assessed the implications of this

137 redistribution for marine Cr budgets, ocean isotope mass balance, and the use of Cr isotopes as a

138 proxy for the oxygenation state of the oceans.

139

140 2.0 Methodology

141   The three sediment cores used in this study were collected during DSDP Leg 92 in 1984.

142 They were previously used by Lyle (1986), to investigate the bulk sediment major element

geochemistry and the history of hydrothermal sedimentation on the south-eastern flank of the SEPR. Poulton and Canfield (2006) conducted a study of the association of P with Fe (oxyhydr)oxides and other phases in the upper 5.5 m at site 598. This site represents the most distal location from the ridge crest and via seafloor spreading is now located 1130 km from the active vent. Using splits from the same sample suite (Poulton and Canfield (2006)) we constructed a profile from the core surface to 5.5 m depth, corresponding to an age of 5.5 Myr at 5.5 m depth (Poulton and Canfield, 2006). To investigate vent particle alteration processes, Mn-oxide and Fe concentrations were determined in 5 samples across the top 20 cm of cores from the other sites (599 and 600), which are closer to the ridge crest, allowing us to track chemical changes in the Mn:Fe ratio of surface sediments in relation to the proximity to the ridge crest. The sediments at all three sites are reported to be compositionally simple, mainly comprising two phases, namely foraminferal and nannofossil carbonates (37- 95%) and metalliferous hydrothermal precipitates (3-40% of bulk sediment) (Barrett et al., 1987). Importantly, the sediments contain only small amounts of lithogenous detrital material as the sample locations are well removed from continental input sources (Barrett et al., 1987).

2.1 Chemical extraction techniques

A selective extraction scheme was used to quantify Cr in the different operationally defined phases of the hydrothermal sediment. Figure 2 is a schematic illustration of these procedures. We employed four different leaches in sequence, adapted from the procedures of Poulton and Canfield (2005), and two separate bulk digests. Table 1 contains a detailed breakdown of our leaching procedures and how they relate to the nomenclature employed in Poulton and Canfield (2006). The first leach in sequence (L_{Carb}) targeted the carbonate fraction. Powdered samples of ~200 mg were weighed into centrifuge tubes and leached with 10% acetic acid (Barrett et al., 1987). The acid addition was in excess of that needed to dissolve 200 mg of pure $CaCO_3$. Samples were placed on a shaker for 4 hours and subsequently centrifuged. An aliquot of supernatant was taken and diluted for Cr concentration analyses via inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). A subset of sediment samples were analysed for total inorganic carbon via coulometry before and after application of the first leach to ensure all $CaCO_3$ was successfully dissolved. Following removal of carbonate, the residual sediment was subjected to

174   the second leach in sequence, which targets poorly crystalline Fe-(oxyhydr)oxide phases

175   (lepidocrocite, ferrihydrite) (Thamdrup et al., 1994) using trace metal grade 0.5 N HCl

176   (Thamdrup et al., 1994) (L_{HFO}, which is broadly analogous to the Fe_{HFO} fraction in Poulton and

177   Canfield (2006)). The supernatant was decanted, filtered, and diluted for measurement via ICP-

178   MS.

179   Following the L_{HFO} extraction, the remaining sediment contained more crystalline metal

180   (oxyhydr)oxides as well as refractory detrital components. In order to differentiate between the

181   more crystalline authigenic metal (oxyhydr)oxides (e.g., goethite and hematite) and refractory

182   detrital minerals, we first subjected the residual sediment to 0.35 M acetic acid/0.2 M Na-citrate

183   buffered Na-dithionite leach for 2 hours (L_{GOE}, which targets minerals such as goethite and

184   hematite, and is referred to as the Fe_{GOE} fraction in Poulton and Canfield (2006)). The

185   supernatant was decanted following centrifugation, filtered, and diluted for measurement via

186   ICP-OES. We did not directly determine the Cr concentration of this sediment phase analytically

187   due to matrix effects of the L_{GOE} extract in the quadrupole ICP-MS, and we thus estimated the Cr

188   concentration of this leach using a mass balance approach (see Section 3.2 below). Following the

189   L_{GOE} extraction a small volume of greyish residual sediment remained, comprising the refractory

190   component of the sediment (not extractable in the L_{Carb}, L_{HFO} or L_{GOE} fractions). We leached the

191   residual sediment from L_{GOE} with near boiling 6 N HCl for 24 h (L_{Sil}, analogous to the Fe_{Sil}

192   fraction in Poulton and Canfield (2006)). Again, samples were centrifuged and an aliquot of the

193   supernatant was removed and diluted for analysis via ICP-MS and ICP-OES. We also performed

194   a separate bulk digest with 6 N HCl on 200 mg sediment by adding 10 mL of acid in sealed

195   centrifuge tubes (L_{6NHCl}). Again, samples were centrifuged and an aliquot of the supernatant was

196   removed and diluted for analysis via ICP-MS and ICP-OES.

197   The reactive Mn and Fe (oxyhydr)oxide content in sediments from the upper 10 cm at

198   sites 599 and 600, and from 5.5 m at site 598, were determined following the method of Neaman

199   et al. (2004) and Chao (1972). Samples of 7.5 mg were weighed into centrifuge tubes and

200   leached for 2 h with 0.1 M hydroxylamine hydrochloride (L_{MnOx}). The amount of NH_2OH-HCl

201   added was in a 1:2000 solid − solution ratio. Samples were centrifuged and an aliquot of

202   supernatant was taken for analysis by ICP-OES. Reaction time was limited to 2 h to restrict

203   dissolution of poorly crystalline iron-oxides (Neaman et al., 2004). Iron concentrations in these

204   extracts accounted for only 0.01% of the bulk Fe in the sediments.

205

2.2 Analytical methods

Chromium concentrations in our leachates were determined by ICP-MS, while major elements Al, Fe and Mn were determined by ICP-OES. The error on [Fe] measurements was ± 8% RSD based on the difference between triplicate measurements, and the detection limit, calculated as three times the standard deviation of the blank (n = 5) was 8 ppb in solution and roughly 35 mg kg^{-1} in the solid phase based on our dilutions. The error on our ICP-OES [Mn] measurements was ± 5% RSD based on the difference between triplicate measurements, and the detection limit, calculated as three times the standard deviation of the blank (n = 5) was 6 ppb in solution and roughly 30 mg kg^{-1} in the solid phase based on our dilutions. The error on [Cr] measurements is ± <1% RSD based on the difference between triplicate measurements, and the detection limit, calculated as three times the standard deviation of the blank (n = 5), translates to 0.028 mg kg^{-1} in the solid phase.

218

2.3 XRD analysis

We used quantitative X-ray diffraction (qXRD) methods on 6 bulk sediment samples to determine the sediment mineralogy. The samples were smear mounted with ethanol on non-diffracting silica plates. Continuous-scan X-ray powder-diffraction data were collected over a range 3-80°2θ with CoKα radiation on a Bruker D8 Focus Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°. We analyzed the X-ray diffractograms using the International Centre for Diffraction Database PDF-4 and Search-Match software by Bruker. X-ray powder-diffraction data of the samples were refined with Rietveld program Topas 4.2 (Bruker AXS).

2.4 Cr purification and isotope ratio determination

Chromium isotope ratios were determined on a Multi-Collector Inductively-Coupled Plasma Mass Spectrometer (MC-ICP-MS, Thermo Neptune) at the Yale Metal Geochemistry Center using a double-spike correction for isotope fractionation during column chemistry and instrumental mass bias. The spike was added to acid splits after the digestion procedure (bulk

236 sediment 6 N HCl digestion, L_{6NHCl} leachate as well as the L_{GOE} and L_{Sil} 6 N HCl digestion

237 performed sequentially). Although isotope effects due to leaching in Na-dithionite and 6 N HCl

238 have not been tested directly, we do not expect any measurable isotope fractionation during

239 acidic digestions of Cr, even at higher acid molarity (see Crowe et al. (2013) and Reinhard et al.

240 (2013)). We note that previous studies on Fe isotope ratios in rocks and sediments have also

241 shown that there appears to be no isotope effect during proton-promoted acid leaching of Fe

242 oxides, which is in contrast to ligand promoted dissolution (Wiederhold et al., 2006). We used

243 three separate column separations (Reinhard et al., 2014; Schoenberg et al., 2008) to ensure

244 complete removal of Fe, Ti, and V during chemical purification. Initially, a split of the 6 N HCl

245 sample solution was spiked, evaporated to dryness, and the residues brought up in 1 N HCl. The

246 amounts of ^{50}Cr-^{54}Cr double-spike ($^{50}Cr/^{52}Cr$ = 462.917, $^{53}Cr/^{52}Cr$ = 0.580, $^{54}Cr/^{52}Cr$ = 354.450,

247 calibrated in the Department of Geology, University of Illinois at Urbana-Champagne and added

248 as Cr(III)), were adjusted so that the spike/sample ratio (i.e., $(^{54}Cr)_{spk}/(^{52}Cr)_{smp}$) was 0.5. Prior to

249 the first column step (AG1-X8 anionic resin, 100-200 mesh), Cr(III) was oxidized to Cr(VI)

250 using potassium peroxidisulfate (heating the samples for 2 h at 110 °C). The AG1-X8 resin was

251 cleaned with mQ water, 3 N HNO_3 and 6 N HCl. The matrix was eluted with 24 ml of 0.2 N HCl

252 and 4 ml 2 N HCl, with Cr subsequently reduced with 5% H_2O_2 and eluted with 5 ml of 2 N

253 HNO_3. The second step removes traces of Fe that may remain after the first elution.

254 Microcolumns were filled with 0.2 ml AG1-X8 resin. The columns were cleaned using mQ water

255 and 3 N HNO_3, and samples were loaded and collected with 1.2 ml of 6 N HCl. Traces of Ti are

256 often left after the first two column steps. Therefore, as the last step, a cation resin AG50W-X8

257 (200-400 mesh) was used to ensure complete Ti and Cr separation. The resin was cleaned with

258 mQ water, 3 N HNO_3 and 6 N HCl, followed by sample loading in 3 ml of 0.5 N HNO_3 and by

259 matrix elution with 1 ml of 0.5 N HNO_3, 2 ml of 0.5 N HF and 6 ml of 1 N HCl. Cr was

260 collected after elution with 5 ml of 1.8 N HCl.

261   Chromium isotopes were run in high-resolution mode to resolve polyatomic interferences

262 such as $^{40}Ar^{12}C^+$, $^{40}Ar^{14}N^+$ and $^{40}Ar^{16}O^+$. Although our chemical procedure results in nearly

263 complete removal of Fe, Ti and V, these elements were monitored by measuring ^{56}Fe, ^{49}Ti and

264 ^{51}V, and samples were corrected for potential interferences of ^{54}Fe on ^{54}Cr, as well as ^{50}Ti and ^{50}V

265 on ^{50}Cr. Samples at a concentration of ~100 ng/g were introduced into the plasma with a PFA

266 μFlow nebulizer (~50 μL/min) coupled with an Apex IR (Elemental Scientific) without

267   additional N_2 gas or membrane desolvation. With a standard sample cone and X skimmer cone

268   under high-resolution mode, the sensitivity obtained was ~3×10^{-10} A ^{52}Cr on 100 ng/g solution.

269   All ion beams were measured on faraday detectors. The double-spike data reduction model is

270   based on the iterative method described by Siebert et al. (2001). A spiked Cr isotope standard

271   NIST SRM 979 was measured bracketing every three natural samples to ensure machine

272   stability. Chromium isotope ratios are reported relative to bracketing standards using

273   conventional delta notation (δ^{53}Cr = [(^{53}Cr/^{52}Cr)$_{sample}$/(^{53}Cr/^{52}Cr)$_{NIST-979}$ – 1] x 1000‰).

274   External precision is reported as two sigma (2σ) uncertainty, calculated based on

275   duplicate analysis of geological reference materials (GRMs) processed through ion-exchange

276   chromatography columns along with samples (BHVO-2 and Nod-A-1 were systematically

277   processed with 70 samples). The δ^{53}Cr value for BHVO-2 is -0.11 ± 0.07‰ (n = 3), which is

278   similar to published values in the literature for BHVO-1 (geostandard collected at the same

279   location as BHVO-2) (Schoenberg et al., 2008), and Nod-A-1 yielded a δ^{53}Cr value of 0.08 ±

280   0.05‰ (n = 4). Sample duplicates, including column procedure duplicates, digested duplicates,

281   and replicate measurements on the MC-ICP-MS revealed a 2σ uncertainty similar to that

282   determined for GRMs, i.e. ≤ 0.09‰ and an average duplicate offset of 0.043‰. Measurement

283   precision is calculated via replicate measurements of the isotopic standard NIST SRM 979

284   during each analytical session (two standards bracket every sample), and 2σ values are better

285   than 0.04‰. In addition, a two-standard deviation of the mean (2se) was systematically

286   calculated using the 50 cycles of measurement obtained for each sample during MC-ICP-MS

287   analysis, and was generally 0.04-0.06‰ on the delta values. This precision and accuracy are

288   comparable to long term means at the Yale Metal Geochemistry Center.

289

290   3.0 Results

291   3.1 Mineralogical analyses

292   Quantification of the relative mineral proportions via qXRD on 6 sub-samples (Table 2)

293   shows that the sediment samples examined here consist almost entirely of calcite and goethite,

294   with very small contributions from crystalline lithogenic minerals (<12%; Table 2), which are

295   inversely proportional to calcite concentration. The detrital fraction is dominated by the feldspar

296 albite, a felsic mineral, in addition to about 1% hercynite, a spinel phase ($Fe^{2+}Al_2^{3+}O_4$) into

297 which Cr can substitute for Al ($Fe^{2+}Cr_2^{3+}O_4$) (Table 2).

298

299 3.2 Site 598 elemental concentrations and Cr mass balance.

300   Within our sequential leach scheme we first targeted the carbonate phase (L_{Carb}, Table 1).

301 Sediments from site 598 have $CaCO_3$ contents ranging from 42.8 to 93.3 ± 0.1 wt% (Poulton and

302 Canfield, 2006). As noted previously, this fraction is dominated by coccoliths (comprising

303 roughly 85%), with a small (up to 4%) fraction of planktonic foraminifera (Barrett et al., 1987;

304 Lyle, 1986). Carbonate concentrations in the sediment are inversely related to metalliferous

305 phases and this leads to mutual dilution of both authigenic and detrital metals in carbonate rich

306 intervals. Triplicate measurements of Cr concentrations in the carbonate phase were below our

307 detection limit (0.03 mg kg^{-1}) in all of the samples from site 598. These low Cr concentrations in

308 the carbonates contribute to a consistent linear relationship between Cr and Fe in the L_{6NHCl} bulk

309 sediment leachate (Table 1), for samples deeper than 150 cm (Fig. 3) where the average molar

310 Cr:Fe ratio remains nearly constant (Fig. 3). This linear relationship is the result of mixing

311 between Cr deficient carbonate and Cr-rich metalliferous Fe-rich phases. The intercept (0.041 ±

312 0.2 mg kg^{-1}) provides an independent estimate of the Cr concentration in the $CaCO_3$, which is

313 near the detection limit of our analytical method (0.03 mg kg^{-1}).

314   The bulk sediment (6 N HCl extractable phases, L_{6NHCl}, Table 4) Fe concentration

315 determined in this study is within ± 5% of the Fe_{TOT} values reported by Poulton and Canfield

316 (2006) and the mass balance of Cr in the individual metalliferous sediment phases is plotted in

317 Fig. 4. Chromium concentrations in the bulk sediment L_{6NHCl} leach range from 0.4 – 3.6 mg kg^{-1},

318 and are strongly correlated with Fe (Poulton and Canfield, 2006) – the highest Cr concentrations

319 are associated with Fe-rich samples (Fig. 5e), whereas carbonate-rich samples are low in Cr.

320 There is a minor fraction of the Cr contained in the L_{HFO} fraction (Fig. 5b), dominantly

321 comprised of highly reactive hydrous ferric oxide minerals such as ferrihydrite (Poulton and

322 Canfield, 2006), and this is mostly restricted to the upper 150 cm (Fig. 4). The Cr concentration

323 of the L_{Sil} fraction ranges from 0.3 – 2.5 mg kg^{-1} (Fig 5d), indicating that a refractory Cr pool,

324 accounts for 37 – 82% of the total Cr (L_{6NHCl}, Table 4). As discussed in section 2.1, we were

325 unable to analytically determine the Cr concentration of the L_{GOE} leachate, and thus we estimate

326 this via mass balance; $LCr_{GOE} = LCr_{6NHCl} − (LCr_{HFO} + LCr_{Sil}$; Table 3). The majority of Cr in the

327   site 598 sediments is thus mainly contained in two fractions; the L_{GOE} (Na-dithionite extractable,

328   Table 3) sediment fraction, comprising crystalline Fe-(oxyhydr)oxide mineral phases such as

329   goethite, and the refractory L_{Sil} fractions (Fig. 5c-d and Table 3).

330   The average Cr:Fe ratio of the sediments is 4.8 x 10^{-5}, with a maximum value of 10.2 x

331   10^{-5} and minimum value of 1.9 x 10^{-5}. In the upper 150 cm of the sediment pile there is a clear

332   and systematic decrease in the ratio of total Cr:Fe (L_{6NHCl}, Fig. 5j), below which the ratio remains

333   relatively constant (Fig. 5g-h). These more deeply buried intervals have a Cr:Fe ratio ($\sim$ 2.0 x 10^{-}

334   ^{5}), which is 5.5 times lower than those at the core top ($\sim$ 10.2 x 10^{-5}), and 20 times lower than

335   fresh hydrothermal vent plume particles ($\sim$ 40 x10^{-5}, Feely et al. (1996), Fig. 6). Within the upper

336   150 cm, we also observe a decrease in the amount of L_{HFO} extractable Cr, and an increase in

337   L_{GOE} extractable Cr (Fig. 4 and Fig. 5h).

338

339   3.3 Mn-oxide concentrations

340   To directly test the capacity of the SEPR sediments to oxidize Cr, we also determined

341   reactive Mn-oxide concentrations in the sediment. The Mn (oxyhdr)oxide concentrations in the

342   sediment at site 598 follow similar trends to those of bulk Fe_{6NHCl} (Fig. 5f), with a maximum

343   concentration of 3.9 wt% at the sediment water interface. Extractable Mn in the upper 20 cm of

344   sediment at sites 599 and 600 also shows that the total Mn:Fe (oxyhydr)oxide ratio increases

345   with distance from the ridge crest (Table 5).

346

347   3.4 Chromium isotopes

348   Chromium extracted from bulk SEPR site 598 sediments with a 6 N HCl (L_{6NHCl}) leach

349   (Table 4, Fig. 7) has $\delta^{53}Cr$ values that are significantly lower (-0.24 to -0.57‰, 2 tailed t-test p-

350   value = 4 x 10^{-6} at the 95% confidence level) than the ISE (-0.12 ± 0.10‰) and oxic abyssal

351   ocean sediments (0.23 to -0.14‰; Gueguen et al. (2016); Schoenberg et al. (2008)). The bulk

352   L_{6NHCl} leach contains both the authigenic reactive Cr phases (L_{HFO} and L_{GOE}) as well as the

353   refractory Cr (L_{Sil}). There is a general decrease in $\delta^{53}Cr$ with increasing sediment depth and

354   decreasing Cr:Fe ratios (Fig. 7). The lightest $\delta^{53}Cr$ values come from samples below 150 cm. We

355   also determined the Cr isotope composition of four select L_{GOE} samples, comprising authigenic

356   Cr contained in more crystalline Fe mineral phases. The $\delta^{53}Cr$ composition of these samples is

357   very isotopically light relative to the ISE with an average $\delta^{53}Cr$ composition of -1.1 ± 0.1‰ (Fig.

358   7a). Additionally, we determined the Cr isotope composition of the L_{Sil} sediment fraction,

359   comprising only the refractory sediment phases, of which almost all δ^{53}Cr values fall within error

360   of the ISE with an average δ^{53}Cr composition of -0.05 ± 0.04‰ (Table 3, Fig. 7). The L_{Sil} leach

361   was performed after extraction and removal of the more reactive and likely authigenic phases of

362   Cr (L_{HFO} and L_{GOE}), and thus we consider Cr contained in the L_{Sil} fraction to represent detrital

363   Cr. The isotopic composition of the detrital L_{Sil} Cr in site 598 sediments is not significantly

364   different than the ISE composition (2 tailed t-test p-value = 0.26 at the 95% confidence level).

365   To estimate the Cr isotopic composition of the reactive and likely authigenic component

366   of the site 598 sediment (the sum of L_{HFO} and L_{GOE} extractable Cr), we corrected for detrital Cr

367   with its ISE composition using a mass balance calculation;

368

369         $$\delta^{53}Cr_{authigenic} = (\delta^{53}Cr_{measured} - (\delta^{53}Cr_{detrital} * X)) / (1-X) \qquad (1)$$

370

371   where $\delta^{53}Cr_{authigenic}$ is the calculated Cr isotopic composition of authigenic Cr, $\delta^{53}Cr_{measured}$ is the

372   bulk Cr isotope composition represented by our L_{6NHCl} leach (Table 4), and $\delta^{53}Cr_{detrital}$ is the Cr

373   isotope composition of the detrital fraction of the sediment, which we take from our L_{Sil} isotope

374   values. X is the fraction of detrital Cr in the Fe_{6NHCl} leach. As described above, the Cr

375   concentration in our L_{Sil} leachates from our sequential extractions is our best estimate of the

376   detrital Cr contribution to the L_{6NHCl} bulk measurements (Tables 3 and 4). The results of our

377   mass balance calculation are shown in (Fig. 7a). We note that there are large uncertainties (0.1 -

378   0.3‰ SE) on the δ^{53}Cr composition of the calculated authigenic component that result from error

379   propagation in our mass balance calculation and these are not plotted to maintain figure clarity,

380   but instead are presented in (Table 4). Our calculation demonstrates that once corrected for the

381   contribution from detrital Cr, the $\delta^{53}Cr_{authigenic}$ values of the SEPR sediments are even lighter

382   than the measured L_{6NHCl} bulk Cr isotope compositions. These estimates, furthermore, are within

383   analytical error of the four measured δ^{53}Cr L_{GOE} samples, which thus satisfies mass balance.

384   We performed a similar calculation to test whether the isotopic composition of the bulk

385   sediment at site 598 (Cr isotopic composition of the L_{6NHCl} leach; sum L_{HFO}, L_{GOE} and L_{Sil}

386   extractable Cr) can be obtained via mass balance and is similar to our measured δ^{53}Cr L_{6NHCl}

387   values;

388

389 $$\delta^{53}Cr_{Bulk} = (\delta^{53}Cr_{authigenic} * X_{authigenic}) + (\delta^{53}Cr_{detrital} * X_{detrital}) \qquad (2)$$

390

391 where $\delta^{53}Cr_{Bulk}$ is the calculated Cr isotopic composition of the bulk sediment, $\delta^{53}Cr_{authigenic}$ is the

392 Cr isotopic composition of the authigenic L_{GOE} leach (4 samples), and $X_{authigenic}$ is the fraction of

393 authigenic Cr in the L_{6NHCl} leach. $\delta^{53}Cr_{detrital}$ is the Cr isotope composition of the detrital fraction

394 of the sediment, which we take as our L_{Sil} isotope values. X is the fraction of detrital Cr in the

395 L_{6NHCl} leach. We use the Cr concentration of our L_{Sil} leachates from our sequential extractions as

396 best estimates of the detrital Cr contribution (Table 3). The results of this mass balance

397 calculation are also shown in (Fig. 7a). This calculation demonstrates that for the four samples

398 analyzed, the calculated $\delta^{53}Cr_{Bulk}$ values are the same as the measured L_{6NHCl} $\delta^{53}Cr$ compositions

399 within error, satisfying isotopic mass balance and giving further confidence in our conclusion

400 that authigenic Cr buried in the SEPR sediments is isotopically light relative to the ISE and

401 detrital Cr.

402

403 4.0 Discussion

404 4.1 Cr in the carbonate phase

405   Poulton and Canfield (2006) attribute the variability in metal concentrations in the

406 sediment at site 598 to changes in the accumulation rate of $CaCO_3$ rather than to fluctuations in

407 the deposition rate of the metalliferous hydrothermal component. This biogenic carbonate carries

408 a negligible fraction of the sediment Cr despite the fact that it is the dominant component of the

409 sediment at site 598. We considered the possibility that calcite bound Cr released during the

410 carbonate leach might have been re-adsorbed onto the remaining Fe-phases. Davis and Leckie

411 (1980) found that Cr adsorption to Fe (oxyhydr)oxides is maximal in a pH range of 5-6 and less

412 than 30% below pH 4. Although re-adsorption of calcite bound Cr to Fe-(oxyhydr)oxides during

413 our carbonate leach cannot explicitly be ruled out, our 10% acetic acid leach was at pH ~4, and

414 hence we do not expect adsorption of more than 30%. Modern planktonic foraminifera,

415 furthermore, typically exhibit Cr concentrations between 0.05 and 0.3 mg kg^{-1} (Wang et al.,

416 2017), which is consistent with biogenic carbonates having lower Cr concentrations than

417 limestones (Gilleaudeau et al., 2016). Experimental studies show that Cr(VI) incorporation into

418 calcite (as CrO_4^{2-}) increases with increasing Cr(VI) concentration in solution (Tang et al., 2007).

419   We applied the partition coefficient (K_d^*) from this experimental work (Tang et al., 2007),

420   where;

421

422                           $$K_d^* = [Cr(VI)]_{solid}/[Cr(VI)]_{solution} \qquad (3)$$

423

424   and when $[Cr]_{solution}$ drops below a minimum of 10 mmol l^{-1}, Kd^* reaches a maximum value of

425   ~95. If this value is extended to Cr(VI) concentrations of 1.95 ± 0.15 nmol l^{-1} observed by

426   Jeandel and Minster (1984) in surface waters above the East Pacific Rise, we calculate an

427   expected $[Cr]_{solid}$ of 0.2 mg kg^{-1} in calcite, which is below our detection limit. Together, our

428   observations imply that a negligible fraction of the Cr in SEPR sediments is associated with

429   carbonate phases.

430

431   4.2 Oxygenated deep-sea sediments and authigenic Cr

432   The authigenic Cr in the SEPR sediments has a δ^{53}Cr isotopic composition that is lighter

433   than other oxygenated marine sediments measured to date. The δ^{53}Cr composition of the

434   majority of previously measured marine sediments deposited from oxygenated seawater fall

435   within the ISE range (-0.12 ± 0.10‰, Gueguen et al. (2016); Schoenberg et al. (2008)), while

436   ferromanganese nodules accumulating beneath oxygenated seawater are isotopically light (Table

437   6) (Wei et al., 2018). Together, these yield an average δ^{53}Cr value of -0.15 ± 0.05‰ for oxic

438   marine sediments. Prior leaching experiments conducted to target the authigenic Cr pool from

439   these sediments also yielded δ^{53}Cr values that were not statistically different from the bulk

440   sediment (-0.01 ± 0.05‰, Gueguen et al. (2016)). Current data for oxic deep-sea sediments,

441   therefore, suggest that fractionated authigenic Cr pools likely comprise a very minor fraction of

442   the total sediment Cr, and thus the δ^{53}Cr composition of these sediments reflects a detrital input

443   with composition identical to the ISE (Gueguen et al., 2016; Schoenberg et al., 2008). The

444   sediments at site 598 were also deposited under oxygenated deep-sea conditions yet they contain

445   an appreciable (up to 56%) authigenic component, and in contrast to other oxygenated

446   sediments, are overwhelmingly isotopically light. Similar leaching techniques designed to target

447   authigenic Cr in the SEPR sediments, reveal that this authigenic Cr is mostly contained in the

448   L_{GOE} fraction, is heavily fractionated, and is demonstrably isotopically light (-0.9 ± 0.3‰ to 1.2

449 ± 0.1‰). Mass balance calculations (section 3.4) further affirm that the isotopically light δ^{53}Cr

450 composition of the bulk sediment is due to this authigenic fraction (Fig 7 and Table 3).

451

452 4.2 Cr isotope composition of detrital inputs at the SEPR

453 An appreciable component of the Cr in the SEPR sediments can be attributed to a detrital

454 source likely delivered as eolian dust. The eolian dust flux at site 598 has been estimated (Rea

455 and Bloomstine, 1986) and comprises only 0.8 – 4.0 wt% of the bulk sediment in the upper 6 m

456 of the sediment column. Our qXRD measurements verify that the mineralogy of the sediment is

457 mainly biogenic calcite and authigenic goethite, with trace amounts of albite (0 - 8%), which

458 likely represents the major mineralogical component of the eolian dust (Table 2). Albite

459 ($NaAlSi_3O_8$) is not likely to contain Cr in its crystal lattice, but we have also detected the detrital

460 spinel mineral hercynite ($Fe^{2+}Al_2O_4$), which can contain Cr(III). We find, furthermore, that an

461 appreciable amount of the total Cr in the site 598 sediment is contained in the L_{Sil} fraction (Table

462 4). Some of the Cr in our bulk L_{6NHCl} leachates is thus likely detrital rather than hydrothermal

463 and/or authigenic, and the bulk Cr isotope composition of the SEPR sediments was partly

464 inherited from eolian dust. Aluminium is typically employed as a tracer for detrital inputs to

465 many types of marine sediments, and positive correlations between Al and other elements of

466 interest have been attributed to a common detrital source (McLennan, 2001). The positive

467 correlation between Fe, Al and Cr concentrations in the SEPR sediments may thus indicate a

468 similar source for these metals, with mutual dilution by carbonate components controlling metal

469 concentrations as a function of depth. An authigenic origin for Al is also a possibility, however,

470 given that a considerable fraction (~70%) of the total Al in the sediment, as reported in (Lyle,

471 1986), is contained in the more reactive L_{HFO} and L_{GOE} sediment fractions. Correlations between

472 Cr and Al concentrations and Cr:Al ratios in our leach fractions thus cannot be solely attributed

473 to detrital contributions to the sediment, and are likely not a robust means of discriminating

474 between authigenic and detrital Cr. We further suggest that the relatively large component of

475 authigenic Al in the SEPR sediments may be hosted by authigenic clay minerals (Heath and

476 Dymond, 1977; Michalopoulos and Aller, 2004), a link needing further study at the SEPR.

477 The detrital Cr in most of the SEPR sediments carries a δ^{53}Cr indistinguishable from ISE

478 values (Fig. 7). This further shows that even though refractory Cr phases of likely detrital origin

479 comprise an appreciable proportion of the hydrothermal sediment Cr, their isotopic composition

480   is not responsible for imparting the isotopically light δ^{53}Cr composition of the bulk sediment,

481   and instead, detrital Cr effectively mutes the isotopically light authigenic Cr in measurements of

482   the bulk sediments. Our Cr:Fe ratios, furthermore, point to little Cr redistribution occurring in the

483   detrital L_{Sil} fraction (Fig. 5i). Co-variation between Cr and Fe concentrations in the L_{Sil} fraction

484   and intervals with the highest [Cr] and [Fe], however, do correspond to hercynite mineral

485   occurrences in the sediment and such correlations suggest similar origins for Cr in L_{Sil} fraction

486   and hercynite, both of which are likely supplied as eolian dust (Figure 5d and Table 2).

487   Collectively, our observations suggest that eolian dust in this part of the Pacific ocean carries the

488   δ^{53}Cr of ISE, which has remained relatively constant over the last 5.7 million years and is

489   consistent with previous studies of Cr in marine sediments (Gueguen et al., 2016; Schoenberg et

490   al., 2008).

491

492   4.3 Cr(III) oxidation in serpentinizing environments

493   The delivery of detrital Cr to the SEPR sediments (Section 4.2 above) tends to mute bulk

494   δ^{53}Cr compositions bringing them closer to the ISE, and yet, the bulk δ^{53}Cr compositions are

495   light due to an isotopically light authigenic Cr source. We thus considered whether the light

496   authigenic δ^{53}Cr recorded in the hydrothermal sediments at site 598 could have been inherited

497   directly from the hydrothermal fluids. The δ^{53}Cr composition of hydrothermal fluids is likely set

498   by alteration reactions (serpentinization) occurring within the hydrothermal vent system, and so

499   we consider whether these reactions could theoretically impart light δ^{53}Cr. Two previous studies

500   that investigated the δ^{53}Cr composition of serpentinized ocean crust found it to be isotopically

501   heavy (up to +1.22‰) relative to the igneous silicate earth (ISE) (Farkas et al., 2013; Wang et

502   al., 2016). The authors interpreted these findings to be the result of a complex series of Cr redox

503   reactions, whereby seawater Cr(VI) entrained into the hydrothermal vent environment

504   experiences partial reduction in the immediate vicinity of the serpentinization site, leading to

505   isotopically heavy residual δ^{53}Cr(IV) in the hydrothermal fluids and shifting the δ^{53}Cr

506   composition of any serpentinite captured Cr(III) to heavier δ^{53}Cr values. Hydrogen peroxide can

507   be present in serpentinizing systems (Oze et al., 2016), with the potential to oxidize Cr(III) and

508   thereby contribute heavy Cr(IV) to hydrothermal fluids, leaving residual serpentinites

509   isotopically light (Oze et al., 2016). Such a mechanism, however, is inconsistent with all current

510   data, which instead suggest that the net result of hydrothermal alteration processes is to produce

511   serpentinites and hydrothermal fluids with heavy $\delta^{53}Cr$ compositions ((Farkas et al., 2013; Wang

512   et al., 2016). It therefore remains unclear as to whether serpentinization reactions can generate

513   hydrothermal fluids with a light $\delta^{53}Cr$ composition and we thus consider the possible role of

514   other processes in setting the $\delta^{53}Cr$ composition of the sediments deposited at site 598.

515

516   4.4 Reduction of Cr(VI) in open vs. closed systems

517   Hydrothermal fluids provide a flux of Cr to seawater (Reinhard et al., 2013), though the

518   degree to which seawater Cr may be reduced and scavenged by hydrothermal fluids remains

519   uncertain. This means that hydrothermal systems may in fact be a net sink rather than a source of

520   Cr to seawater. To assess the extent to which Cr(III) in the SEPR sediments might originate from

521   hydrothermal vs. seawater sources we consider concentrations of Cr in vent fluids, seawater and

522   fresh plume particles. Cr(III) can be enriched in plume fluids by up to 10 times compared to

523   seawater (Sander and Koschinsky, 2000). Adopting a conservative end member Cr of 5 times

524   ambient seawater concentration (similar to measured vent fluid concentrations (Sander and

525   Koschinsky, 2000; Sander et al., 2003), would give a vent fluid Cr content of up to 50 nM Cr,

526   prior to dilution with seawater. Typical Fe concentrations in SEPR hydrothermal fluids are on

527   the order of 10 mM (Charlou et al., 1996). Using these values, the molar Cr:Fe ratio in SEPR

528   hydrothermal fluids is at most 5×10^{-6}, which is two orders of magnitude lower than the Cr:Fe

529   ratio of on axis plume particles (Feely et al., 1996) (Fig. 6) and three orders of magnitude lower

530   than the SEPR sediments at Site 598. This suggests that most Cr in hydrothermal plume particles

531   is not derived from vent fluids but rather comes from seawater in the immediate vicinity of the

532   vent, consistent with studies conducted on other hydrothermal systems (German et al., 1999;

533   Trocine and Trefry, 1988). Other estimates indeed suggest that 8 - 10% of all Cr supplied to the

534   ocean by rivers is removed via hydrothermal plume scavenging and deposited in ridge crest

535   sediments (Rudnicki and Elderfield, 1993). This suggests that scavenging of seawater Cr is a

536   non-negligible part of the global marine Cr budget, and the resulting redox reactions involved

537   may impart important isotopic effects, as we explore below.

538   Partial reduction of seawater Cr(VI) provides one likely explanation for the light $\delta^{53}Cr$

539   values we observed in the SEPR sediments. Partial reduction of seawater Cr(VI) upon mixing

540   with Fe(II) (and H_2S) laden vent fluids, and subsequent co-precipitation of Fe-(oxyhydr)oxides

541   has the potential to impart large Cr isotope fractionations, as observed in previous laboratory

542   experiments (Basu and Johnson, 2012; Dossing et al., 2011). While the extent to which evolving

543   vent plumes mix with seawater, and hence how open the plume is to Cr exchange with seawater,

544   is difficult to estimate, we consider two end-member scenarios in which Cr isotope fractionation

545   at the SEPR results from fully open or fully closed system behaviour. A fully open, well-mixed

546   system would most likely be achieved during reaction between Cr(VI) and Fe(II) in the water

547   column. This would occur when the rate of mixing between seawater and the hydrothermal

548   plume is so fast that the concentration and δ^{53}Cr composition of Cr(VI) in the latter remains the

549   same as the former (i.e. a lack of reservoir effects). In this scenario, [Cr(VI)] and δ^{53}Cr in the

550   plume water is constant in time and space, and the δ^{53}Cr of particles produced during seawater

551   Cr(VI) reduction can be described by:

552

553 $$\delta^{53}Cr(III)_{product} = \delta^{53}Cr(VI)_{seawater} - \varepsilon \qquad (4)$$

554

555   where the Cr isotopic composition of seawater and the isotope fractionation factor (ε) do not

556   change with distance from the vent.

557   To estimate the possible range of δ^{53}Cr(III)$_{product}$ values, we have compiled relevant

558   isotope fractionation factors (ε) from the literature, which span a suite of appropriate reductants

559   for Cr(VI) in hydrothermal systems (Table 7). Under open system behaviour, the smallest

560   fractionation factor ($\varepsilon = 0.8$‰), proposed by Scheiderich et al. (2015) for Cr(VI) reduction in

561   ocean surface waters, would only yield δ^{53}Cr(III)$_{product}$ values as light as the δ^{53}Cr observed in

562   the SEPR sediments if the initial δ^{53}Cr$_{seawater}$ is only mildly heavy to begin with (δ^{53}Cr = 0.13‰).

563   Given, however, that the modern average δ^{53}Cr$_{seawater}$ is 0.66‰, and more specifically, average

564   Pacific ocean water is also 0.66‰ (Paulukat et al., 2016; Scheiderich et al., 2015), then Cr(VI)

565   reduction in the SEPR system would need to be accompanied by an isotope fractionation >0.8‰

566   to account for the light δ^{53}Cr values in the SEPR sediments, if partial Cr(VI) reduction was

567   exclusively responsible. Larger isotope fractionation factors, however, are expected. Dissolved

568   ferrous iron is a potent and likely reductant of Cr(VI) in the vicinity of hydrothermal vents, as are

569   mixed valence Fe (oxyhydr)oxides that form as direct products of Fe(II) oxidation (Table 7).

570   Reduction of Cr(VI) by ferrous iron carries a fractionation in the range of $\varepsilon = 3.6 - 4.2$‰

571   (Dossing et al., 2011; Kitchen et al., 2012). These larger isotope fractionation factors produce

572 δ^{53}Cr(III) values lighter than our data over the entire range of known δ^{53}Cr$_{seawater}$ compositions,

573 including the highest values measured to date (δ^{53}Cr $_{seawater}$ = 1.24‰, Scheiderich et al. (2015)).

574 In contrast, particulate Fe(II)-bearing phases carry more muted isotope fractionation factors in

575 the range of ε = 2.11 – 2.65‰ (Table 7). Thus reduction via such particles could account for the

576 observed range of Cr isotope fractionation at the SEPR if seawater Cr(VI) had an isotopic

577 composition between δ^{53}Cr$_{seawater}$ = 0.62 and 2.41‰, consistent with current measurements of

578 δ^{53}Cr$_{seawater}$. Therefore, based on isotope data alone, our data can be described by partial

579 reduction of Cr(VI) in a hydrothermal system that is entirely open, using isotope fractionations

580 that fall in a continuum between 0.8‰ and 2.65‰ – magnitudes consistent with isotope

581 fractionation factors derived from laboratory experiments with a variety of ferrous Fe reductants

582 (Table 7). Variability in the isotope fractionation factor, δ^{53}Cr composition of local seawater, and

583 the extent of fluid mixing may also explain some of the variability observed in the δ^{53}Cr values

584 down core at the SEPR.

585 In contrast to a fully open system where partial Cr(VI) reduction occurs in a vigorously

586 mixed water column, a fully closed system would be approached if Cr(VI) reduction occurred

587 within the sediment pile at site 598. In this scenario, increasing burial and continued Cr(VI)

588 reduction within the sediment would drive the authigenic δ^{53}Cr of Cr(III) formed deeper in the

589 sediment towards the initial δ^{53}Cr composition of seawater at the sediment water interface. This

590 process would also tend to cause Cr:Fe ratios of the sediment to increase with depth. Neither

591 relationship is observed (Fig. 5g-h), and thus Cr(VI) reduction within the sediment pile is

592 unlikely to be the dominant process driving Cr isotope fractionation at site 598. In fact, we

593 observe the opposite relationship between sediment δ^{53}Cr composition and burial depth, finding

594 that the lightest δ^{53}Cr values measured come from samples with the lowest Cr:Fe ratios. We also

595 observe a relatively coherent relationship in which δ^{53}Cr decreases with increasing burial depth

596 and decreasing Cr:Fe ratios. We also recognize, however, that our data may fall somewhere on a

597 continuum between fully open and fully closed system behaviour, and thus record a combination

598 of water column and diagenetic Cr redox processes, the latter of which we explore below.

599

600 4.5 Diagenetic oxidation of Cr(III)

601   Oxidation of Cr(III) to Cr(VI) by manganese oxides has been shown under laboratory

602   conditions ((Eary and Rai, 1987; Nakayama et al., 1981; Schroeder and Lee, 1975) and in natural

603   soils (Oze et al., 2007), and can be described by the following reaction (Eary and Rai, 1987;

604   Manceau and Charlet, 1992):

605

606                    $$Cr^{3+} + 3MnOOH \rightarrow HCrO_4^- + 3Mn^{2+} + 2OH^-$$ (5)

607

608   which produces soluble Cr(VI) oxyanions. In sediments, this Cr(VI) would be mobile and could

609   ultimately escape by diffusion to overlying seawater. Shaw et al. (1990) determined the

610   distribution of porewater [Cr] in the upper 20 cm of multiple continental margin sites off the

611   coast of California, suggesting Cr loss in Mn-oxide rich surface sediments, and demonstrating

612   low retention of Cr in sediments under oxic conditions in the presence of Mn-oxides. We observe

613   manganese oxides throughout the sediment profile and these are present in excess of that

614   necessary to oxidize all oxide bound Cr, based on the stoichiometry noted above. We also find

615   the total Mn:Fe-oxide ratio decreases with distance from the ridge crest (Table 5), and this

616   "telescoping" effect we attribute to the slower oxidation kinetics of Mn(II) with O_2 relative to

617   Fe(II) (Dymond and Roth, 1988). Therefore, we expect more ferrous iron to be oxidized and

618   deposited closer to the ridge crest compared to Mn, and more distal sediments, with relatively

619   higher Mn-oxide contents, are likely to have higher potential for Cr remobilization. The

620   diagenetic interaction of Mn-oxides with hydrothermal Cr(III) to induce oxidative remobilization

621   as Cr(VI) is therefore a plausible and likely explanation for the apparent redistribution of Cr.

622   Based on our current understanding of Cr isotope fractionation, and by analogy to oxidative Cr

623   mobilization in weathering environments (Crowe et al., 2013; Frei et al., 2009; Frei and Polat,

624   2013), oxidatively remobilized Cr(VI) from SEPR sediments is expected to be isotopically

625   heavier than the residual Cr(III), either due to fractionation imparted directly during oxidation

626   (e.g., Zink et al. (2010)) or due to partial reduction back to Cr(III), which favours the light Cr

627   isotope (Crowe et al., 2013; Ellis et al., 2002).

628   Chromium oxidation and remobilization from mineral phases hosting Cr(III) is dependent

629   on the solubility of the host minerals (Rai et al., 1989). There is a progressive change in the

630   fraction of total Fe represented in L_{HFO} and L_{GOE} at site 598 (Poulton and Canfield, 2006), and

631   this is interpreted as a progressive transformation of reactive Fe-minerals (ferrihydrite) to more

632 stable phases. This is largely complete by a depth of 150 cm at site 598. We observe that the
633 Cr:Fe molar ratio decreases steadily through the top 150 cm of sediment (Fig. 5j), which
634 coincides with the zone of ferrihydrite transformation to goethite (Fig. 4b). Ferrihydrite
635 transformation to goethite takes place via dissolution-reprecipitation reactions, which
636 presumably release Cr from ferrihydrite and redistribute it to porewaters where it can be
637 sequestered by less reactive Fe phases or become mobile through diffusive transport. Assuming a
638 constant Cr:Fe ratio during deposition suggests progressive Cr loss relative to Fe with increasing
639 depth in the upper 150 cm of sediment (Fig. 5j). The downcore changes suggest that Cr in
640 ferrihydrite is redistributed into goethite by a depth of 150 cm, and that Cr loss and
641 remobilization from ferrihydrite is complete by this depth, with less than 5% of the total Cr
642 remaining in L_{HFO} phases (Fig. 4, Table 3). Cr(III) oxidation driven by release of Cr from L_{HFO}
643 and subsequent reaction with Mn-oxides provides a likely explanation for the observed
644 distribution of Cr within the upper 150 cm of the sediment and it's apparent loss from the
645 sediment. Such a scenario is also consistent with the downcore trends in δ^{53}Cr which are strongly
646 correlated to Cr:Fe (Fig. 7b), implying a genetic link between these two geochemical features.
647 δ^{53}Cr values indeed become progressively lighter as Cr is lost relative to Fe, and this is
648 consistent with the directionality of fractionation expected during oxidative Cr remobilization
649 and the δ^{53}Cr composition of authigenic Cr captured in the L_{GOE} fraction. Thus, partial reduction
650 of seawater Cr(VI) in the hydrothermal plume and diagenetic Cr(III) oxidation can together
651 account for the light δ^{53}Cr values and Cr(VI) loss observed in the sediment at the SEPR.

652   Remobilization of Cr below 150 cm appears limited, indicating that sediments older than
653 2.5 Myr are poorly reactive towards Cr dissolution and consequently Cr(III) oxidation and
654 redistribution. In these deeper sediments, Cr is dominantly hosted by goethite and residual poorly
655 reactive detrital phases, although in other marine sediments reactive Fe phases such as
656 ferrihydrite often convert to hematite as the stable end member (Schwertmann and Murad, 1983).
657 At the SEPR, we expect this goethite phase to be the primary carrier of both the Cr isotope signal
658 derived from seawater and any subsequent early diagenetic reactions, for ultimate preservation in
659 the geologic record. Cr isotope signals imparted through partial reduction of seawater Cr(VI) and
660 subsequently overprinted through Cr remobilization and isotope fractionation in hydrothermal
661 sediments may thus be partly controlled by Fe (oxyhydr)oxide mineral ageing.

662

663   4.6 Isotopically light Cr in hydrothermal sediments

664   The light δ^{53}Cr values of the hydrothermal sediments at site 598 are unique compared to

665   most oxygenated marine sediments studied to date (Bonnand et al., 2013; Gueguen et al., 2016;

666   Reinhard et al., 2014; Wei et al., 2018). Based on our results from DSDP site 598, we argue that

667   partial reduction of seawater Cr(VI) and oxidative diagenesis combine to leave hydrothermal

668   sediments isotopically light (depleted relative to the ISE). Importantly, both of these mechanisms

669   require oxygenated seawater in the vicinity of the hydrothermal system, opening the possibility

670   that isotopically light Cr values measured in hydrothermal sediments may be diagnostic of

671   oxygen-bearing deep ocean water. In an anoxic deep ocean, Cr(III) sourced from hydrothermal

672   vents would enter seawater and precipitate in hydrothermal sediments without undergoing redox

673   cycling. The resulting hydrothermal precipitates would carry an ISE δ^{53}Cr composition (Fig. 8a).

674   In strong contrast to the anoxic deep ocean scenario, the modern oxygenated deep oceans contain

675   isotopically heavy Cr(VI), as the result of oxidative weathering on land (Frei et al., 2009, Crowe

676   et al., 2013, Scheiderich et al., 2015, D'Arcy et al., 2016, Paulukat et al., 2016, Wu et al., 2017).

677   Cr(VI) readily reacts with reductants (H_2S, Fe(II)) that accumulate in the ocean under anoxic

678   conditions, and thus Cr(VI) accumulation in the deep ocean only occurs when it is oxygenated.

679   The isotopically light signals we find in modern hydrothermal sediments develop due to

680   the local interaction of hydrothermal reductants with Cr(VI) in oxic seawater, with a possible or

681   likely partial overprint through oxidative Cr(III) diagenesis (Fig. 8b). These observations set up a

682   framework for using negative δ^{53}Cr isotope anomalies in iron oxide dominated deep-sea

683   hydrothermal sediments, as a proxy for deep-water oxygenation. Light δ^{53}Cr compositions have

684   only been observed as the result of oxidative remobilization of Cr(III) in paleosols and modern

685   soils, and in strongly oxidizing ferromanganese nodules (e.g., Crowe et al., 2013, Babechuk et al.

686   (2017); Berger and Frei (2014), Wei et al. (2018)), and here through Cr redox cycling in

687   hydrothermal plume fallout sediments. Examination of existing δ^{53}Cr records reveals

688   occurrences of isotopically light δ^{53}Cr values in Neoproterozoic hydrothermal sediments (Sial et

689   al., 2015), implying deposition from oxygenated deep ocean waters at this time. We propose that

690   this framework can be expanded through further measurements of δ^{53}Cr in older hydrothermal

691   sediments. In principle this should enable reconstruction of deep ocean oxygen dynamics

692   through geologic history.

693

694 5.0 Summary

695   Sediments deposited at the SEPR are enriched in hydrothermal Fe and Mn

696 (oxyhydr)oxides. In the vicinity of hydrothermal vents, seawater-sourced Cr(VI) is likely

697 reduced by Fe(II) laden vent fluids and the Cr(III) produced is scavenged by freshly-formed Fe

698 precipitates and deposited in the sediments. This partial reduction of Cr(VI) from oxygenated

699 seawater imparts a light δ^{53}Cr fingerprint in the plume particles, which are deposited with δ^{53}Cr

700 values lighter than the ISE range (-0.12 ± 0.10‰). Sedimentary Mn oxides may subsequently

701 catalyze the oxidation of sediment Cr(III), inducing the release of as much as 80% of Cr in the

702 form of soluble Cr(VI) to the overlying water column. This remobilization may also carry an

703 isotopic fractionation, with potential to enhance the overwhelmingly light δ^{53}Cr imparted during

704 partial reduction. Overall, these processes combine to set a variable, but distinctly light, range in

705 bulk sediment δ^{53}Cr of between -0.24 and -0.57‰, dictated by a heavily fractionated and

706 isotopically light authigenic sediment fraction. The δ^{53}Cr composition of the detrital fraction of

707 the sediment, moreover, is unfractionated and has remained relatively constant for the last 5.7

708 Myr. Iron diagenesis transforms less stable Fe phases (e.g., ferrihydrite) to more stable goethite

709 by a depth of 150 cm (2.5 Myr), slowing subsequent diagenetic Fe alteration and likely locking

710 in the δ^{53}Cr composition below this transition. Together, these processes leave a diagnostic

711 record of isotopically light δ^{53}Cr that signals deposition from Cr(VI) bearing oxygenated deep

712 seawater – a signal that can potentially be tracked through time, thus providing impetus to further

713 explore ancient hydrothermal sediments as archives of δ^{53}Cr that may demarcate deep ocean

714 oxygenation in the geologic record.

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756   Figure Captions

757

758   Figure 1. The modern chromium cycle, modified from Crowe et al. (2013). We display the two

759   main Cr fluxes to the ocean, as well as the four main redox reactions, numbered in the box, that

760   control isotope fractionation. The isotopic compositional range of each flux is provided, and it is

761   of note that with the exception of the hydrothermal flux, all are potentially ^{53}Cr enriched. Black

762   arrows indicate a flux of Cr that has not undergone a redox reaction, whereas grey arrows

763   indicate a flux of Cr that has undergone a redox transformation.

764

765   Figure 2. Leach procedure schematic. **a)** Sediment extraction techniques applied in this study.

766   The chemical extraction techniques are denoted beside each operationally defined sediment

767   phase with the leach designation abbreviation in brackets (refer to Table 1). **b)** Sediment

768   extraction techniques applied in Poulton and Canfield (2006) on identical sediment sections. We

769   note that in Poulton and Canfield (2006) metal contents of the detrital silicate fraction of the

770   sediment (Fe_{Sil}) was calculated as the difference between Fe_{TOT} and ($Fe_{GOE} + Fe_{HFO}$) fractions.

771

772   Figure 3. Two end member-mixing diagram. Displayed are the Cr and Fe concentrations in the

773   L_{6NHCl} leach for samples below 250 cm, where the Cr:Fe ratio remains constant. The intercept of

774   0.04 ± 0.3 mg kg^{-1} provides the [Cr] expected in the carbonate phase. The dotted lines represent a

775   90% confidence belt on the regression.

776

777   Figure 4. Mass balance of Cr in the site 598 sediments. **a)** Concentrations of Cr in the L_{HFO}, L_{GOE}

778   and L_{Sil} sequential leaches. We also plot the bulk Cr concentration of the sediment (L_{6NHCl} leach)

779   **b)** Relative abundance of Cr in each sediment fraction normalized to the bulk Cr in the L_{6NHCl}

780   leach. We note that depth intervals where [Cr] was not determined in all leach fractions (see

781   Tables 3 and 4) have been omitted from the profiles.

782

783   Figure 5. Element concentrations at site 598. **a)** Carbonate concentration (Poulton and Canfield,

784   2006). **b)** Cr (blue data points) and Fe (orange data points) in the L_{HFO} fraction. **c)** Cr and Fe in

785   the L_{GOE} fraction. **d)** Cr and Fe in the L_{Sil} fraction. **e)** Cr and Fe in the bulk L_{6NHCl} fraction. **f)**

786   Mn-Oxide (purple) and Mn-Oxide:Fe_{6NHCl} (red data points). **g)** Cr:Fe ratio of the L_{HFO} fraction.

787   **h)** Cr:Fe ratio of the L_{GOE} fraction. **i)** Cr:Fe ratio of the L_{Sil} fraction. **j)** Cr:Fe ratio of the L_{6NHCl}

788   fraction.

789

790   Figure 6. Cr:Fe composition of vent particles and sediments deposited at site 598. Displayed is a

791   comparison of the Cr:Fe molar ratios of suspended vent particles measured by Feely et al.

792   (1996), compared to the Cr:Fe composition of hydrothermal sediments at site 598 (Cr and Fe

793   concentrations from the L_{6NHCl} leach).

794

795   Figure 7. Cr-isotope composition of sediments deposited at site 598. **a)** Cr isotope composition

796   of the site 598 sediments. The grey shaded region represents the ISE range (-0.12 ± 0.10‰). The

797   open diamonds represent the estimated authigenic $\delta^{53}Cr$ composition calculated using a mass

798   balance approach (section 3.4). The closed squares represent the estimated bulk $\delta^{53}Cr$

799   composition calculated using a mass balance approach (section 3.4). The large errors on the mass

800   balance obtained $\delta^{53}Cr$ values result from error propagation. **b)** Relationship between the Cr:Fe

801   ratio and $\delta^{53}Cr$ composition of the bulk L_{6NHCl} leach for sediments deposited below 150 cm. Grey

802   shaded region represents a 95% confidence belt on the linear regression with an r^2 value of 0.80.

803

804   Figure 8. Cr cycling in an anoxic vs. oxic deep ocean. Depicted are schematics detailing the

805   expected $\delta^{53}Cr$ composition of hydrothermal sediments deposited in both an anoxic and oxic

806   deep ocean. Blue arrows indicate Cr that has undergone redox cycling whereas black arrows

807   indicate no redox state change. **a)** In a dominantly anoxic ocean, no Cr(VI) reduction takes place

808   in the plume vicinity. This deposits unfractionated hydrothermally sourced Cr(III) in the

809   sediment and preserves the initial ISE $\delta^{53}Cr$ composition liberated from vent efflux. **b)** In an

810   oxygenated ocean, the heavy Cr(VI) reservoir may be partially reduced during interaction with

811   electron donor rich hydrothermal plumes. Depending on the magnitude of the fractionation factor

812   associated with this reaction (see Table 7), this is expected to precipitate depleted $\delta^{53}Cr$ in the

813   sediment, making light $\delta^{53}Cr$ values diagnostic of oxygenated deep ocean waters that have

814   interacted with hydrothermal plumes. This light $\delta^{53}Cr$ signal is only further reinforced during

815   diagenesis with manganese oxides in the sediment pile.

816

817

818 Table 1. Summary of extraction techniques. [1](Barrett et al., 1987), [2](Poulton and Canfield, 2006),

819 [3](Thamdrup et al., 1994), [4](Poulton and Canfield, 2005), [5](Neaman et al., 2004).

Fraction designation	Sediment fraction	Extractant
Sequential Digests		
L_{Carb}	Carbonate	10% acetic acid, 4 h[1]
L_{HFO}	Poorly crystalline hydrous ferric oxides (Fe_{HFO} in [2])	0.5 N HCl, 1 h[3]
L_{GOE}	Ferric (oxyhydr)oxides (Fe_{GOE} in [2])	0.35 M acetic acid/0.2 M Na-citrate Na-dithionite, 2 h[4]
L_{Sil}	Silicates (Fe_{Sil} in [2])	Near boiling 6 N HCl, 24 h[4]
Bulk Sediment Digests		
L_{6NHCl}	Fe_{TOT}	Near boiling 6 N HCl, 24 h[4]
MnOx	Mn Oxides	0.1 M NH_2OH-HCl, 2 h[5]

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823 Table 2. Mineralogical analyses of the sediments from site 598.

	Sample Depth (cm)					
	2.5	**42.5**	**75.6**	**246.5**	**398**	**499.5**
% Albite	1	2	4	8		2
% Calcite	99	85	78	56	97	83
% Goethite		11	14	33	2	15
% Hercynite		1		2	1	
% Kaolinite			2	1		
% Quartz low			2			
Total	100	100	100	100	100	100

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832 Table 3. Element concentrations determined via sequential extractions in site 598 sediments. We
833 note that Cr concentration of the L_{GOE} fraction was determined as the difference between total Cr
834 (Cr_{6NHCl}, Table 4) and the sum of the sequential phases; thus
835 $Cr_{GOE} = Cr_{6NHCl} - (Cr_{HFO} + Cr_{Sil})$. ND "Not Determined", BLD "Below Detection".
836

| | | | | Sequential Extractions | | | | | | | | | |
| | Element concentrations in L_{HFO} (0.5 N HCl) fraction | | | Element concentrations in L_{GOE} (Na-Dith) fraction | | | | | Element concentrations in L_{Sil} (6 N HCl) | | | | |
Depth (cm)	Cr (mg kg^{-1})	Fe (wt%)	Al (wt%)	Cr (mg kg^{-1})	Fe (wt%)	Al (wt%)	δ^{53}Cr (‰)	2se (‰)	Cr (mg kg^{-1})	Fe (wt%)	Al (wt%)	δ^{53}Cr (‰)	2se (‰)
0.5	0.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4.5	0.7	0.2	0.0	0	1.0	0.1	-1.11	0.07	0.6	0.1	0.1	-0.01	0.02
8.5	0.3	0.2	0.0	0.2	1.1	0.1	ND	ND	0.5	0.1	0.1	-0.28	0.11
21	0.3	0.3	0.1	0.3	2.4	0.1	ND	ND	1.0	0.2	0.1	-0.07	0.03
26.5	0.20	0.3	0.1	0.2	2.7	0.1	ND	ND	1.2	0.2	0.1	ND	ND
34.5	0.16	0.3	0.1	0.5	3.6	0.1	ND	ND	1.3	0.3	0.1	-0.10	0.02
42.5	0.19	0.4	0.2	0.8	5.6	0.2	ND	ND	2.1	0.5	0.2	-0.06	0.03
52.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
68.5	ND	0.7	0.2	ND	7.3	0.3	ND	ND	ND	0.5	0.3	0.04	0.06
76.5	0.19	0.4	0.3	0.7	7.3	0.3	ND	ND	2.5	0.7	0.3	-0.04	0.03
84.5	0.09	0.4	0.2	0.7	6.6	0.3	-1.2	0.1	2.4	0.7	0.3	-0.06	0.03
101	0.3	0.4	0.2	0.1	5.4	0.2	ND	ND	2.2	0.3	0.2	-0.05	0.03
110.5	0.09	0.2	0.1	0.8	4.1	0.1	ND	ND	1.1	0.3	0.1	-0.06	0.03
121.5	0.08	0.2	0.1	0.3	4.0	0.1	ND	ND	1.5	0.3	0.1	-0.22	0.05
138.5	0.10	0.2	0.1	0.4	2.3	0.1	ND	ND	0.7	0.2	0.1	-0.08	0.03
150.5	0.06	0.2	0.1	0.5	3.0	0.1	-0.9	0.3	0.8	0.2	0.1	0.15	0.03
166.5	0.05	0.1	0.1	0.6	2.9	0.1	ND	ND	0.7	0.2	0.1	-0.08	0.03
186.5	0.05	0.2	0.1	0.5	3.6	0.1	ND	ND	0.7	0.2	0.1	ND	ND
196.5	0.03	0.2	0.1	0.6	4.6	0.1	-1.1	0.2	0.8	0.2	0.1	0.32	0.05
206.5	0.05	0.3	0.2	0.6	7.0	0.2	ND	ND	1.1	0.4	0.2	ND	ND
216.5	0.08	0.3	0.2	0.8	9.7	0.2	ND	ND	1.4	0.5	0.2	-0.04	0.05
236.5	0.07	0.5	0.4	0.6	12.0	0.3	ND	ND	2.0	0.7	0.3	-0.01	0.03
246.5	0.10	0.4	0.4	0.7	13.3	0.3	ND	ND	1.8	0.9	0.3	-0.03	0.03
266.5	0.05	0.4	0.3	0.9	11.7	0.2	ND	ND	1.3	0.7	0.2	-0.07	0.03
277.5	0.07	0.3	0.2	1.0	9.7	0.2	ND	ND	1.1	0.5	0.2	-0.08	0.03
286.5	0.04	0.2	0.1	0.7	6.4	0.1	ND	ND	0.7	0.3	0.1	-0.07	0.03
306.5	0.03	0.1	0.1	0.4	3.2	0.1	ND	ND	0.4	0.1	0.1	ND	ND
326.5	BLD	0.1	0.1	ND	2.3	0.0	ND	ND	0.4	0.1	0.0	ND	ND
347.5	0.05	0.2	0.1	0.7	6.1	0.1	ND	ND	0.7	0.3	0.1	-0.11	0.03
398.5	0.11	0.1	0.0	0.3	2.6	0.0	ND	ND	0.3	0.1	0.0	ND	ND
424.5	0.07	0.1	0.0	0.2	2.5	0.0	ND	ND	0.3	0.1	0.0	ND	ND

499.5	0.03	0.3	0.1	0.9	8.9	0.1	ND	ND	0.7	0.3	0.1	-0.05	0.05
549.5	0.03	0.1	0.0	0.1	1.5	0.0	ND	ND	0.3	0.0	0.0	ND	ND
Average												-0.04	0.04

837

838 Table 4. Element concentrations and Cr isotope composition determined in the bulk (L_{6NHCl}
839 leach) site 598 sediments. We note that the detrital Cr concentration was determined as the ratio
840 of Cr_{Sil} to total Cr in the Cr_{6NHCl} leach; thus % Cr detrital = $(Cr_{Sil} / Cr_{6NHCl}) * 100\%$. ND "Not
841 Determined".

842

Bulk Sediment Leach							
Depth (cm)	Element concentrations in L_{6NHCl} (6 N HCl)					Calculated Detrital fraction	Calculated $\delta^{53}Cr$ Authigenic (‰)	Calculated 2se (‰)
	Cr (mg kg-1)	Fe (wt%)	Al (wt%)	$\delta^{53}Cr$ (‰)	2se (‰)	Cr (%)	$\delta^{53}Cr$ (‰)	2se (‰)
0.5	1.1	1.3	ND	-0.35	0.05	ND	ND	ND
2.5	1.2	1.2	ND	-0.37	0.05	ND	ND	ND
4.5	1.3	0.9	0.1	-0.32	0.05	0.64	-0.9	0.2
8.5	1.0	1.1	0.2	-0.33	0.05	0.53	-0.4	0.2
21	1.5	2.5	0.3	-0.3	0.05	0.64	-0.7	0.3
26.5	1.6	2.3	0.3	-0.29	0.05	0.75	ND	ND
34.5	2.0	3.7	0.5	-0.28	0.05	0.66	-0.6	0.3
42.5	3.1	4.7	0.6	-0.37	0.04	0.68	-1.0	0.2
52.5	3.2	5.5	0.7	-0.28	0.04	ND	ND	ND
68.5	3.6	6.5	0.8	-0.24	0.05	ND	ND	ND
76.5	3.4	7.2	0.9	-0.3	0.05	0.74	-1.1	0.2
84.5	3.2	6.6	0.8	-0.34	0.05	0.74	-1.1	0.2
101	2.6	4.8	0.6	-0.36	0.04	0.84	-2.0	ND
110.5	2.0	3.7	0.4	-0.34	0.05	0.57	-0.7	0.2
121.5	1.9	3.4	0.4	-0.35	0.11	0.80	-0.9	0.4
138.5	1.2	2.3	0.3	-0.27	0.06	0.56	-0.5	0.3
150.5	1.4	2.8	0.3	-0.27	0.06	0.57	-0.8	0.3
166.5	1.3	2.9	0.3	-0.28	0.05	0.52	-0.5	0.3
186.5	1.3	3.4	0.4	ND	ND	0.57	ND	ND
196.5	1.4	3.8	0.4	-0.37	0.06	0.59	-1.3	0.2
206.5	1.8	7.1	0.7	ND	ND	0.62	ND	ND
216.5	2.3	8.9	0.8	-0.38	0.05	0.60	-0.9	0.2
236.5	2.7	ND	ND	-0.5	0.04	0.75	-1.9	ND
246.5	2.6	15.0	1.4	-0.37	0.04	0.71	-1.2	0.2
266.5	2.3	11.2	1.0	-0.45	0.04	0.58	-1.0	0.2
277.5	2.1	9.1	0.8	-0.57	0.04	0.51	-1.1	0.2
286.5	1.5	6.4	0.5	-0.47	0.04	0.48	-0.8	0.2
306.5	0.9	2.8	0.2	ND	ND	0.47	ND	ND

326.5	0.8	2.6	0.2	NA	NA	0.48	ND	ND
347.5	1.4	5.7	0.5	-0.44	0.05	0.50	-0.8	0.2
398.5	0.7	2.3	0.2	ND	ND	0.48	ND	ND
424.5	0.6	2.4	0.2	ND	ND	0.50	ND	ND
499.5	1.6	7.1	0.5	-0.56	0.05	0.44	-1.0	0.2
549.5	0.4	1.2	0.1	ND	ND	0.63	ND	ND

843

844 Table 5. Mn-oxide:Fe molar ratios in the upper 20 cm of the three samples sites.

Site	Distance from ridge crest (km)	Mn:Fe Molar Ratio of Upper 20 cm
600	340	0.28
599	640	0.24
598	1130	0.39

845

846 Table 6. Compilation of modern oxic pelagic sediment and ferromanganese crust Cr isotope

847 values.

$\delta^{53}Cr_{bulk}$ (‰)	$\delta^{53}Cr_{leach}$ (‰)	2se (‰)	Reference
-0.06	NA	0.04	
0.06	NA	0.04	
-0.06	NA	0.04	
-0.06	NA	0.04	
-0.01	0.02	0.04	
-0.05	NA	0.04	
-0.07	NA	0.04	
-0.08	NA	0.04	
-0.08	NA	0.04	
-0.13	NA	0.04	
-0.14	NA	0.04	
-0.13	NA	0.04	Gueguen et al., (2016)
-0.08	NA	0.04	
-0.06	NA	0.04	
-0.02	NA	0.04	
-0.03	0.01	0.04	
-0.03	0.01	0.04	
-0.07	NA	0.04	
0	0.1	0.04	
0.23	NA	0.04	
0.02	NA	0.04	
-0.01	NA	0.04	
-0.1	-0.21	0.04	

-0.11	NA	0.04	
-0.1	NA	0.04	
-0.016	NA	0.048	**Schoenberg et al., (2008)**
-0.053	NA	0.048	
-0.007	NA	0.048	
-0.54	NA	0.03	
-0.48	NA	0.04	
-0.85	NA	0.04	
-0.41	NA	0	
-0.37	NA	0.03	
-0.47	NA	0.04	**Wei et al., (2018)**
-0.38	NA	0.02	
-0.34	NA	0.02	
-0.15	NA	0.04	
-0.34	NA	0.03	
-0.32	NA	0.05	
Average	**-0.15**	**-0.014**	**0.05**

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Table 7. Compilation of fraction factors during reduction of Cr(VI) adapted from Scheiderich et al., (2015).

Reference	Fractionation factor (‰)	Reductant
Scheiderich et al., (2015)	0.8‰	Organic matter in ocean surface water
Bauer et al. (2018)	1.8‰	Dissolved and solid phase Fe(II)
Basu and Johnson (2012)	3.91; 2.67; 2.65; 2.11	Goethite; siderite; green rust; FeS
Døssing et al. (2011)	3.60; 1.50	Ferrous Fe; 'Green rust'
Ellis et al. (2002)	3.51	Magnetite
Kitchen et al. (2012)	4.20; 3.11	Low-pH Fe(II); organic reductants
Sikora et al. (2008)	4.11; 1.75	*Shewanella oneidensis* bacteria
Zink et al. (2010)	3.54; 5.0	Acidic H_2O_2; pH-neutral H_2O_2 (kinetic)

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1038

Continental runoff

$Cr(VI)_{aq}$, $\delta^{53}Cr$ = -0.12 – 5.00‰

Soils

$Cr_2O_3 \xrightarrow{MnO_2} Cr(VI)_{aq}$

[1]

Continental weathering

$Cr(VI)_{aq}$, $\delta^{53}Cr$ = 0.13 – 1.24‰

Fe(II), H_2S

$Cr(VI)_{aq} \longrightarrow Cr(OH)_3$

[4]

Hydrothermal vents

$Cr(OH)_3 \longleftarrow Cr(III)_{aq}$ $\delta^{53}Cr$ BSE

[3]

[1]

Reactions
1. Cr(III) oxidation
2. Acid Cr(III) dissolution
3. Hydrolysis
4. Cr(VI) reduction

Chemical sediments

$\delta^{53}Cr$ = -0.57 – 5.00‰ $Cr_2O_3 \xrightarrow{H^+} Cr(III)_{aq}$

[2]

Seafloor weathering

a)

6 N HCl
(L_{6NHCl})

Bulk Sediment Leach 1

NH$_2$OH-HCl
(MnOx)

Bulk Sediment Leach 2

6 N HCl
(L_{Sil})

Na-dithionite
(L_{GOE})

0.5 N HCl
(L_{HFO})

Acetic Acid
(L_{Carb})

Sequential Extraction 1

b)

6 N HCl
(Fe_{TOT})

Bulk Sediment Leach 1

Fe_{TOT} - (Fe_{GOE} + Fe_{HFO})
(Fe_{Sil})

Na-dithionite
(Fe_{GOE})

Hydroxylamine HCl
(Fe_{HFO})

Na-Acetate
(Fe_{Carb})

Sequential Extraction 1

a

- ● $\delta^{53}Cr$ L_{GOE}(‰)
- ● $\delta^{53}Cr$ L_{6NHCl} (‰)
- ● $\delta^{53}Cr$ L_{Sil} (‰)
- ◇ Mass Balance Authigenic $\delta^{53}Cr$
- ■ Mass Balance Bulk $\delta^{53}Cr$

b

a

Anoxic Deep Ocean

Reactions
1. Hydrolysis

Anoxic Seawater, Dissolved Fe(II), H$_2$S

Fe(II)   Fe(II)   Fe(II)

no Cr(VI) reduction within plume

Cr(OH)$_3$ Cr(OH)$_3$ ← Cr(III)$_{aq}$
                                              1
Fe(II)   Fe(II)

Anoxic Sediments

Cr$_2$O$_3$ Cr$_2$O$_3$ → Cr(III)$_{aq}$

Seafloor weathering

$\delta^{53}Cr_{sediments}$ ≈ -0.121‰ (ISE)

b

Oxygenated Deep Ocean

Reactions
1. Cr(III) oxidation
2. Cr(VI) reduction
3. Hydrolysis

Cr(VI)$_{aq}$ $\delta^{53}Cr_{seawater}$ ≈ 1.0‰   Oxygenated Seawater

Fe(II)   Fe(II)   Fe(II)

Partial seawater Cr(VI) reduction within plume

Fe(II), H$_2$S: ε = 1.57‰

Cr(VI)$_{aq}$ → Cr(OH)$_3$ Cr(OH)$_3$ ← Cr(III)$_{aq}$
            2   3
Fe(II)

Cr(VI)$_{aq}$

Oxygenated Sediments

MnO$_2$

Cr$_2$O$_3$ → Cr(VI)$_{aq}$ Cr$_2$O$_3$ → Cr(III)$_{aq}$
            1

Seafloor weathering

$\delta^{53}Cr_{sediments}$ < -0.2‰