Chemical Characteristics of Modern Deep-Sea Metalliferous Sediments in Closed

versus Open Basins, with Emphasis on Rare-earth Elements and Nd Isotopes

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38 **Abstract**

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4 41 Metalliferous sediments deposited on and near spreading ridges show contrasting
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6 42 geochemical signatures depending on whether deposition occurred in a restricted basin filled
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8 43 with anoxic dense brines, or in an open ocean characterized by oxidized and well-circulated
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10 44 seawater. Metalliferous sediments of the Atlantis II Deep, which are precipitated from ca. 60°C
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12 45 dense brines, display a wide range of mineralogical and chemical facies. The most abundant
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14 46 facies are enriched in Fe-oxyhydroxides or Fe-silicates or metal sulphides; Mn-oxides and
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16 47 anhydrite are locally important. Terrigenous and biogenic components are minor. Base and
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18 48 precious metals are notably enriched in the sulphide-rich facies. By contrast, chemical
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20 49 precipitates in open-ocean settings consist of Fe-Mn-oxyhydroxides that were deposited from
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22 50 dilute hydrothermal plumes, commonly admixed with biogenic carbonate-rich ooze. On a
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24 51 carbonate-free basis, open-ocean metalliferous sediments show much less enrichment in
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26 52 trace metals relative to sediments in the Atlantis II Deep but have higher contents of rare-
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28 53 earth elements (REEs).
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33 55 The shale-normalised REE patterns of metalliferous sediments in the Atlantis II Deep show
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35 56 positive Eu anomalies, but lack Ce anomalies. Due to the low REE content of the precipitates,
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37 57 even minor aluminosilicate detritus (10%) can affect REE patterns. The 'baseline' of the REE
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39 58 pattern is determined mainly by the aluminosilicate component of the metalliferous sediment,
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41 59 with the Eu anomaly resulting from the hydrothermal component. Nd isotopic variations can
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43 60 be explained largely by the mixing of Nd provided by aluminosilicate detritus with lesser
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45 61 dissolved Nd derived from a basaltic-hydrothermal source. These two sources can also
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47 62 account for the Pb isotopic variations reported in previous studies. The majority of Sr is
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49 63 derived from evaporites that flank the brine deep, with a smaller contribution from the
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51 64 basalts.
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55 66 In open-ocean settings, plume particulates that formed above high-temperature vents acquire
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57 67 seawater-type REE patterns and Nd isotope ratios soon after discharge; these features are
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59 68 maintained as the plume drifts hundreds to a few thousand kilometres from the ridge axis.
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61 69 Departures from seawater isotopic and REE signatures can occur if detrital material (basaltic
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70   or terrigenous) is present in the metalliferous sediment. The Sr-isotope ratios of open-ocean

71   sediments are, like Nd, dominated by seawater Sr. For Pb, a basaltic component can be

72   isotopically identified in metalliferous sediments up to 1000 km from the axis.

73

74   Where low-temperature fluids discharge through biogenic sediments on ridge flanks, as at the

75   Galapagos hydrothermal mounds, Fe-rich smectites (nontronite) are formed, together with

76   minor Mn-oxides. The nontronites have very low contents of REEs, with seawater-type

77   patterns, although Ce anomalies are less negative than those of deep Pacific seawater.

78   Nontronites formed in high-temperature vent fields, and on intra-plate seamounts, display a

79   range of REE patterns resulting from mixtures of hydrothermal fluid and normal seawater.

80

81   In open-ocean basins, the REE patterns and Nd-Sr isotope ratios of chemical precipitates

82   generally reflect those of ambient deep seawater. In closed (or restricted) anoxic basins

83   subject to hydrothermal input, the precipitates can have REE patterns and Nd-Sr-Pb isotope

84   ratios that differ considerably from those of ambient seawater. These results bear on the

85   interpretation of geochemical data from ancient exhalative deposits.

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87

88   **Keywords: Geochemistry, metalliferous sediments, REEs, Nd isotopes, Red Sea, Pacific Ocean**

1. Introduction

Chemical sedimentation resulting from hydrothermal activity in deep marine environments can be considered in terms of two end-member settings: (1) closed basins up to a few tens of kilometres across that lie on spreading axes, and contain up to 100 m of hot (20–68°C) anoxic brines as near- bottom layers from which metal-rich sulphides, silicates and oxyhydroxides precipitate (Degens and Ross, 1969; Bäcker and Richter, 1973; Laurila et al., 2014a, b, 2015, and references therein); and (2) broad flanks of open–ocean spreading ridges where bottom waters are well circulated and oxic, and where Fe-Mn-oxyhydroxides precipitate from dilute, low-temperature plumes that can extend up to a few thousand kilometres from the spreading axis (cf. Boström et al., 1969; Sayles and Bischoff, 1973; Jarvis, 1985; Barrett et al., 1987; Owen and Olivarez, 1988; Feely et al., 1994a, 1996; Resing et al., 2015; Fitzsimmons et al., 2017; Gartman and Findlay, 2020).

Fe-rich sediments may also form:

(i) at distances of up to a few tens of km from spreading axes where uprising low-temperature fluids react with biogenic sediments to form thick, nontronite-rich deposits (Corliss et al., 1978; Hékinian et al., 1978; Dymond et al., 1980; Honnorez et al., 1981; McMurtry et al., 1983; Moorby and Cronan, 1983; Barrett, 1983, 1992);

(ii) on seamounts as thin, nontronite-rich deposits encrusting volcanic rocks (De Carlo et al., 1983; Alt, 1988; McMurtry et al., 1993; Dekov et al., 2007; Lubetkin et al., 2018);

(iii) directly on spreading axes, either by surface oxidation of high-temperature sulphide deposits (Barrett, 1990; German et al., 1993; Damyanov et al., 1998; Dias et al., 2008; Pan et al., 2018), or by precipitation from low-temperature fluids (Murnane and Clague, 1983; Mills et al., 2001; Severmann et al., 2004; Dekov et al., 2010; Sun et al., 2012, 2018; Zeng et al., 2012; Ta et al., 2017).

In order to assess chemical differences between the two end-member settings, we first review the characteristics of metalliferous sediments from the brine-filled deeps of the Red Sea versus those that formed in open-ocean settings of the eastern Pacific Ocean (Fig. 1). In the Atlantis II Deep of the Red Sea, metalliferous sediments form almost pure

119 accumulations (5–20 m thick) of Fe oxyhydroxides, Fe-rich hydrous silicates, Fe-Cu-Zn-Pb

120 sulphides, Fe-Mn carbonates and oxides, and amorphous compounds that overlie axial

121 basalts (e.g., Bäcker and Richter, 1973). In the eastern Pacific Ocean, metalliferous

122 sediments occur as laterally extensive, fine-grained Fe-Mn oxyhydroxides dispersed within

123 biogenic ooze-dominated sediments (up to 50 m thick) that accumulated over millions of

124 years as the seafloor spread away from the East Pacific Rise (Lyle, 1986). In both of these

125 settings, a small but chemically significant component of terrigenous detritus is also

126 present within the metalliferous sediments.

127

128 For the Atlantis II Deep, we present previously unpublished chemical analyses of 53 samples of

129 metalliferous sediments from 13 cores in the western to southwestern portion of the Deep. In

130 addition, a subset of 14 samples has been analysed for Nd isotope ratios with the aim of

131 identifying the different possible sources of Nd (e.g., basalt, seawater, continental detritus),

132 and to assess relationships between rare earth element (REE) patterns and Nd isotope ratios.

133 For the eastern Pacific Ocean, 40 new chemical analyses of metalliferous sediments, including

134 REEs, from Leg 92 of the Deep Sea Drilling Project (DSDP) are reported. We also review

135 published REE and Nd-Sr-Pb isotope data for metalliferous sediments from these two settings.

136

137 In addition to the end-members, REE and Nd isotopic data for Fe-silicate-rich, low-temperature

138 seafloor precipitates are reviewed, with emphasis on: (i) the nontronite-rich Galapagos

139 hydrothermal mounds on the flank of the Galapagos Rift in the eastern Pacific Ocean; and (ii)

140 Fe-rich sediments formed on the axes of spreading ridges, including nontronite-rich precipitates

141 and Fe-oxide-hydroxide-rich material derived from the oxidation of massive sulphides.

142

143 The overall objective of this paper is to characterise the main chemical features of modern

144 metalliferous sediments deposited in contrasting ocean-floor settings, with an emphasis on the

145 interpretation of REE patterns and Nd isotopic compositions. This survey focuses on sediments

146 containing a significant hydrothermal component, and therefore does not include largely

147 hydrogenous metalliferous deposits such as ferromanganese nodules of the abyssal plains, or

148 ferromanganese crusts overlying basalts at spreading centres or on seamounts. We also briefly

149 discuss the REE patterns and Nd isotopic compositions of some ancient exhalative rocks on land

150 that were originally deposited in deep-ocean settings, e.g., Palaeozoic umbers overlying

151 massive sulphide deposits, and Precambrian banded iron formations.

152

1.1. Previous studies

154

155 The brine-filled deeps of the axial portion of the Red Sea (Figs. 1, 2) have been of interest to

156 oceanographers and geologists since the first research cruises to the area in the 1960s and

157 1970s (Miller et al., 1966; Degens and Ross, 1969; Bäcker and Schoell, 1972). Numerous studies

158 of the Atlantis II Deep sediments have since produced a detailed picture of their stratigraphy,

159 mineralogy, chemistry and potential economic value (Bischoff, 1969; Bischoff and Manheim,

160 1969, 1972; Bäcker and Richter, 1973; Hackett and Bischoff, 1973; Delevaux and Doe, 1974;

161 Steinkamp and Schumann, 1974; Bäcker, 1976; Bignall et al., 1976; Lupton et al., 1977; Shanks

162 and Bischoff, 1977, 1980; Pottorf and Barnes, 1983; Mustafa et al., 1984; Zierenberg and

163 Shanks, 1983, 1988; Karbe, 1987; Oudin, 1987; Singer and Stoffers, 1987; Cole, 1988; Dupré et

164 al., 1988; Guney et al., 1988; Ramboz et al., 1988; Butuzova et al., 1990; Cocherie et al., 1994;

165 Blanc et al., 1998; Pierret et al., 1998; Taitel-Goldman and Singer, 2001, 2002; Badaut et al.,

166 2002; Taitel-Goldman and Singer, 2009; Bertram et al., 2011; Laurila et al., 2014a, b, 2015;

167 Brueckmann et al., 2017; Quadros et al., 2018). The metalliferous sediments of the Atlantis II

168 Deep constitute a major deposit of base and precious metals with an estimated in-situ value of

169 US$ 11 billion (Brueckmann et al., 2017); mining schemes have been proposed for piping the

170 sediments to a surface ship, with primary processing carried out at sea (Mustafa and Amann,

171 1980; Nawan, 1984; Thiel et al., 2015; Hamer, 2017).

172

173 Detailed investigations have been made on the temperature and chemical composition of the

174 brine layers that overlie the metalliferous sediments in the Atlantis II Deep (Ross, 1972; Schoell

175 and Faber, 1978; Danielsson et al., 1980; Hartmann, 1985; Zierenberg and Shanks, 1986;

176 Anschutz et al., 1995, 1998, 2000; Anschutz and Blanc, 1996; Winckler et al., 2000, 2001; Pierret

177 et al., 2001; Swift et al., 2012; Anschutz, 2015; Schardt, 2016), and on microbial communities

178 both in the hot brines (Eder et al., 2001; Qian et al., 2011; Wang et al., 2011, 2013), and in the

179 underlying sediments (Siam et al., 2012). Several other brine pools along the spreading axis of

180 the Red Sea (shown in Fig. 2) have also been studied, although in less detail than the Atlantis II

181 Deep (Bignell, 1975; Blum and Puchelt, 1991; Sholten et al., 1991; Pierret et al., 2010). Tectonic,

182 igneous and sedimentological events during the opening of the Red Sea, which bear on the

183 formation and seafloor setting of the brine pools, have been described by Bonatti and Seyler

184 (1987), Bosworth et al. (2005), Ligi et al. (2012, 2015, 2018), Augustin et al. (2014, 2016, 2019),

185 Bonatti et al. (2015), Bosworth (2015) and Bosworth and Stockli (2016).

186

187 In the eastern Pacific Ocean, detailed chemical studies have been carried out on surficial (<9 m

188 depth) Fe-Mn-oxyhydroxide-rich metalliferous sediments occurring on and near the crest of the

189 East Pacific Rise (EPR; Boström et al., 1969; Bender et al., 1971; Marchig and Gundlach, 1982;

190 Walter and Stoffers, 1985), and Fe-smectite-rich sediments within the Bauer Deep several

191 hundred km east of the EPR (Dasch et al., 1971; Sayles and Bischoff, 1973; Sayles et al., 1975).

192 Metalliferous sediments have also been recovered at depth in the Bauer Deep by Leg 34 of the

193 DSDP (Fig. 1; Boström et al., 1976; Dymond et al., 1976) and in drill holes located up to 1700 km

194 west of the EPR by Legs 85 and 92 of the DSDP (Fig. 1; Jarvis, 1985; Lyle, 1986; Ruhlin and

195 Owen, 1986; Barrett et al., 1987). Chemical features of basal metalliferous sediments from

196 DSDP drillholes in the eastern Pacific Ocean have been reported by Cronan (1976) and Jarvis

197 (1985). Metalliferous sediments from drilled holes and near-axial surface locations span an age

198 range from Middle Eocene to Pleistocene, and were derived from colloidal Fe-Mn

199 oxyhydroxides that settled out of laterally spreading hydrothermal plumes originating at either

200 the EPR or the earlier-active Galapagos and Mendoza Ridges (Dymond et al., 1973; Dymond et

201 al., 1976; Leinen and Stakes, 1979; Marchig and Gundlach, 1982; Lyle, 1986; Rea and Leinen,

202 1986; Marchig and Erzinger, 1986; Lyle et al., 1987). During sediment burial, early diagenetic

203 reactions between Fe-Mn oxyhydroxides and biogenic silica can lead to the formation of Fe-rich

204 smectitic silicates plus Mn micronodules, particularly in areas of slow sedimentation such as the

205 Bauer Deep (Sayles and Bischoff, 1973; Heath and Dymond, 1977, 1981; Jarvis, 1985).

206

207 In contrast to metalliferous sediments derived from Fe-Mn-oxyhydroxide-bearing plumes, the

208 Galapagos hydrothermal mounds, located 20–30 km from the modern Galapagos Rift, consist

209 mainly of Fe-rich, Al-poor (nontronitic) silicates, first recovered by dredging (Corliss et al.,

210 1978). The mounds were investigated by rotary drilling on DSDP Leg 54 (Hékinian et al., 1978;

211 Dymond et al., 1980; Schrader et al., 1980; Varnavas and Cronan, 1981) and in more detail

212 using piston coring on DSDP Leg 70 (Honnorez et al., 1981; Barrett and Friedrichsen, 1982;

213 Moorby, 1983; Moorby and Cronan, 1983). Nontronite has also been recovered locally from the

214 flanks of seamounts in the Pacific Ocean (Singer et al., 1984; Lubetkin et al., 2018) and in the

215 Mediterranean Sea (Dekov et al., 2007).

216

217 1.2. Sample material and analytical methods

218

219 Locations of the Atlantis II Deep, the EPR Transect, and other metalliferous sediment and brine

220 sites discussed in this paper are shown in Fig. 1. Geographic coordinates of the sampled sites

221 are listed in Table 1. All cores from the Atlantis II Deep, except one, were sampled by TJB at

222 Preussag AG's archival storage facility in Berkhöpen, Germany. These cores were recovered on

223 R/V Valdivia cruises VA-01 (1971) and VA-03 (1972). One core (274 KS) was taken on R/V

224 Valdivia cruise VA 29 in 1980. This last core, stored at the Bureau de Recherches Géologiques et

225 Minières (BRGM) in Orléans, France, was sampled by TJB. All sediment samples were obtained

226 from intervals of homogeneous colour and texture (featureless muds, with the exception of

227 anhydrite layers/veins; see Section 2.1). Samples from the Atlantis II Deep were washed with

228 distilled water prior to analysis to remove crystallized salts.

229

230 Forty-three of the 53 Red Sea samples were analysed for major and trace elements; 10 samples

231 were analysed for trace elements only, due to limited amounts of sample material.

232 Determination of major and trace elements by inductively coupled plasma (ICP)

233 spectrochemical techniques was based on total dissolution of 0.5–1 g of sample using a mixed-

234 acid digestion of nitric (HNO_3), hydrochloric (HCl), perchloric ($HClO_4$) and hydrofluoric (HF) acids

235 followed, if necessary, by a lithium metaborate-tetraborate ($LiBO_2 - Li_2B_4O_7$) fusion and

236 dissolution of any residual material (Bouvier, 1991). Major elements and selected trace

237 elements were determined by ICP-based atomic emission spectrometry (ICP-AES). Other trace

238 elements including metals were analysed by ICP-based mass spectrometry (ICP-MS) at the

239 Analytical Laboratories of the Geological Survey of Canada, Ottawa

240 (https://navigator.innovation.ca/en/facility/natural-resources-canada/trace-inorganic-

241 geochemistry-research-laboratory). Pb was determined by atomic absorption (AA).

242 Instrumental neutron activation analysis (INAA) of selected trace elements was carried out at

243 Activation Laboratories, Ancaster, Ontario (https://actlabs.com/). INAA measurements were

244 made on 1-g samples irradiated by thermal neutrons in a high-flux reactor, using gamma-ray

245 spectrometry with a solid-state detector. Total sulphur was determined by combustion

246 followed by infrared spectrophotometry (LECO), and loss on ignition (LOI) by gravimetry at

247 900°C; CO_2 (t) is the total carbon measured by LECO and is reported as CO_2. The LECO

248 measurements were also made at the Geological Survey of Canada. Carbonate carbon was

249 determined by dissolving the sample in hot HCl, decanting the liquid, weighing the dried

250 residue, and calculating the carbonate fraction by difference. C (org) is the non-carbonate

251 carbon fraction, calculated as the difference between CO_2 (t) and carbonate carbon. All data for

252 the Red Sea sediments, excluding REEs, are given in Supplementary Data Table 2.

253

254 Sediment samples from holes drilled by DSDP Leg 92 (EPR Transect) were provided by the Deep

255 Sea Drilling Project. Prior to analysis, samples were washed using distilled water, dried at 110°C,

256 powdered in an agate mortar, subjected to a 10 % acetic acid leach to remove the calcium

257 carbonate component, then dried at 105°C and re-powdered (further details in Barrett et al.,

258 1987). Leg 92 samples were analysed for major and trace elements by the same methods as

259 outlined above for the Red Sea samples; REEs were determined by ICP-MS. In addition,

260 lanthanum, yttrium and zirconium were also determined by ICP-AES. For these three elements,

261 we have used the ICP-AES results as several of the Leg 92 samples could not be measured by

262 ICP-MS due to insufficient material. The ICP-MS results are, however, also reported in

263 Supplementary Data Table 2. For those samples measured by both techniques, the results

264 agree to within 5 % of their average value (r^2 values for La-La, Y-Y and Zr-Zr as measured by the

265 two methods are 0.967, 0.870 and 0.975, respectively). All data for the Leg 92 sediments are

266 given in Supplementary Data Table 2.

267

268 Owing to the very low content of REEs in metalliferous sediments of the Atlantis II Deep, as well

269 as elevated Ba concentrations due to the presence of barite, a specific procedure was

270 developed by Jarvis et al. (1989) to ensure accurate analysis of such samples (cf. Barrett et al.,

271 1990). Splits (0.2–0.5 g) of sample powders were digested in open PTFE

272 (polytetrafluoroethylene) beakers using a $HF-HClO_4$ mixture (Totland et al., 1992; Jarvis, 2003,

273 p. 185), with final solutions taken up in 1 M HCl. Samples with visible residues following

274 digestion were filtered, the residues fused with 0.25 g $LiBO_2$ in platinum crucibles, and the melt

275 dissolved in 1 M HCl. The two solutions were then combined. The REEs and Y were extracted

276 using a cation-separation procedure (Jarvis and Jarvis, 1985; Jarvis, 2003, p. 210), and

277 determined using a VG Elemental PlasmaQuad PQ2 Plus ICP-MS, at the NERC-ICP-MS Facility,

278 then at Royal Holloway University of London, UK. Operating conditions followed Totland et al.

279 (1992).

280

281 The cation-exchange extraction utilized does not completely separate Ba from the REEs. The

282 determination of low levels of Eu (typically 2–50 ng ml^{-1}), in the presence of up to 100 ng ml^{-1} of

283 Ba, required a large correction to compensate for the overlap of refractory $^{135}Ba^{16}O$ on ^{151}Eu.

284 Therefore, Eu was determined independently by adjusting the ICP-MS to give a maximum

285 amount of doubly charged M^{2+} ions (Jarvis et al., 1989). Results obtained by the two techniques

286 were generally in good agreement; however, data obtained using the "doubly charged"

287 technique have been shown to be more precise and more accurate (Jarvis et al., 1989) and are

288 reported here. The precision of the REE and Y analyses is estimated to be better than ±10 %

289 RSD for all elements. Accuracy of the data is judged to be close to the precision (Totland et al.,

290 1992; Jarvis, 2003).

291

292 The Nd isotope ratios of 13 selected samples of metalliferous sediment from the Atlantis II

293 Deep were measured at the London University Radiogenic Isotope Facility. The method used

294 was that described by Thirlwall (1991). Six analyses of the laboratory Aldrich standard gave a

295 mean value of 0.511423 ± 5 (2 sd), slightly higher than the standard value of 0.511420, which in

296 turn is equivalent to the La Jolla standard value of 0.511855. Measured values are reported

297 relative to a CHUR value of 0.512646. The total blank for the analyses was 200–400 pg Nd,

298 which has an insignificant effect on the measured values.

299

300 **2. Metalliferous Sediments in Closed Ocean Basins – Atlantis II Deep, Red Sea**

301 2.1. Tectonic setting and stratigraphy

302

303 Locations of the Atlantis II Deep and five other deeps along the axis of the Red Sea are

304 indicated in Fig. 2a; the inset shows plate boundaries and spreading directions. The history of

305 opening of the Red Sea, and the important influence of evaporite deposits on seafloor

306 topography, as well as on brine generation, have been described by Cochran (2005), Ligi et al.

307 (2012, 2015, 2018), Augustin et al. (2014, 2016), Mitchell and Park (2014), Bonatti et al. (2015),

308 Bosworth (2015), Ehrhardt and Hübscher (2015), Hovland et al. (2015, 2019) and Stockli and

309 Bosworth (2019). Seafloor topography in the region of the Atlantis II Deep is illustrated in Fig.

310 2b (after Augustin et al., 2016), where the locations of the 15 cores sampled in the present

311 study are also shown (yellow-filled circles). Figure 3 gives a schematic section across the Red

312 Sea, showing the brine layers, metalliferous sediments and underlying axial basalts of the

313 Atlantis II Deep with respect to laterally bounding Miocene evaporite and Pliocene-Pleistocene

314 siliciclastic sequences. The thickness of metalliferous sediment in the Atlantis II Deep generally

315 ranges from 10 to 25 m. Most of this sediment lies at depths of 2000 to 2200 m below sea level.

316 Accumulation rates during periods of heightened hydrothermal activity were in the order of

317 100 cm/kyr (Shanks and Bischoff, 1980), in contrast to the normal Red Sea hemipelagic

318 sedimentation rate of about 10 cm/kyr (Ku, 1969).

319

320 Early studies of gravity cores led to the recognition of seven main sediment facies within the

321 Atlantis II Deep (Bischoff, 1969; Hackett and Bischoff, 1973). These facies were named

322 according to the dominant minerals (detrital material, iron-montmorillonite, goethite-

323 amorphous, sulphide, manganosiderite, anhydrite, manganite), although each facies can

324 contain mineralogically contrasting layers in places. Subsequently, they were grouped into five

325 main lithostratigraphic units by Bäcker and Richter (1973) and Bäcker (1976): AM = amorphous

326 silicate zone; SU2 = upper sulphidic zone; CO = central oxide zone; SU1 = lower sulphidic zone;

327 DOP = detrital-oxide-pyrite zone. These units have been employed by most studies of Atlantis II

328 Deep sediments since then (e.g., Shanks and Bischoff, 1980; Pottorf and Barnes, 1983; Oudin et

329 al., 1984; Laurila, 2015). It should be noted, however, that these broad lithostratigraphic units

330 commonly display internal variations in the form of colour-banded layers and laminations of

331 contrasting mineralogy. Schematic sediment columns for the Atlantis II Deep as a whole, and

332 the Southwest Basin in particular, are shown in Fig. 4 [after Laurila (2015), based on Bäcker and

333 Richter (1973)'s classification of lithological units]. In the Southwest Basin – the focus of the

334 present study – most cores intersected only the upper three lithological units, owing to the

335 presence of a major basalt sill that prevented core penetration to the basaltic basement.

336

337 Blanc et al. (1998) suggested revisions to the lithological units proposed by Bäcker and Richter

338 (1973), based on detailed study of two complete cores, one from the Southwest Basin, the

339 other from the West Basin. Blanc et al. (1998) argued that only two main sedimentary units

340 (Lower and Upper) can be distinguished in the Southwest Basin, whereas elsewhere in the

341 Atlantis II Deep the vertical sequence is more complex, but broadly comparable to that

342 suggested by Bäcker and Richter (1973), with the main difference being Blanc et al. (1998)'s

343 subdivision of the Central Oxide (CO) zone into six subunits.

344

345 In the Bäcker and Richter (1973) scheme, the oldest sedimentary unit, the detrital-oxide-pyrite

346 (DOP) facies, overlies MOR-type basalts (Fig. 3). The DOP facies was deposited from 23,000 to

347 12,000 years ago, during the time of the last glacial maximum (Anschutz, 2015). It is dominated

348 by Fe-Mn carbonates, siliceous plankton tests, detrital clays and pyrite, but also includes Fe-

349 oxyhydroxide layers. The DOP facies is overlain by SU1, the first sulphide facies (Figs. 3, 4). The

350 contact between these two facies approximately corresponds to the Pleistocene–Holocene

351 boundary (Anschutz, 2015). The SU1 facies is overlain by the central oxic (CO) zone, which is

352 dominated by Fe- and Mn-oxides and oxyhydroxides, then by the SU2 zone containing

353 significant sulphides, and finally by the AM zone dominated by amorphous Fe-silicates. In the

354 classification of Blanc et al. (1998), the SU2 and AM zones are combined into one, as sulphides

355 and amorphous silicates are present throughout both. In the Southwest Basin, this combined

356 zone (SU2 + AM) is much thicker than elsewhere in the Atlantis II Deep, reaching at least 10 m.

357

358 Fe-bearing phases in the Atlantis II Deep are commonly amorphous or poorly crystallized,

359 especially in the upper 5 to 10 m of the sedimentary sequence, and include metastable Fe-

360 OOH-Si compounds that transform to Fe-oxides and Fe-rich clays during burial diagenesis

361 (Taitel-Goldman and Singer, 2002; Laurila et al., 2015). The silica is probably derived from both

362 hydrothermal and biogenic sources (Anschutz and Blanc, 1995a). Local enrichments in detrital

363 clays, authigenic carbonates and Mn oxides occur below the SU2 zone, mainly in the lowest

364 (DOP) zone (Anschutz and Blanc, 1995b). Detailed features and distributions of the main

365 minerals of the Atlantis II Deep have been reported by Thisse (1982), Zierenberg and Shanks

366 (1983), Cole (1988), Badaut et al. (1992), Blanc et al. (1998), Schwertmann et al. (1998), Taitel-

367 Goldman and Singer (2001), and Taitel-Goldman et al. (2004, 2009). The origin of the fine

368 layering that develops below depths of a few metres, often in the form of colour banding within

369 Fe-oxyhydroxide-rich sediments, has been ascribed to diagenetic processes by Laurila et al.

370 (2015).

371

372 Chemical analyses in the 1970s and 1980s were commonly made on bulk samples over core

373 lengths of 100 cm, as a major objective of the coring was to determine average metal grades

374 and tonnages throughout the Atlantis II Deep (Guney et al., 1984, 1988). Given that many

375 lithological units can contain intervals with distinct mineralogical layering on a scale of

376 centimetres or less, bulk chemical analyses over lengths of 100 cm therefore often represent

377 averages of a number of layers of contrasting mineralogy and chemistry.

378

379 Detailed studies of 100 short sample intervals (< 2 cm) from nine cores in different parts of the

380 Atlantis II Deep were undertaken by Laurila et al. (2014a, b, 2015). These studies, which

381 documented variations in major elements, metal contents, REE patterns and mineralogy

382 throughout the Deep, have added significantly to our understanding of chemical sedimentation

383 in hot brine pools. Variations in sediment facies were interpreted by these authors to be the

384 result of changes in temperature, pH and Eh of the brines from which the sediments

385 precipitated, which in turn reflect variable hydrothermal input within the basin due to factors

386 such as distance from the source vent(s) and change in hydrothermal discharge rate. In

387 addition, diagenetic effects can modify the mineralogy of the primary precipitates

388 (Schwertmann et al., 1988; Taitel-Goldman and Singer, 2002; Laurila et al., 2015). Typical

389 examples of metalliferous sediments from the Atlantis II Deep are shown in Fig. 5 (from Laurila

390 et al., 2015).

391

392 Locations of the 16 cores sampled in the present study are shown in Fig. 6 and listed in Table 1.

393 Twelve cores are from the Southwest Basin, and three from the West Basin (345, 369, 436). The

394 main minerals present in each sample are given in Table 2. Sample depths ranged from 0.3–

395 10.8 m below the seafloor. Samples were selected from intervals of differing colour and

396 mineralogy, and included red, brown and yellow Fe-oxyhydroxide-rich layers, greenish Fe-

397 silicate-rich layers, purplish metal sulphide-rich layers and (uncommon) whitish-grey anhydrite-

398 rich layers. Apart from the anhydrite-rich layers, which contain coarse crystals, the sediments

399 ranged from soft muds (greater depths) to gelatinous oozes (uppermost few metres). Some of

400 the Fe oxyhydroxide-rich layers are colour laminated on a mm-scale due to differing

401 proportions of phases such as goethite, limonite and lepidocrocite, and locally Fe-silicate clays

402 and Mn-oxyhydroxides (Laurila et al., 2015). All samples but two were from the upper three

403 sedimentary units as defined by Bäcker and Richter (1973), that is, units AM, SU2 and CO (Fig.

404 4). In the Southwest Basin, using the classification of Blanc et al. (1998), all cores but one

405 belong to their Upper (U) unit, which corresponds to the AM and SU2 zones of Bäcker and

406 Richter (1973). The exception is Core 274 in the Southwest Basin, which intersected the SU1

407 and DOP zones at, 7.5 m and 10.2 m, respectively, below the seafloor (the hole terminated at

408 11.0 m, still in sediment). Given that the boundary between the upper Pleistocene and

409 Holocene occurs at the top of the DOP unit (Anschutz, 2015), all analysed samples in this study,

410 apart from the lowest sample in Core 274, are thus of Holocene age (<11.7 ka).

411

412 2.2. Major elements

413

414 Detailed chemical analyses for 43 samples of metalliferous sediment from the Atlantis II Deep

415 are given in Supplementary Data Table 1. Although the sediments were washed with distilled

416 water prior to analysis, some salts remained, as indicated by high Na + Cl contents of 2–10 %

417 (Supplementary Data Table 1). The main chemical features of the bulk sediments are the high

418 contents of Fe (commonly 25–55 wt % Fe_2O_3t), combined with very low amounts of detritally-

419 supplied elements such as Al (typically ≤2 % wt Al_2O_3). As shown in Fig. 7, the Atlantis II Deep

420 sediments have Fe/Mn ratios higher than those of metalliferous sediments on the spreading

421 axis of the southern East Pacific Rise (SEPR) and most plume particulates from the northern

422 East Pacific Rise (NEPR), and much higher than those of slowly accumulating, deep-sea

423 ferromanganese nodules. A few samples from the Atlantis II Deep are notably enriched in Mg

424 (talc-bearing), Ca (anhydrite) or Mn (Mn oxides) relative to most samples from the Deep. Our

425 major-element results are broadly comparable to those reported by Laurila et al. (2015), who

426 analysed samples from a different set of cores, which included the Southwest Basin, East Basin

427 and West Basin (our samples are mainly from the Southwest Basin).

428

429 Iron in the Atlantis II Deep sediments occurs in both Fe^{2+} and Fe^{3+} states, in the form of

430 oxyhydroxides (goethite, limonite, hematite), Fe-rich hydrous silicates, and iron sulphides. The

431 proportions of these phases vary vertically and laterally within the Deep (Fig. 4). The Al_2O_3

432 content of the metalliferous sediments, which serves as a proxy for the siliciclastic detrital

433 component, ranges from 0.2–4.0 wt %. Other detritally supplied elements such as Ti and Zr

434 show positive correlations with Al_2O_3 (Fig. 8a, b).

435

436 The main source of the detrital component is wind-borne dust derived from the arid

437 continental terranes that flank the Red Sea (Stein et al., 2007; Palchan et al., 2018). Detrital

438 material has a strong influence on the REE content of the metalliferous sediments, as shown by

439 a plot of ∑REE versus Al_2O_3 (Fig. 8c), and as previously reported by Laurila et al. (2014a). Most

440 of the metalliferous sediments contain 25–55 wt % Fe_2O_3t and 15–30 wt % SiO_2 (Fig. 8d). Much

441 of this silica is probably hydrothermal in origin, although some could be supplied by dissolution

442 of detrital quartz and biogenic silica (radiolaria, diatoms) in the sediments, based on

443 calculations by Anschutz and Blanc (1995a). Several samples are notably enriched either in

444 nontronite, a hydrous, low-Al, Fe^{+3}-rich silicate, or in Fe-oxyhydroxides, based on chemical

445 trends (Fig. 8d). Nontronite is formed in the lowest brine layer of the Atlantis II Deep, as silica of

446 mainly hydrothermal origin combines with hydrothermal Fe-oxyhydroxides (cf. Schwertmann et

447 al., 1998; Taitel-Goldman et al., 2009; Cuadros et al., 2018).

448

449 2.3. Metals

450

451 Metalliferous sediments in the Atlantis II Deep are enriched in base and precious metals, as

452 documented by numerous studies since the 1970s (e.g., Bäcker and Richter, 1973; Shanks and

453 Bischoff, 1977; Pottorf and Barnes, 1983; Mustafa et al., 1984; Oudin, 1987; Guney et al., 1988;

454 Laurila et al., 2014a). Zinc, Cu and Pb contents in the Southwest Basin are up to 15 wt %, 3 wt %

455 and 0.3 wt % respectively, while Au and Ag reach 5 ppm and 300 ppm, respectively. Sediments

456 are enriched in most trace metals, containing up to 900 ppm As, 500 ppm Mo, 400 ppm Co, 120

ppm Ni, 200 ppm Sb, 50 ppm Tl and 7 ppm Hg (Oudin, 1987; Laurila et al., 2014a; Supplementary Data Table 1).

In the present sample set, Au correlates well with Cu (Fig. 9a), and also appears to correlate with Zn, apart from samples with < 1 ppm Au (Fig. 9b). This suggests that the gold is associated with chalcopyrite and sphalerite, although it is not necessarily hosted solely by these sulphides. Overall, gold correlates positively with total sulphur (not shown); samples consisting mainly of Fe oxyhydroxides contain low Au (<1 ppm) (Fig. 9). According to Laurila et al. (2014a, 2015), Au shows a general association with Cu-Zn and Fe sulphides in vent-proximal sediments, and is also enriched (together with As) in diagenetic pyrite in distal sediments. Silver correlates best with Cu (Fig. 9c), whereas Cd correlates strongly with Zn (Fig. 9d).

Although not shown, moderate positive correlations also exist between the following metal pairs: Ag–Pb, Ag–Zn, Co–Cu, Sb–Cu, and U–Fe. Silver therefore is associated with all three sulphides (Cu–Pb–Zn), whereas Sb and Co are mainly associated with Cu sulphide. Similar correlations were found by Laurila et al. (2014a), who considered all of these metals to be dominantly hydrothermal in origin, with the exception of U. The U–Fe correlation results mainly from the absorption of seawater U by hydrothermal Fe-bearing oxyhydroxides, as originally proposed by Ku (1969). According to Laurila et al. (2014a), Ni, Cr and V (not shown here) are associated mainly with diagenetic pyrite, are largely of non-hydrothermal origin, and were mainly sourced from, respectively, biological material, detrital siliciclastics, and seawater.

In the present sample set, the bulk-sediment ratio of Ag to Au is about 40, similar to the average value of 50 reported by Oudin (1987), while the ratios of Zn to Cd, and Pb to Ag, are about 330 and 10, respectively. As noted above, trace metals correlate mainly with the proportion of Cu–Zn–Pb sulphides, which formed either as primary precipitates on the seafloor or during early diagenesis (Oudin, 1987; Laurila et al., 2014a). Metals initially brought into the Atlantis II Deep by hot saline fluids can be precipitated in the lower brine layer either as sulphides, or by absorption onto Si-Fe-OOH particles. During burial, metals associated with the Si-Fe-OOH particles are released and incorporated into diagenetic sulphides (Anschutz et al.,

487 2000; Laurila et al., 2014a). Possible sources of metals (basaltic crust, continental detritus,

488 evaporites) are discussed in Sections 2.5 and 5.2, where Nd-Sr-Pb isotopic data are assessed.

489

490 2.4. Rare-earth elements

491

492 The REE contents of 39 samples of metalliferous sediment from the Southwest and West basins

493 of the Atlantis II Deep are given in Table 2. Shale-normalized REE patterns are nearly flat or

494 slightly depleted in the light REE, and display moderate to large positive Eu anomalies (2–4 and

495 4–7, respectively; Figs. 10, 11); the Eu anomaly is defined as Eu_N/Eu_N^*, where Eu_N^* =

496 $(Sm_N^*Gd_N)^{0.5}$ and N is the shale-normalized value. Total REE contents are very low, ranging

497 from 2–20 ppm for most samples. Exceptions are three anhydrite-rich layers with < 2 ppm

498 ∑REE, and three siliciclastic-bearing sediments with 24–112 ppm ∑REE. These results are

499 broadly similar to those previously reported for metalliferous sediments in various parts of the

500 Deep (Courtois and Treuil, 1977; Oudin and Cocherie, 1988; Cocherie et al., 1994; Laurila et al.,

501 2014b). One difference, however, is the presence, in the data sets of Oudin and Cocherie (1988)

502 and Cocherie et al. (1994), of several samples with high contents of P_2O_5 and REEs (up to 1.8 wt

503 % P_2O_5 and 1000 ppm ∑REE). This association was ascribed to the presence of phosphatic fish

504 debris that had scavenged REEs from hydrothermal fluids after deposition on the floor of the

505 Deep (Oudin and Cocherie, 1988). Although our study lacks P_2O_5 data, most of the 100 samples

506 reported by Laurila et al. (2014b) contained only 0.1–0.5 wt % P_2O_5 (maximum of 0.77 wt %

507 P_2O_5). As shown by Laurila et al. (2014b), variations in REE abundances are instead largely due

508 to the amount of siliciclastic material in each sample (cf. Fig. 8c), whereas variations in the Eu

509 anomaly reflect the chemical state of the brine from which the metalliferous particulates

510 precipitated.

511

512 Figure 10 shows shale-normalized REE patterns for samples from different depths and chemical

513 facies in a single core (274). Also shown for comparison are data for three types of vent fluids

514 from the Mid-Atlantic Ridge (after Bau and Dulski, 1999). Large positive Eu anomalies and low

515 La/Yb ratios are typical of high-temperature vent fluids from various types of spreading ridges

516 (Michard and Albarede, 1986; Mitra et al., 1994). In Fig. 10, four of the five sediment samples in

517 Core 274 have nearly flat REE patterns with moderate positive Eu anomalies, differing only in

518   absolute contents of REEs. The exception is a near-surface sample (depth of 1.0 m), which has

519   the highest content of REEs, and also the smallest positive Eu anomaly. These features suggest

520   that the shallow sample at 1.0 m depth is enriched in detrital material, given that Holocene

521   detritus entering the Red Sea (as aeolian dust) has a high REE content and nearly flat REE

522   pattern (Greaves et al., 1994; Palchan et al., 2013). The REE pattern of the sample at 1.0 m also

523   closely resembles that of biodetrital sediment from a Red Sea core (1016) taken outside of any

524   known deeps (Pierret et al., 2010). Based on the very small Eu anomaly of the sample at 1.0 m,

525   the hydrothermal component is minor.

526

527   The Southwest Basin is considered, on the basis of mineralogy (anhydrite, hematite) and the

528   presence of epigenetic veins and high-temperature fluid inclusions, to be the main site of

529   Holocene hydrothermal input to the Atlantis II Deep (Zierenberg and Shanks, 1983; Ramboz et

530   al., 1988; Laurila et al., 2014a, b). REE patterns for metalliferous sediments from the Southwest

531   Basin are shown in Fig. 11a–d. All patterns but one have a large positive Eu anomaly, and in

532   most cases, show slight depletion in light relative to heavy REEs. The exception is sample 397-4

533   from the eastern part of the Southwest Basin (Fig. 11d). This sample is notably enriched in total

534   REEs due to its high content of aluminosilicate detritus, but still displays a positive Eu anomaly,

535   although not as large as those of the purest metalliferous sediments (see also Fig. 11f).

536

537   Core 436 is located on the eastern side of the West Basin, some 3 km north of the Southwest

538   Basin (Fig. 6). If the main input of hydrothermal fluids in the Atlantis II Deep is in the southern

539   portion of the Southwest Basin, as suggested by metal distribution patterns (Laurila et al.,

540   2014a), then Core 436 would represent the most "distal" site in our sample set. Four samples

541   from depths of about 2.2 to 10.0 m have moderate Eu anomalies (Fig. 11e). These four samples

542   differ significantly in mineralogical composition, but share essentially the same REE pattern,

543   which is similar to the REE pattern of most sediments in the Southwest Basin. Based on Eu

544   anomalies, the hydrothermal signal in the West Basin is, however, weaker.

545

546   The effect of aluminosilicate detritus on the bulk REE patterns of metalliferous sediments in the

547   Atlantis II Deep is shown in Fig. 11f, for samples containing 0.4 to 3.9 wt % Al_2O_3. As the amount

548   of detritus increases, REE patterns are shifted to higher absolute levels, while the positive Eu

549   anomalies become smaller in size. The sample having the highest detrital content shows a

550   minor depletion in light relative to heavy REE. Similar light REE depletion is also seen in sample

551   274-1 (Fig. 10), which contains the largest detrital component in our data set (Al_2O_3 estimated

552   as 7 wt %; see Section 2.5), and in hemipelagic (biodetrital) sediment from the central Red Sea

553   (Pierret et al., 2010). The light REE depletion is presumably due to a small difference in the

554   composition of the aeolian dust entering the Red Sea relative to PAAS (post-Archean Australian

555   shale: Taylor and McLennan, 1985).

556

557   The detrital contribution of REE to the bulk sediment can be calculated using the content of a

558   lithophile element such as Al, Ti, Zr, Th or Sc, and an assumed end-member REE pattern for the

559   detrital component. Laurila et al. (2014b) used the average REE pattern of their most Al-rich

560   samples (ca. 7 wt % Al_2O_3) as a proxy for this component, which when subtracted from the bulk

561   sediment REE pattern should yield an estimate of the 'residual' hydrothermal REE pattern. The

562   calculated hydrothermal REE patterns were generally nearly flat, with Eu anomalies being

563   slightly more positive than those of the bulk metalliferous sediment. However, it is conceivable

564   that the Al-rich samples used by Laurila et al. (2014b) contained a small hydrothermal

565   component, as they were also taken from the Atlantis II Deep. In the present study, a similar

566   approach was adopted, but differed in using the carbonate-free fraction (Al_2O_3 = 13.8 %, $\sum$REE =

567   180 ppm, Nd = 34.4 ppm) of Holocene sediment from Core KL-23 in the northern Red Sea

568   (Palchan et al., 2013) as a proxy for the detrital REE component. The calculated hydrothermal

569   REE patterns (not shown) are flatter than the calculated patterns of Laurila et al. (2014b) but

570   display the same moderate to large positive Eu anomalies. Such calculations are, however, very

571   sensitive to the percentage of detritus in the bulk sediment, and to the REE pattern of this

572   detritus, both of which can only be estimated. Because the metalliferous sediments have very

573   low REE contents to begin with, removal of the estimated detrital REE component can leave

574   residual hydrothermal values that are close to zero or even slightly negative for most of the

575   REEs, thus producing irregular "baselines" to the patterns, although the positive Eu anomalies

576   remain well defined.

577

578   2.5. Nd isotopes

579

580 The Nd isotope ratios of oceanic sediments reflect the relative contributions from old

581 continental detritus (supplied by wind and rivers), young volcanic detritus (oceanic ridges and

582 island arcs), biogenic fallout, and hydrothermal plume-derived authigenic precipitates (mainly

583 Fe-Mn-oxyhydroxides). Biogenic components such as fish debris (Grandjean et al., 1987; Martin

584 and Haley, 2000) and foraminifera (Palmer and Elderfield, 1985) normally carry the Nd isotopic

585 signatures of ambient seawater, and also concentrate Nd relative to its very low levels in

586 ambient seawater. Metalliferous sediments deposited from plumes more than 10 km from

587 ridge-axial vents carry a seawater Nd isotopic signature due to efficient scavenging of REEs

588 from seawater (Halliday et al., 1992). Sediments deposited within 10 kilometres of the vents

589 can, however, contain a small component of basaltic-hydrothermal Nd (German et al., 1993;

590 Chavagnac et al., 2006; Sun et al., 2018).

591

592 Potential sources of Nd in the metalliferous sediments of the Atlantis II Deep include underlying

593 basaltic oceanic crust, flanking Miocene siliciclastic rocks and evaporites, and Pliocene–

594 Pleistocene hemipelagic sediments that overlie the Miocene sequence (Fig. 3). Literature data

595 on the Nd isotopic ratios and Nd contents of various potential source rocks and hydrothermal

596 fluids are presented and discussed in more detail, together with analogous data for Sr and Pb,

597 in Section 5.2, below). The brine layers within the Atlantis II Deep from which the chemical

598 sediments precipitated exhibit rather low and stable temperatures (currently 44°C to 68°C;

599 Anschutz, 2015). However, the fluids that brought metals and Nd into the basin may have

600 reached temperatures of 300°C, based on fluid inclusion data for veins that cut the

601 metalliferous sediments of the Southwest Basin (Ramboz et al., 1988).

602

603 As a first approximation, we assume that the Nd in the metalliferous sediments is derived from

604 mixtures of leached radiogenic basalt on the one hand, and unradiogenic terrigenous material

605 and/or seawater on the other. Given that high-temperature fluids venting at spreading ridges

606 have essentially the same εNd values as underlying basalts (Hegner and Tatsumoto, 1987;

607 Hinkley and Tatsumoto, 1987), we use an εNd value of +9.7 for our hydrothermal end-member,

608 based on the average value for two basalts from the Atlantis II Deep at 21.4°N (Volker et al.,

609 1993). For comparison, seven basalts from the axis of the central to northern Red Sea

610 (18.15°N–25.55°N) have an average εNd value of +8.4, and a layer of basaltic glass in a

611 sediment core from the Shaban Deep in the northern Red Sea (26°N; Fig. 2a) has a value of +8.5

612 (Cocherie et al., 1994). The εNd value of +9.7 is preferred here for the hydrothermal end-

613 member as it leads to a more conservative estimate of the proportion of basaltic Nd in the

614 Atlantis II metalliferous sediments.

615

616 Unradiogenic Nd could, in theory, be contributed to the metalliferous sediments of the Atlantis

617 II Deep by the hemipelagic sediment that slowly accumulates throughout the Red Sea. This

618 hemipelagic sediment includes both fine-grained terrigenous material (aeolian dust) and

619 biogenic grains such as planktonic tests and fish teeth (Arz et al., 2003; Coulibaly et al., 2006).

620 Biogenic material initially concentrates Nd relative to seawater levels but maintains the Nd

621 isotopic composition of seawater. In the Shaban Deep of the northern Red Sea (Fig. 2a), five

622 samples from a "biodetrital" sediment core have an average εNd value of -4.9 ± 0.2 which is

623 thought to be representative of average seawater in that region (Cocherie et al., 1994).

624 Terrigenous dust settling into northern Red Sea sediments over the last 10 kyr has a similar Nd

625 isotopic composition, with an average εNd value of -5.8 (Palchan et al., 2013). We have

626 therefore used an intermediate εNd value of -5.3 as the unradiogenic end-member for the

627 Atlantis II Deep mixing model. The εNd value of normal Red Sea water has not been measured

628 directly, but eastern Mediterranean seawater at various depths has εNd values of -7 to -6 (Frost

629 et al., 1986; Tachikawa et al., 2004). The use of an εNd value of -5.3 for the unradiogenic end-

630 member, rather than a more negative number, leads to more conservative estimates of the

631 percentage of basaltic Nd in the metalliferous sediments in the mixing model discussed below.

632

633 In the present study, 14 samples of metalliferous sediment from the Atlantis II Deep have εNd

634 values of -2.7 to +0.1 (Table 3). Ten of these samples show a restricted range of values from -

635 2.24 to -1.48. Based on a simple two-phase mixing model between basaltic-hydrothermal and

636 terrigenous/seawater end-members, the metalliferous sediments contain 17–36 % basaltic-

637 hydrothermal Nd (Table 3). The remaining 64–83 % Nd is probably contributed mainly by

638 terrigenous material (as the Nd content of normal seawater is orders of magnitude lower).

639 Assuming that the 0.5–1.0 wt % Al_2O_3 content of the purest metalliferous sediments is due

640 entirely to a component of siliciclastic detritus containing 13.8 % Al_2O_3 and 36 ppm Nd (5–6 ka

641 dust: Palchan et al., 2013), this component could contribute about 1.3 to 2.6 ppm Nd to the

642 bulk sediment, or 40–100 % of the total Nd (based on Nd data from the present study; and

643 Laurila, 2015). Thus, even a small terrigenous (dust) component within the metalliferous

644 sediments can adequately account for the appreciable unradiogenic component implied by the

645 εNd mixing model.

646

647 The terrigenous component must mix with a low-Nd hydrothermal component having εNd

648 values in the -2 to +2 range in order to produce the εNd values and Nd concentrations observed

649 in the bulk metalliferous sediments. The low-Nd hydrothermal component could be produced

650 by mixing between high-temperature fluid having a basaltic εNd value (e.g., +9) and much

651 lower-temperature seawater or brine having an εNd value of about -5. Unfortunately, there are

652 no data on the Nd contents of hydrothermal fluids or brines in the Atlantis II Deep, although

653 even high-temperature fluids at vent sites on open-ocean ridges have very low Nd contents of

654 <0.01 ppm (lower-temperature fluids would contain even less Nd). Thus, the metalliferous

655 precipitates must concentrate Nd by a few orders of magnitude relative to the source

656 hydrothermal fluid (which itself contains both basaltic and seawater Nd). In theory, absorption

657 of Nd by precipitates could occur either in the brine pool or shortly after their deposition on the

658 seafloor. Mixing of a small component of terrigenous dust with the precipitates then produces

659 an εNd trend towards the terrigenous dust. Although unmodified seawater in theory could

660 contribute some Nd to the metalliferous precipitates, seawater Nd would have an εNd value

661 similar to that of detritus entering the Red Sea, and therefore would not be isotopically

662 distinguishable from the Nd contributed by the detritus.

663

664 The ten samples of metalliferous sediment having εNd values of -2.24 to -1.48 all show

665 moderate to large, positive Eu anomalies (Fig. 12), even though they contain only 20–25 %

666 basaltic Nd according to the simple mixing model. The ten samples represent various chemical

667 facies of metalliferous sediment (given in Table 3). Three samples from depths of 1.0 to 9.5 m in

668 Core 274 (Southwest Basin) have εNd values of -2.48 to -1.76 (Fig. 13a, Table 3), with the

669 shallowest sample having the most negative εNd value. This sample appears to have the

670 highest terrigenous content in the entire data set (ca. 7 wt % Al_2O_3, and based on Zr and Th

671 contents and their positive correlations with Al_2O_3 in the overall data set; Supplementary Data

672   Table 1). Nonetheless, this sample still contains 19 % basaltic-hydrothermal Nd based on our

673   simple mixing model.

674

675   The two highest εNd values in the data set (+0.12 and -0.68) are for mineralogically distinct

676   samples dominated by anhydrite and talc, respectively (Fig. 13b; Table 3). Based on the mixing

677   model, these two samples contain the highest proportion of basaltic-hydrothermal Nd (31–36

678   %). The increased basaltic-hydrothermal component conceivably could be caused by a later

679   phase of much hotter fluid passing through the sediment. Anhydrite and talc occur sporadically

680   within the Southwest Basin as veins and as replacements within the metalliferous sediments

681   and are inferred to have formed from high-temperature fluids (Zierenberg and Shanks, 1983;

682   Oudin et al., 1984; Ramboz et al., 1988).

683

684   The magnitude of the positive Eu anomaly in the metalliferous sediments generally increases as

685   the inferred component of basaltic-hydrothermal Nd increases (Fig. 14). However, several

686   samples show little correlation. A strict correlation is not expected, as the height of the Eu

687   anomaly also depends on the level of the flanking REEs – an increase in the proportion of

688   siliciclastic detritus in the bulk sediment will raise the "background" REE values, and thus

689   decrease the relative height of the Eu anomaly. This effect, however, is probably minor in most

690   of the metalliferous sediments, as their contents of detritus are uniformly low (<2 wt % Al_2O_3).

691

692   Two biodetrital-rich samples, one from outside the Atlantis II Deep, have Eu anomalies close to

693   that of seawater (small blue-filled squares in Fig. 14), but contain about 15 % basaltic Nd,

694   presumably due to a small metalliferous component. One of these samples (KS-01: 604 cm) is

695   from the Shaban Deep and contains goethite, whereas the other (198: 745–750 cm) is from the

696   detrital-oxide-pyrite facies of the Atlantis II Deep (Cocherie et al., 1994). The lack of positive Eu

697   anomalies in these two samples suggests that the metalliferous component precipitated from

698   relatively oxidizing brines, consistent with their overall mineralogy.

699

700   Two samples from the Atlantis II Deep with high contents of phosphatic fish debris (Cocherie et

701   al., 1994) plot well to the right of the general metalliferous sediment trend in Fig. 14. Oudin and

702   Cocherie (1988) and Cocherie et al. (1994) have shown that where phosphatic fish debris is

703   present in the sediments, it can preferentially scavenge REEs from hydrothermal fluids in

704   porewaters or overlying brine, leading to an increase in the proportion of basaltic Nd within the

705   sediments (this process eliminates the original seawater Nd signature of the fish debris).

706

707   In Fig. 15, calculated proportions of basaltic Nd in each metalliferous sediment sample are

708   plotted on a map of the Atlantis II Deep, together with calculated Eu anomalies. Percentages of

709   basaltic Nd are represented by bubble size, and values of Eu anomalies by red numbers (data in

710   Table 3). The samples come from a range of depths (1.0–9.7 m) and represent a variety of ages,

711   although all are younger than 12 ka, apart from one sample from the DOP facies (Core 71). No

712   spatial trend within the basin is obvious in either εNd or Eu anomaly, probably because the

713   samples represent different stratigraphic levels and therefore likely formed under differing

714   conditions of temperature, Eh and basin chemistry. However, it is worth noting that the two

715   samples with the largest basaltic Nd component are from the southern and northern margins of

716   the Southwest Basin (Cores 64 and 367, respectively). A higher proportion of basaltic Nd could

717   conceivably be the result of proximity to a site of hydrothermal discharge. Higher-temperature

718   phases such as talc and hematite have been found in cores from, respectively, the northern and

719   southern margins of the Southwest Basin (Zierenberg and Shanks, 1983), although these phases

720   are not present in the samples mentioned above. The sample with the smallest proportion of

721   basaltic Nd in our data set (Fig. 15) is from the middle of the West Basin (sample 436-6).

722

723   2.6. Other anoxic basins

724

725   Anoxic, brine-filled basins are common on the continental slopes of passive margins, for

726   example the Orca Basin in the northern Gulf of Mexico (Fig. 1), where up to 180 m of low-T (ca.

727   6°C), very saline brine is present at seafloor depths of >2200 m (Shokes et al., 1977; Trabant

728   and Presley, 1978; Sheu and Presley, 1986; Sheu, 1990; Pilcher and Blumstein, 2007; Schijf,

729   2007). Sediments in the Orca Basin consist of laminated carbonaceous muds and siltstones,

730   which contain iron sulphides (Hurtgen et al., 1999; Tribovillard et al., 2008). Brines are anoxic

731   and enriched in Fe and Mn relative to normal bottom waters (Trefry et al., 1984). Where the

732   top of the brine layer intersects the basin margin, additional reddish, Fe-oxide-bearing layers

733   are deposited. As part of the present study, we obtained REE data for three 1-cm-long samples

734   from the top 7 cm of Core 87-G-2 from the margin of the Orca Basin. The samples consisted of

735   dark muds with faint laminations. REE patterns are very close to that of average shale (PAAS),

736   with no Ce or Eu anomalies (data in Table 3). Thus, there is no obvious normal-seawater or

737   volcanic-hydrothermal contribution to the REE signature, which appears to result instead from

738   fine-grained terrigenous detritus (minor organic material is also present), at least in the upper

739   several centimetres of the core.

740

741   Several seafloor deeps in the Mediterranean Sea contain strongly saline, anoxic bottom brines,

742   some of which, e.g the Bannock, Tyro and Urania Basins, contain significant amounts of H_2S and

743   thus are euxinic brines (Luther et al., 1990; De Lange et al., 1990; Cita, 1991; Vengosh et al.,

744   1999). In the Bannock Basin (Fig. 1), the brine layer is some 450 m thick and has a temperature

745   of 14–15°C. There is no evidence of volcanism in the region. Normal seawater above the

746   Bannock brine layer shows a large negative Ce anomaly, as expected, but the brine itself carries

747   a positive Ce anomaly (Schijf et al., 1995). Interestingly, the brine, although reduced, lacks a

748   positive Eu anomaly (which is also the case for the Orca Basin brine). This suggests that even in

749   euxinic brines, a positive Eu anomaly is not generated unless there has been some input of a

750   hydrothermal fluid that previously reacted with volcanic basement – as for example in the

751   Atlantis II Deep. To our knowledge, no REE data have been reported as yet for the sediments of

752   the Bannock, Tyro and Urania Basins.

753

754   In the Thetis Deep of the Red Sea (location in Fig. 1a), the upper 1 m of metalliferous

755   sediments, which consist mainly of Fe-oxyhydroxides, have strong positive Eu anomalies

756   (Butuzova and Lyapunov, 1995; Pierret et al., 2010). However, there is no brine within this

757   deep, only normal seawater. The chemical precipitates (and the positive Eu anomalies) of the

758   Thetis Deep are interpreted to result from the rapid cooling of hydrothermal fluids that

759   discharged into a topographic low and mixed with seawater (Pierret et al., 2010). In the Kebrit

760   Deep of the Red Sea (Fig. 1a), small massive sulphide chimneys with common bituminous

761   impregnations have been recovered by dredging; these lie within a low-temperature, H_2S-

762   bearing brine layer (Blum and Puchelt, 1991). Occasional limonite-rich sediment layers are also

763   present within cored, near-surface hemipelagic sediments of this deep (Botz et al., 2007). No

764   REE data, or Nd-Sr-Pb isotopic data, have been reported from the Kebrit Deep.

765

3. Metalliferous Sediments in Open Ocean Basins – East Pacific Rise DSDP Leg 92 Transect

3.1. Tectonic setting and stratigraphy

768

DSDP Leg 92 drilled at four main locations to the west of the EPR (Figs. 1, 16; Sites 597 – 602).

At these sites, Fe-Mn-oxyhydroxide-bearing, nannofossil oozes up to 50 m thick lie on basaltic

crust ranging in age from 28 Ma to 3 Ma (Rea and Leinen, 1986). The metalliferous component

of the sediments consists of fine particulates supplied by dilute hydrothermal plumes that drift

westwards from the EPR for up to a few thousand kilometres (Lupton and Craig, 1981; Baker et

al. 1995; Resling et al., 2015; Fitzsimmons et al., 2017). As the metalliferous sediments are

buried, the Fe-Mn-oxyhydroxides are diagenetically transformed to goethite and minor clay

minerals (Kastner, 1986; Poulton and Canfield, 2006). There is no evidence for diagenetic loss of

Mn (or P) from the sediments with burial (Lyle, 1986; Poulton and Canfield, 2006). Simplified

stratigraphic columns for the four Leg 92 holes are shown in Fig. 17, together with locations of

the samples analysed in the present study. Detailed stratigraphic and sedimentological features

of the Leg 92 drill cores are given in Leinen, Rea et al. (1986). Colour photographs of all cores

are available at http://deepseadrilling.org/cores/leg092/.

782

Although the sampled Leg 92 metalliferous sediments range in age from about 27 Ma to 0–2

Ma, each sample was initially deposited at surface. The deepest samples in each hole were

deposited closest to the axis of the EPR, with the shallowest samples deposited farthest from

the axis. The age of the lowest sediment in each of the sampled holes corresponds to, or is

slightly younger than the time at which the underlying basaltic crust was generated at the EPR

axis. Upward changes in chemical composition in each hole reflect continuous plate motion

away from the East Pacific Rise (Rea and Leinen, 1986; Lyle, 1986). With increasing distance

from the axis, the proportion of laterally drifting hydrothermal precipitates that settle into the

sediment will change, as will the proportion of biogenic tests, the latter varying according to

surface productivity as well as depth of the seafloor relative to the lysocline. One of the major

chemical changes that occurs upsection in Leg 92 metalliferous sediment (i.e., with increasing

794 palaeo-distance from the ridge axis) is an increase in the Fe/Mn ratio at about 200–300 km

795 from the axis; this is attributed to a relative decrease in Mn as a result of chemical and

796 sedimentation processes in the more ridge-proximal part of the plume (Lyle, 1986; Marchig and

797 Erzinger, 1986).

798

799 Major- and trace-element data for Leg 92 sediments are presented in Supplementary Data

800 Table 2; REE data are listed in Table 4. Due to the large component of biogenic carbonate in

801 these sediments (78–97%, Barrett et al., 1987), all analyses are reported here on a carbonate-

802 free basis. Although this carbonate-free residue is mainly composed of metalliferous sediment

803 (Fe-Mn oxyhydroxides), a minor terrigenous component is also present in the form of aeolian

804 dust derived from South America (Rea and Leinen, 1986).

805

806 Previous chemical studies of the Leg 92 sediments, including REEs, have been carried out by

807 Lyle (1986), Marchig and Erzinger (1986), Ruhlin and Owen (1986), and Barrett and Jarvis

808 (1988). The REE analyses in Table 4 of the present paper are for a different set of samples than

809 those reported by Barrett and Jarvis (1988), but cover the same range of lithologies. Nd-

810 isotopic data for the Leg 92 sediments have been reported by Halliday et al. (1992), while Pb-Sr-

811 compositions were determined by Barrett et al. (1986, 1987); results are discussed in Sections

812 3.4 and 5.2, respectively.

813

814 The compositional range of the carbonate-free fraction of the Leg 92 metalliferous sediments,

815 in terms of molar proportions of Fe, Mn and Al normalized to 100 %, is shown Fig. 18. Many of

816 the Leg 92 samples cluster around the average value of surface metalliferous sediments on the

817 southern EPR (SEPR: Marchig and Erzinger, 1986). These latter sediments, which come from

818 within 50 km of the spreading axis, can be considered a compositional end-member for

819 precipitates that settle from low-temperature hydrothermal plumes in open oxidized oceans. It

820 is of interest that both the Leg 92 and SEPR metalliferous sediments contain a higher

821 proportion of Mn than sediments derived from the SEPR axial plume, which are dominated by

822 Fe-rich particulates. The "additional" Mn was presumably either adsorbed onto initial Fe-rich

823 particulates within the plume as it drifted westwards, or adsorbed from seawater after the

824 particulates settled to the seafloor.

825

826 Plume particulates along the axis of the northern EPR (NEPR) show a compositional trend

827 extending from an Fe-dominated, SEPR plume-type end-member towards on-axis water column

828 particulates (Fig. 18), the latter representing re-suspended bottom sediments (Sherrell et al.,

829 1999). The on-axis particulates themselves appear to contain a component of normal pelagic

830 clay. All but five of the Leg 92 metalliferous sediments are enriched in Mn relative to the NEPR

831 plume particulate trend. Metalliferous sediments from Leg 92 are also enriched in Mn relative

832 to most metalliferous sediments in the Atlantis II Deep (compare Figs. 18 and 7).

833

834 3.2. Major- and trace-elements

835

836 On a carbonate-free basis, most Leg 92 metalliferous sediments contain 30–50 wt % $Fe_2O_3(t)$,

837 10–18 wt % MnO, and <2.0 wt % Al_2O_3 (Supplementary data Table 2). Similar abundance levels

838 were reported by Marchig and Erzinger (1986) for the "lower" portions of the Leg 92 holes, and

839 also for a transect of surficial metalliferous sediments up to 50 km from the crest of the EPR at

840 about 18.5°S (GEOMETEP cores: see also Marchig and Gundlach, 1982). Plots of $Fe_2O_3(t)$ vs

841 MnO, and Al_2O_3 vs. $Fe_2O_3(t)$ are shown in Fig. 19a and b, respectively. There is no obvious

842 correlation between Fe and Mn, or between Fe and Al. Two subsets of samples plot away from

843 the main group: (1) several near-surface, sub-lysocline sediments that are low in MnO (5.5–7.5

844 wt %) but high in Al_2O_3 (3.2–7.4 wt %); the latter feature is attributed to an increased

845 proportion of terrigenous detritus; and (2) several near-basement sediments from Site 597 with

846 elevated Al_2O_3 contents (3–4 wt %) that are mainly due to a component of intermixed basaltic

847 detritus (as recorded in shipboard logs). Most Leg 92 metalliferous sediments contain only 5–10

848 wt % SiO_2 on a carbonate-free basis, with the exception of a few near-surface samples and the

849 Site 597 near-basement samples mentioned above. This indicates that phases such as Fe

850 smectites and biogenic silica must be only minor components of the metalliferous sediment.

851

852 The contribution of detrital material to the composition of Leg 92 metalliferous sediments can

853 be examined using cross-plots of selected elements versus Al_2O_3. A TiO_2–Al_2O_3 plot (Fig. 19c)

854 suggests that the metalliferous sediments contain both basaltic and terrigenous detrital

855 components, based on the TiO_2/Al_2O_3 ratio of Leg 92 basalt (Erzinger, 1986) and the average

856 TiO$_2$/Al$_2$O$_3$ ratio of pelagic clay (Li and Schoonmaker, 2003). Fe-smectite-bearing metalliferous

857 sediment from the Bauer Basin, shown by the two squares, clearly contains a significant

858 component of terrigenous detritus. In a plot of SiO$_2$ versus Al$_2$O$_3$ (Fig. 19d), by contrast, only

859 one main detrital trend is obvious; departures from this trend are probably due to the presence

860 of 'excess' biogenic silica and/or aeolian quartz.

861

862 The total REE contents of carbonate-free Leg 92 metalliferous sediments (<2.0 wt % Al$_2$O$_3$)

863 range from about 100 to 350 ppm, excluding 3 near-surface sediments (Table 4). Similar levels

864 of REE were reported for a different set of samples by Ruhlin and Owen (1986). Total REEs

865 show no obvious correlation with P$_2$O$_5$ (Fig. 20a), or Fe$_2$O$_3$(t) (Fig. 20b). Based on a strong

866 positive correlation with Ca (not shown), P mainly resides in apatite, which in deep-sea

867 sediments is derived chiefly from fish debris (although P can also be adsorbed from seawater by

868 Fe-rich plume particulates: Feely et al., 1998). Biogenic apatite can also absorb large amounts

869 of REEs from bottom waters after settling on the seafloor, especially if sedimentation rates are

870 low (Dubinin and Sval'nov, 2001). However, the lack of correlation between total REEs and P$_2$O$_5$

871 in the metalliferous sediments (apart from three samples discussed below) suggests that the

872 abundance of biogenic apatite does not control the final REE content of the sediment. It may be

873 that the length of time during which the apatite was in contact with REE-bearing porewaters is

874 a more important control. The abundance of Fe$_2$O$_3$(t) also does not seem to determine the

875 total REE content of the metalliferous sediment (Fig. 20b). This suggests that detrital material is

876 the main source of REEs in the metalliferous sediments. As discussed in Section 3.3, seawater

877 has also contributed some REEs to the metalliferous component of the sediment.

878

879 Three near-surface sediments from Leg 92 (Fig. 20) with notably higher REE contents than the

880 main metalliferous group (800–1300 ppm vs. 100–350 ppm) also contain a larger detrital

881 component (4.7–7.4 wt % Al$_2$O$_3$) and a larger phosphatic component (3.0–3.2 wt % P$_2$O$_5$).

882 These three samples, which are from depths of 0.7 to 5.2 m at Site 598, accumulated slowly as

883 a result of being deposited at or below the lysocline (Rea and Leinen, 1986). This allowed more

884 time for detrital aluminosilicates, authigenic phosphate and fish debris to accumulate. These

885 three samples are also elevated in Zr (250–470 ppm) relative to the main group of metalliferous

886 sediments (40–90 ppm), and relative to terrigenous material as represented by average shale

887 (which could supply up to 100 ppm Zr in the highest-Al sample). The excess Zr in these three

888 samples could conceivably be due to post-depositional absorption of Zr from porewaters by the

889 phosphatic component of the sediment (cf. Tlig et al., 1987; Oudin and Cocherie, 1988).

890

891 On a carbonate-free basis, most of the Leg 92 metalliferous sediments have much lower

892 contents of metals (Cu = 1000–2000 ppm, Zn = 500–1500 ppm, Pb = 50–150 ppm, As = 300–500

893 ppm, Au = 5–50 ppb, Ag = 2–50 ppm) than those of the Atlantis II Deep (Supplementary Data

894 Tables 1 and 2). Exceptions are: (i) Mo, which is enriched in most of the Leg 92 sediments

895 relative to typical pelagic sediments; and (ii) Ba, Co and Ni, which are enriched in near-surface

896 sediments deposited at or below the lysocline.

897

898 Binary plots involving elements such as Al, Mo, Ba and Co (Fig. 21) can be used to help

899 recognize contributions from detrital, hydrothermal and hydrogenous sources. Leg 92

900 metalliferous sediments contain 50–600 ppm Mo (Fig. 21a), with the four highest values

901 occurring in sediments just above basement basalts at Site 597 (Fig. 21b). These latter Mo

902 values (500–600 ppm) are notably higher than the average of 134 ppm Mo for ridge-proximal

903 metalliferous sediments on the EPR (Marchig and Gundlach, 1982; large red-filled circle in Fig.

904 21a). Some of the Mo in the four near-basement samples could be contributed by hydrogenous

905 Fe-Mn micronodules, which in pure form can contain 300–600 ppm Mo (filled circle with N in

906 Fig. 21a; Dubinin and Sval'nov, 2001; Li and Schoonmaker, 2003). However, Mn micronodules

907 are rare in Leg 92 sediments (Marchig and Erzinger, 1986). The detrital component in these four

908 samples (3–4 % wt Al_2O_3) cannot add more than a few ppm Mo to the sediment, as the Mo

909 contents of pelagic clay and seafloor basalt are ca. 27 ppm and <1 ppm, respectively (Sun and

910 McDonough, 1989; Li and Schoonmaker, 2003). Although Mo can also be enriched in seafloor

911 sediments where porewaters are euxinic and FeS precipitation occurs (Scott and Lyons, 2012),

912 the basal Leg 92 sediments are characterized by oxidized mineral assemblages with low

913 contents of organic carbon (see Site Reports in Leinen, Rea et al., 1986). Thus some input of

914 hydrothermal Mo is required. The five sub-lysocline samples, in contrast to the main group of

915 metalliferous sediments, outline a trend extending from low-Mo pelagic clay towards the ideal

916 Fe-Mn micronodule line (Fig. 21a). The intersection of the two trends suggests that the

917 maximum hydrogenous Mo contribution to the metalliferous sediments is about 250 ppm.

918

919 The vertical distribution of Mo in two of the drillholes (Sites 597 and 599) that reached basaltic

920 basement on Leg 92 is shown in Fig. 21b. Downhole trends in the two holes are similar: high Mo

921 contents (300–600 ppm) in the lowest few metres of sediment above basement, a central

922 interval about 20 m thick with lower Mo values (60–120 ppm), and an upper interval (1–8 m

923 below surface) of moderate Mo values (180–360 ppm). We suggest that the near-basement Mo

924 enrichment results from scavenging of hydrothermal and seawater Mo by Fe-Mn-rich

925 oxyhydroxides that precipitated from a hydrothermal plume close to an axial vent, with the

926 lower Mo values in the central interval of the two holes reflecting deposition from a distal,

927 diluted plume as the sites moved away from the EPR. The moderate Mo values observed in

928 near-surface samples (1–8 m below the seafloor) could be the result of increased amounts of

929 hydrogenous plus detrital material (cf. Fig. 21a), as might be expected when seafloor descends

930 below the lysocline and bulk sedimentation rates become much slower.

931

932 Sub-lysocline sediments are enriched in Ba (0.7–1.1 wt % in 4 of 5 samples) and Co (250–410

933 ppm in 4 of 5 samples) relative to the underlying metalliferous sediments (Fig. 21c). The

934 enrichment in Ba would seem to require the presence of either minor authigenic barite, or Ba

935 substitution in biogenic apatite, although neither phase was specifically reported in the Leg 92

936 shipboard studies (Leinen, Rea et al., 1986). The Co enrichment could be due to the presence of

937 hydrogenous Fe-Mn micronodules (cf. Dubinin and Sval'nov, 2001).

938

939 A plot of ∑REE versus Al_2O_3 (Fig. 21d) suggests that that REE enrichment in the sub-lysocline

940 sediments is partly due to detrital material. This detrital material is of aeolian derivation (Rea

941 and Leinen, 1986). However, shale and pelagic clay contain only 200–250 ppm ∑REE (Li and

942 Schoonmaker, 2003) and therefore a 50 % detrital component (7.5 % Al_2O_3) should only

943 contribute about 100–125 ppm REE to the sediment. Therefore another source of REE must be

944 present in the sub-lysocline sediments, for example biogenic apatite or authigenic Fe-Mn

945 micronodules, which can respectively contain in the order of 5000 and 1000 ppm ∑REE (Dubinin

946 and Sval'nov, 2001).

947

948 3.3. Rare-earth element patterns

REE data for Leg 92 sediments have been reported by Barrett et al. (1986), Ruhlin and Owen (1986) and Owen and Olivarez (1988). The new REE analyses discussed below are for a different set of samples than those reported by Barrett et al. (1986). Shale-normalized REE patterns for the carbonate-free fraction of metalliferous sediments from Sites 599 and 598 are shown in Fig. 22a and b, respectively. Sediments from Site 599 range in age from ≈ 1–8 Ma, whereas those from Site 598 (excluding the three samples from Core 1) range in age from ≈ 11–16 Ma. The Leg 92 REE patterns are closely comparable to those of Eocene – Oligocene metalliferous sediments cored at Sites 573 and 574 of Leg 85 in the central equatorial Pacific (Jarvis, 1985).

Almost all of the Leg 92 metalliferous sediments, regardless of age, share the same basic REE pattern (Fig. 22). This pattern is similar to that of deep Pacific seawater, but with a flatter slope from the middle to heavy REE, especially in the older sediments (compare the ca. 10–17 Ma patterns from Site 598 with the 3.7–8.6 Ma patterns from Site 599). The minor flattening of REE patterns in sediments older than ca. 10 Ma has been ascribed to diagenetic reactions during transformation of Fe-Mn-oxyhydroxides to goethite plus minor Fe-rich smectite and apatite (Barrett and Jarvis, 1988).

Leg 92 metalliferous sediments show a general uphole increase in ∑REE, with near-surface, slowly accumulating sediments in the most axial-distal holes containing the highest abundances of REEs (Ruhlin and Owen, 1986; Owen and Olivarez, 1988). This general upwards trend is the result of two processes affecting surface sediments on the westward-moving plate: (1) as the hydrothermal plume drifts hundreds of kilometres or more from the palaeo-axis, Fe-rich oxyhydroxides within the plume scavenge progressively more REE from seawater before settling to the seafloor; and (2) as the seafloor eventually descends below the lysocline and towards the carbonate compensation depth (CCD), as at Sites 597 and 598, sedimentation rates decrease (Rea and Leinen, 1986); as a result, Fe-oxyhydroxides and biogenic apatite in near-surface sediments are able to more effectively scavenge REEs from seawater and porewaters.

At Site 598, near-surface, sub-lysocline near-surface sediments contain higher proportions of detrital aluminosilicates than underlying metalliferous sediments, which may be the cause of

the slightly flatter REE patterns of the former (the same effect is seen at the top of Site 597: Barrett et al., 1986). Sub-lysocline (and sub-CCD) pelagic sediments, which accumulate very slowly, can also be enriched in phases such as biogenic apatite, authigenic Fe-Mn micronodules and phillipsite (Dubinin and Sval'nov, 2001). Biogenic apatite probably contributes to the elevated REE pattern of the Leg 92 sub-lysocline sediments, as the REE content of this phase can become very high due to post-depositional scavenging of seawater REE (cf. Kon et al., 2014; Liao et al., 2019). The contribution of Fe-Mn micronodules must be minor, as the sediments still retain negative Ce anomalies, whereas micronodules carry positive Ce anomalies (Dubinin and Sval'nov, 2001). Phillipsite, an authigenic Al-silicate, contains low levels of REE (Dubinin, 2000) and therefore cannot be the cause of the REE enrichment in sub-lysocline sediments.

The relationships between Fe, P and REE metalliferous sediments in the eastern South Pacific Ocean have been examined by Kashiwabara et al. (2018), who concluded that after an initial period of scavenging of REEs from seawater by hydrothermal Fe-Mn oxyhydroxides, the REEs were transferred to authigenic apatite during early diagenesis under oxic conditions. These authors also found that biogenic apatite in the form of fish debris is the main host of REE in slowly accumulating, sub-CCD sediments (e.g., those of the central North Pacific Ocean).

3.4. Nd isotopes

The Nd isotopic composition of metalliferous sediments from Site 598 was determined by Halliday et al. (1992), who analysed six samples initially deposited at distances ranging from about 10 to 1000 km from the spreading axis. These samples had near-uniform εNd values of -5.2 to -4.2, reflecting derivation of essentially all of the Nd from Pacific seawater, with no evidence of a basaltic-hydrothermal contribution. This finding is consistent with the seawater-like REE patterns for Site 598 discussed in Section 3.3. Halliday et al. (1992) concluded that any basaltic Nd contained within discharging vent fluids at a spreading axis must be deposited very close to the vents themselves (<10 km from the palaeo-axis for Site 598).

In a study of sediments 2–15 km from a vent site on the Juan de Fuca Ridge, Sun et al. (2018) found that the Fe-Mn oxide fraction, which represents 5–7 % of the bulk sediment, and which

1011 they interpreted as plume-derived, contained 10–20 % of basaltic-hydrothermal Nd, based on

1012 εNd values of -1.6 to -1.0, i.e., somewhat higher than the range of North Pacific Deep Seawater

1013 (-4 to -2). In support of the restriction of dissolved basaltic Nd to the immediate environment of

1014 the ridge axis is Stichel et al.'s (2018) observation that the neutrally buoyant plume above the

1015 TAG hydrothermal field on the Mid-Atlantic Ridge shows only a small increase in εNd (+0.7

1016 units) relative to background deep seawater.

1017

1018 **4. Metalliferous Sediments Near and On Open-Ocean Spreading Axes**

1019 4.1. Near-Axial Locations

1020

1021 Metalliferous sediments can also form in near-axial locations where uprising low-temperature

1022 hydrothermal fluids pass through a thin blanket of pelagic sediment. The best-known example

1023 is the Galapagos hydrothermal mounds field, which overlies young oceanic crust (<600 ka) in

1024 the eastern equatorial Pacific, 18–32 km south of the Galapagos Rift spreading centre (Figs. 1,

1025 23a). In this area, semi-continuous chains of mounds occur above ridge-parallel basement

1026 faults, with individual mounds protruding up to several metres above the sediment cover

1027 (Williams et al., 1979). Piston-core drilling on DSDP Leg 70 determined that the mounds consist

1028 of 10–20 m of nontronite, an Fe^{3+}-rich, Al-poor smectite, interbedded with biogenic ooze,

1029 overlain by a thin surface layer of Mn-oxide-rich crusts and mud (Fig. 23b; Honnorez et al.,

1030 1981). The nontronite commonly occurs as intervals of dark green, unconsolidated granules;

1031 these are separated from cream-coloured biogenic ooze by transitional layers of fine-grained

1032 compact nontronite. Chemical analyses of various types of mounds sediments are given in

1033 Schrader et al. (1980), Barrett and Friedrichsen (1982), Moorby and Cronan (1983), Honnorez et

1034 al. (1983) and McMurtry et al. (1983). Temperatures of nontronite formation are mainly in the

1035 10–40°C range (Barrett and Friedrichsen, 1982; McMurtry et al., 1983). Stratigraphic and

1036 sedimentological descriptions of all Leg 70 drill cores are given by Honnorez, Von Herzen et al.

1037 (1983), with colour photographs available at http://www.deepseadrilling.org/cores/leg070/.

1038

1039 The near-axial nontronite of the Galapagos mounds field is formed as upwelling, Fe^{2+}-bearing

1040 fluids pass through and dissolve much of the biogenic ooze; the dissolved Fe is oxidized and

1041 combines with silica of biogenic and hydrothermal derivation to form an Fe-rich, Al-poor,

1042 hydrous silicate (Honnorez et al., 1981). Although the nontronite is largely authigenic, it is

1043 interlayered with normal pelagic ooze and traditionally has been referred to as a low-

1044 temperature hydrothermal sediment (cf. Honnorez et al., 1981; McMurtry et al., 1983). Locally,

1045 nontronite is exposed on the surface of hydrothermal mounds (Corliss et al., 1978). The general

1046 formula for nontronite can be written as $(Na,K,0.5Ca)_{0.33}Fe^{3+}_2(Si_{3.67},Al_{0.33})_4O_{10}(OH_2)nH_2O)$,

1047 although its composition varies in different seafloor hydrothermal settings (e.g., McMurtry et

1048 al., 1983; Murnane and Clague, 1983; Stoffers et al., 1985; Alt, 1988; Severmann et al., 2004;

1049 Sun et al., 2012; Ta et al., 2017).

1050

1051 Nontronitic sediments and Fe-Mn oxide mud from the Galapagos hydrothermal mounds share

1052 similar REE patterns (Fig. 24; Barrett et al., 1988), but differ from normal seawater (Fig. 22a) in

1053 having flatter slopes from the middle to heavy REE, and notably less negative Ce anomalies. In

1054 the nontronitic sediments, the absolute contents of REE vary considerably. This results from

1055 mass changes in major elements that accompany nontronite growth (cf. Barrett, 1992). Initially,

1056 as biogenic ooze is dissolved by low-temperature fluids, REEs associated with minor detrital

1057 clays (incipient nontronite) are residually concentrated, together with immobile elements such

1058 as Al and Ti, forming dm-thick intervals of transitional nontronite (arrow 1 in Fig. 24). As fluids

1059 continue to pass through the sediment and precipitation of Fe and Si occurs, m-thick intervals

1060 of granular nontronite form; these have very low REE contents owing to the diluting effect of

1061 the added Fe and Si (arrow 2 in Fig. 24). Simultaneously, Al and Ti are also diluted by the added

1062 Fe and Si (Barrett, 1992).

1063

1064 Based on general correlations between total REE, Al and Ti, much of the REE content of the

1065 nontronitic sediments is inherited from the minor component of detrital aluminosilicates

1066 contained within the original biogenic ooze, which provides a shale-like 'baseline' to the REE

1067 patterns. The hydrothermal component of the nontronitic sediment appears to carry a

1068 seawater-like REE signature. The combined components produce a bulk sediment REE pattern

1069 (Fig. 24) having a small negative Ce anomaly, and a somewhat steeper slope from Pr to Lu,

1070 relative to shale. The lack of a positive Eu anomaly suggests that the upwelling fluids that

1071 entered the Galapagos mounds had not previously reacted with basalts at high temperatures.

1072 However, low-temperature interaction likely occurred, as Pb-isotope data indicate that the

1073 nontronite contains variable proportions of basaltic and seawater Pb (Barrett, 1983; Barrett et

1074 al., 1988). The Sr-isotopic composition of the nontronites demonstrates that almost all of the Sr

1075 is seawater-derived (Barrett, 1983).

1076

1077 Nontronite-rich sediments have also been recovered from other open-ocean settings,

1078 commonly seamounts, where they formed mainly at 30–80°C (De Carlo et al., 1983; Murnane

1079 and Clague, 1983; Singer et al., 1984; Alt, 1988; Dekov et al., 2007; Lubetkin et al., 2018). Many

1080 of these nontronite occurrences are found at or near the surface. In such cases, the nontronite

1081 appears to have precipitated directly from diffuse, low-temperature fluids (see also Section

1082 4.2). Nd isotopic data have not been reported for any of these nontronite occurrences, apart

1083 from a sample from the Eolo Seamount in the Mediterranean (Fig. 1), where an εNd value of -

1084 4.5 suggests it contains roughly 30 % local volcanic Nd (Dekov et al., 2007).

1085

4.2. Axial Vent Locations

1086

1088 Nontronite is also found within Fe-oxide-rich sediments of the active TAG hydrothermal field at

1089 26°N on the Mid-Atlantic Ridge (Fig. 1). The nontronite is inferred to form by direct

1090 precipitation from relatively low-temperature fluids (81–96°C) rising through sulphide-rich

1091 mounds (Severmann et al., 2004). The REE patterns of nontronites from both active (TAG)

1092 mounds and nearby inactive (Alvin area) mounds are shown in Fig. 25. Also shown are the REE

1093 patterns of the 'residual' Fe-oxide component of these sediments, calculated from the

1094 difference between bulk sediment and nontronite REE patterns (Severmann et al., 2004).

1095 Nontronite and residual Fe oxide from TAG mounds both carry a hydrothermal signature based

1096 on their large positive Eu anomalies (also a feature of diffuse vent fluids at TAG). At the inactive

1097 Alvin site, nontronite and residual Fe-oxides have notably smaller Eu anomalies, suggesting that

1098 they formed from a hydrothermal fluid that had mixed to a small degree with normal seawater.

1099 The Alvin Fe-oxides additionally display a small negative Ce anomaly (e.g., Fig. 25), consistent

1100 with an even larger seawater component in the precipitating fluid (Severmann et al., 2004).

1101 This type of REE pattern, with a positive Eu anomaly but negative Ce anomaly, has been

1102   reported from the TAG area for vent sulphides (Mills et al., 1993) and Fe-oxide-rich and Mn-

1103   oxide-rich sediments overlying inactive sulphide mounds (Dutrieux, 2020).

1104

1105   REE patterns with positive Eu anomalies but negative Ce anomalies have also been reported

1106   for: (i) carbonate-ooze-rich sediment 2–5 km from the Rainbow vent site at 36°N on the Mid-

1107   Atlantic Ridge (location in Fig. 1; Chavagnac et al., 2005); (2) Fe-oxyhydroxide particulates in

1108   neutrally buoyant plumes at both the TAG and Rainbow sites (German et al., 1990, 1993;

1109   Chavagnac et al., 2005); and (3) low-temperature (30°C) fluids on the Juan de Fuca Ridge (Fig. 1;

1110   Bao et al., 2008). At the TAG site, modelling suggests that sediment REE patterns with small

1111   positive Eu anomalies, but moderately negative Ce anomalies, can be produced by mixing cold

1112   seawater with high-temperature fluids at a ratio of about 1000:1 (German et al., 1990).

1113

1114   Sulphate minerals can also contribute a positive Eu anomaly, provided they are sufficiently

1115   abundant (the REE content of sulphides is very low). Anhydrite with large positive Eu anomalies

1116   is a common mineral in the TAG field on the Mid-Atlantic Ridge (Mills and Elderfield, 1995;

1117   Humphris, 1998) and at 9–10°N on the EPR (Yao et al., 2015). Barite is generally scarce, but has

1118   been reported from 37°N on the Mid-Atlantic Ridge (Langmuir et al., 1997; Dias et al., 2008),

1119   and 49.7°N on the Southern Explorer Ridge in the NE Pacific Ocean (Fig. 1; Barrett et al., 1990).

1120   The Nd isotopic composition of barite-rich sediment at 37°N on the Mid-Atlantic Ridge is close

1121   to that of the associated basalts (Dias et al., 2008).

1122

1123   On the Southern Explorer Ridge, barite forms a component of massive sulphide-sulphate-silica

1124   deposits at the Magic Mountain vent field (Tunnicliffe et al., 1986; Scott et al., 1990). Barite

1125   also occurs as residual sandy material within Fe-oxyhydroxide-rich gossanous sediments

1126   overlying inactive mounds; this barite has a large positive Eu anomaly, but no Ce anomaly

1127   (Barrett et al., 1990). This feature is consistent with the barite originating as a high-temperature

1128   phase that remains in the sediment as a residue after oxidative weathering has converted the

1129   sulphides to Fe-rich oxyhydroxides. Two bulk samples of massive sulphide-sulphate-silica from

1130   the vent field have a moderate positive Eu anomaly, but a moderate negative Ce anomaly (Fig.

1131   26a). These two samples were interpreted by Barrett et al. (1990) to have been deposited from

1132   a roughly 500:1 mixture of normal seawater and high-temperature vent fluid, with the positive

Eu anomaly contributed mainly by the barite, and the negative Ce anomaly by hydrothermal silica (assuming that the silica contains sufficient REEs to impart a seawater-like REE pattern).

Other sulphide-bearing bulk samples in the Southern Explorer Ridge vent field have a negative Ce anomaly, with a small or no Eu anomaly (Fig. 26b), implying that the precipitating fluids were seawater-dominated (Barrett et al., 1990). For these samples, most of the REE content is probably contributed by non-sulphide phases such as sulphates and silica (the REE content of base-metal sulphides is very low). The REE patterns in Fig. 26 differ from that of normal deep seawater, which displays a much steeper slope from Dy to Lu (Fig. 26a). Mixing of hot vent fluids (REE patterns shown in Fig. 10) with normal seawater should act to decrease this slope, while also imparting a positive Eu anomaly to the resulting fluid.

5. Discussion

5.1. Compositional features

The contrasting seafloor settings, REE patterns and Nd-Pb-Sr isotopic ratios of the main types of metalliferous sediment discussed in this paper are summarized in Table 5. Small, closed basins located on a young spreading axis, such as the Red Sea deeps, can become filled with stable, but chemically unusual, brines that undergo little interaction with overlying seawater. As a result, metals delivered by uprising hydrothermal fluids remain within the brines, eventually precipitating to form a variety of metalliferous facies depending upon the prevailing chemical features of the brine. The Atlantis II Deep precipitates are dominated overall by mixtures of Fe-oxyhydroxides, Fe-Si silicates, amorphous compounds, metal sulphides and Ca sulphates. The anoxic nature of the lower brine layer allows metals such as Zn, Cu and Pb to be distributed up to several km from probable vent sites. Where the content of dissolved reduced sulphur in the brine is high, metal sulphides precipitate; if the reduced sulphur content is low, metals carried as chloride complexes may be transported farther from the vent sites, and adsorbed onto precipitating Fe-Si-beating oxyhydroxides (Laurila et al., 2014a). The reduced sulphur is provided dominantly by the hydrothermal brines that enter the Deep; in-situ reduction of

seawater sulphate can only be a minor source of sulphur (Shanks and Bischoff, 1980; Zierenberg and Shanks, 1986). Although hemipelagic biogenic sedimentation takes place throughout the Red Sea, almost no biogenic material (e.g. calcareous and siliceous microfossils) accumulates within the Atlantis II Deep above the lowest DOP facies, and detrital input (aeolian dust) is limited owing to the geographic and climatic features of the central Red Sea and its flanking landmasses.

The Atlantis II Deep deposit is of considerable economic interest as it contains a number of base- and precious-metal-rich intervals, has broad lateral extent, and comprises unlithified sediments that could be recovered from the seafloor relatively easily. Based on data from some 600 Preussag AG drill cores, the Atlantis II Deep was estimated by Barbery et al. (1981) to contain an inferred resource of 89.5 Mt grading 2.06 wt % Zn, 0.44 wt % Cu and 38.4 ppm Ag on a dry, salt-free basis. In a more recent evaluation, the deposit was estimated to contain 3.27–3.75 Mt Zn, 0.74–0.81 Mt Cu, and 6500–7100 t Ag (Bertram, 2011). The gold content has been estimated as 47 tons Au at an average grade of 0.5 g/t Au (Mustafa et al., 1984). At 2016 prices, the in-situ resource had a value of about US$11 billion (Brueckmann et al., 2017). The deposit also contains significant amounts of other metals. For the five chemical facies identified by Laurila et al. (2014a), minimum and maximum average contents of these metals are: Pb (182–1220 ppm), Cd (24–234 ppm), Sb (10–49 ppm), Mo (76–155 ppm) and Hg (484–3700 ppb).

In the Atlantis II Deep, total REE contents of the 'purest' metalliferous sediments (< 2 wt % Al_2O_3) are very low, mostly <25 ppm (Laurila et al., 2014b; this study). In sediments with a substantial detrital component (Al_2O_3 up to 7 wt %), ∑REE can reach 60 ppm. Metalliferous sediments enriched in P_2O_5 (1–2 wt %) can have ∑REE contents as high as 800–3900 ppm (Oudin and Cocherie, 1988). Such P-rich samples appear to be uncommon, however. The high REE contents of the P-rich sediments have been interpreted to be the result of absorption of REEs from hydrothermally influenced porewaters onto biogenic phosphate (fish teeth) following deposition and burial of the phosphate (Cocherie et al., 1994).

Deep-sea pelagic sediments accumulating in open oceans on the broad flanks of spreading ridges typically consist of a dominant biogenic ooze component (carbonate and/or siliceous

1193 tests), with a lesser metalliferous component, and a very minor detrital fraction. The

1194 metalliferous component, which can be isolated by leach treatments, has: (i) high contents of

1195 Fe + Mn, commonly in the form of oxyhydroxides and oxides; (ii) low contents of Al, Ti and Zr,

1196 elements typically associated with detrital material (of continental and/or seafloor basaltic

1197 derivation); and (iii) enrichment of trace metals and REEs relative to normal pelagic sediments.

1198

1199 As a result of the oxidized nature of bottom waters in modern open oceans, metal sulphide

1200 deposition is limited to the immediate vicinity of high-temperature axial vents, either as

1201 massive mounds and chimneys, or as sulphide particulates that settle out of the buoyant plume

1202 (cf. Robb, 2005; Tornos et al., 2015). Most of the precipitates in the buoyant plume are,

1203 however, Fe-oxyhydroxides; minor sulphate phases are also present (Feely et al., 1994b, 1996).

1204 The Fe-rich precipitates of the buoyant plumes contain variable proportions of basalt- and

1205 seawater-derived metals (see Section 5.2). As the plume becomes non-buoyant and is

1206 dispersed by bottom currents over lateral distances up to 4000 km from the source vents

1207 (Resing et al., 2015; Fitzsimmons et al., 2017), trace metals and REEs derived exclusively from

1208 seawater are adsorbed by the Fe-rich precipitates. As these precipitates settle to the seafloor,

1209 they mix with ambient biogenic fallout and siliciclastic detritus (the proportions of which will

1210 depend on latitude, proximity to land, and depth within the ocean basin). Following

1211 sedimentation, the metalliferous component continues to absorb trace metals and REEs from

1212 pore waters (which represent diagenetically modified seawater).

1213

1214 The sediments cored on DSDP Legs 85 and 92 in the eastern Pacific Ocean were deposited

1215 above the CCD and lysocline over much of their history and therefore generally contain a large

1216 component of calcareous ooze. Expressed on a carbonate-free basis, these sediments contain

1217 100–500 ppm each of Cu, Ni, Zn and ∑REE (Jarvis, 1985; Barrett et al., 1988). As such, they are

1218 not likely to be of economic interest. However, in other regions of the Pacific Ocean, especially

1219 those lying below the CCD, REEs and associated high-tech trace metals are sufficiently

1220 concentrated in Mn nodules, Fe-Mn crusts and metalliferous sediments that they are being

1221 considered as future economic resources. (Kato et al., 2011; Hein et al., 2013; Seo et al., 2014;

1222 Nakamura et al., 2015; Iijima et al., 2016; Sa et al., 2018; Takaya et al., 2018; Balaram, 2019;

1223 Maciag and Zawadzki, 2019; Pak et al., 2019). One of the most promising areas in the Japanese

Exclusive Economic Zone, some 1900 km southeast of Tokyo, where deep-sea muds contain

two or three intervals that are very enriched in REE over thicknesses up to 1 m (∑REE contents

reach 5000 ppm). The REE enrichment in this case is due to the presence of biogenic phosphate

debris, which in these slowly accumulating sediments has adsorbed large amounts of REEs from

seawater (Ohta et al., 2016; Yusakawa et al., 2019; Tanaka et al., 2020).

5.2. Nd-Sr-Pb isotopes

The Nd-Pb-Sr isotopic composition of a given sample of deep-sea sediment will depend on the

relative amounts of Nd, Pb and Sr contributed to it by: (1) hydrothermal fluids during

precipitation of the metalliferous phases; (2) locally derived basaltic detritus; (3) continentally

derived clays and dust; and (4) phosphatic fish debris and biogenic tests (especially calcareous

microfossils in the case of Sr). Table 6 provides a compilation of Nd-Pb-Sr isotope ratios and

concentrations in metalliferous sediments and potential sources for both closed-basin and

open-ocean settings. The isotopic ratios of high-temperature fluids discharging from black

smokers indicate that the dissolved Nd-Pb-Sr in these fluids is mainly basalt-derived. However,

mixing of these fluids with seawater in the uprising plume changes the isotopic ratios

dramatically owing to differences in: (i) relative concentrations of Nd-Pb-Sr in vent fluids versus

normal deep seawater (Table 6); and (ii) rates at which various metals and REEs are adsorbed

onto Fe-rich precipitates in the plume.

Lead isotopic data for open-ocean metalliferous sediments show that most of the Pb up to

about 100 km from vents on active ridges has a basaltic source (Bender et al., 1971), with a

small component of basaltic Pb recognisable as far as 1000 km from the ridge (Barrett et al.,

1987). By contrast, the Sr and Nd isotopic compositions of open-ocean metalliferous sediments

such as those cored on Leg 92 indicate that almost all of the Sr and Nd was derived from normal

seawater (Barrett et al., 1987; Halliday et al., 1992); this is also the case for sediments

deposited within a few kilometres of the spreading axis (Chavagnac et al., 2006). In the Bauer

Basin west of the Galapagos Rise (Fig. 1), a hydrogenous-hydrothermal ferromanganese crust

that has grown for 7 Myr contains a significant component of basalt-derived Pb that apparently

1255 was dispersed laterally at least 200 km from the Rise; by contrast the Nd in this crust was

1256 derived from Pacific deep-ocean water (van der Flierdt et al., 2004).

1257

1258 In closed basins with a restricted circulation of bottom waters, such as the Atlantis II Deep, the

1259 situation is different due to the lack of mixing between hydrothermal, basement-derived brines

1260 and overlying, isotopically normal seawater. The brine that enters the Deep from below carries

1261 Pb, Nd and Sr that were derived from the basaltic basement, and possibly also from "old"

1262 seawater trapped within the Miocene evaporitic and Pliocene-Pleistocene hemipelagic

1263 sediments that flank the spreading axis (Fig. 3). The basaltic component is acquired in the

1264 discharge part of the hydrothermal convection cycle as hot brines leach Pb, Nd and Sr from

1265 underlying basalts, whereas the "old" seawater component originates in the recharge part of

1266 the convection cycle, as a result of leaching of sediments (especially evaporites) and mixing

1267 with trapped porewaters by descending Red Sea water (cf. Fig. 3).

1268

1269 Figure 27 summarizes the εNd values of metalliferous sediments from the Red Sea, the eastern

1270 Pacific Ocean and the Mid-Atlantic Ridge, together with comparative data from the literature

1271 on basalts, high-temperature vent fluids, deep seawater, and selected seafloor hydrothermal

1272 deposits. It is worth noting that the εNd values of deep seawater can vary from one ocean basin

1273 to another, and even within basins, due to variations in the average Nd isotopic composition of

1274 detritus entering each basin (cf. van de Flierdt et al., 2016). This point needs to be taken into

1275 account when comparing open-ocean metalliferous sediments on a global scale, but it is

1276 unlikely to be a factor for small basins such as the Atlantis II Deep.

1277

1278 In the Atlantis II Deep, Nd isotopic data for the metalliferous sediments (Cocherie et al., 1994;

1279 this study) suggest that 20–30 % of the Nd is derived from a basaltic source. The remainder of

1280 the Nd in the metalliferous sediments is attributed to Holocene terrigenous detritus (aeolian

1281 dust), although it is conceivable that hydrothermal leaching of the Miocene evaporites and

1282 younger hemipelagic sediments that flank the Deep (Fig. 3) could also introduce unradiogenic

1283 Nd to the brine pool. Unfortunately, the Nd isotopic composition of these flanking sediments is

1284 unknown, although Holocene hemipelagic sediments in the northern Red Sea have an εNd

1285 value of about -6 (Palchan et al., 2013). Low-temperature brine from the Shaban Deep in the

1286 northern Red Sea has an εNd value of -4.5 (Cocherie et al., 1994), although this does not

1287 necessarily represent the composition of Miocene evaporites. Also unknown is the content of

1288 Nd of the hydrothermal (metalliferous) brines that enter the Atlantis II Deep. Thus, the

1289 proportion of Nd in the metalliferous sediments that might have been leached from flanking

1290 sediments (or their porewaters) cannot be determined. However, it may be minor, as the Nd

1291 isotopic composition of the metalliferous sediment can be reasonably accounted for by mixing

1292 between a detrital (aeolian) component that slowly accumulates within the Deep, and a

1293 basaltic-hydrothermal component that is supplied by brines that flow into the Deep. Although

1294 the basaltic-hydrothermal fluid itself could, in theory, contain some Nd derived from Miocene

1295 to Pleistocene seawater, the proportion is not possible to estimate.

1296

1297 Strontium-isotope ratios of both the metalliferous sediments and their porewaters in the

1298 Atlantis II Deep show little variation above the DOP interval (i.e., sediments younger than about

1299 11 ka), and reflect a mixture of seawater-derived Sr and basaltic Sr (Anschutz et al. 1995). The

1300 basaltic Sr component has been estimated as 30 % of the total Sr present in the sediments, the

1301 remainder being derived from the Late Miocene evaporites (Zierenberg and Shanks, 1986). The

1302 fairly limited ranges in Nd and Sr isotopic compositions observed in the metalliferous sediments

1303 suggest that the main brine layer in the Atlantis II Deep has been isotopically near-

1304 homogeneous for much of the Holocene.

1305

1306 Lead-isotope studies of metalliferous sediments in the Red Sea have been made by Dupré et al.

1307 (1988), Bauman (1994) and Pierret et al. (2010). Dupré et al. (1988) concluded that most of the

1308 Pb was not of basaltic derivation, based on isotopic differences with local basalts, whereas

1309 Bauman (1994) suggested that the Pb was basaltic but represented an average of Pb extracted

1310 from regionally isotopically variable basalts. In the study by Pierret et al. (2010), five samples of

1311 metalliferous sediments from the Atlantis II Deep (21.3°N) and four from the Thetis Deep

1312 (22.5°N) shared similar Pb isotopic ratios that could be explained by a dominantly basaltic

1313 source, if the least radiogenic end-member is taken as basalt from the Nereus Deep (23.2°N;

1314 Fig. 2a). However, if basalt from the Atlantis II Deep is taken as the end-member (using data in

1315 Dupré et al., 1988 and Volker et al., 1993), the samples analysed by Pierret et al. (2010) would

1316 instead contain 20–40 % basaltic Pb. In this regard, it is worth noting that basalts located near

1317 hot spots along ridges can have more radiogenic Pb-Sr isotopic compositions than normal

1318 MORBs (Dosso et al., 1999; Ferreira, 2006).

1319

1320 About 20–40 % of the Nd, Sr and Pb in the metalliferous sediments of the Atlantis II Deep

1321 appear to have been derived from a basaltic source. The similar proportions of basaltic

1322 contribution shown by these three elements is likely a coincidence, given the various

1323 components of the hydrothermal system (normal seawater, basalts, evolved brine) would have

1324 varied considerably in terms of their Nd-Sr-Pb concentrations and initial isotopic ratios

1325 (comparative data for different possible sources and fluids are given in Table 6).

1326

1327 5.3. Detrital effects

1328

1329 For metalliferous sediments with low contents of REE, such as those of the Atlantic II Deep and

1330 the Galapagos Hydrothermal Mounds, even a minor siliciclastic component can have a notable

1331 effect on REE patterns and Nd-Sr-Pb isotopic ratios. In the Atlantis II Deep, a 10 % siliciclastic

1332 component could provide as much as three-quarters of the Nd in the bulk sediment. This effect

1333 would result in Nd isotope ratios lying between those of detrital and hydrothermal end-

1334 members, but closer to the former. For Pb, the effect of a 10 % siliciclastic component would be

1335 minor, because it would contribute only about 2 ppm Pb to bulk sediments that contain 10–100

1336 ppm Pb, and locally more (Laurila, 2014a, this study). For Sr, the effect of a 10 % siliciclastic

1337 component would generally be minor, as it would contribute about 30 ppm Sr to bulk

1338 sediments that contain 50–500 ppm Sr (Anschutz et al., 1995).

1339

1340 Ideally, the REE pattern of the siliciclastic component should be subtracted from that of the

1341 bulk metalliferous sediment in order to obtain the true REE pattern of the hydrothermal end-

1342 member precipitate (cf. Laurila et al., 2014a). This is particularly important in metalliferous

1343 sediments where ∑REE <30 ppm, for example those of the Atlantis II Deep (in open-ocean

1344 settings, metalliferous sediments generally contain a few hundred ppm of REE, so the

1345 correction will be minor). In the Atlantis II Deep, removal of the siliciclastic component's

1346 estimated REE pattern can leave a "baseline" metalliferous pattern that, apart from europium,

1347 is close to zero or slightly negative. In such cases, the calculation must be done carefully and

1348 based on accurate data.

1349

1350 5.4. Variations in chemical signatures

1351

1352 At spreading ridges in open, oxidized oceans, the Nd isotope ratios and REE patterns of Fe-

1353 oxyhydroxide precipitates should shift from a dominantly basaltic-hydrothermal signature to a

1354 seawater-like signature within a few kilometres or less of the vents. Relative to high-

1355 temperature vent fluids, the precipitates show a decrease in the proportion of light to heavy

1356 REE, acquisition of a negative Ce anomaly, and loss of the positive Eu anomaly. Depending on

1357 discharge rate and degree of mixing with seawater in the near-vent region, a wide range of

1358 isotopic ratios and REE patterns can be expected in the earliest plume precipitates. As these Fe-

1359 rich precipitates drift away from the vent region, they scavenge Nd, Pb and Sr derived from

1360 normal deep seawater.

1361

1362 The metalliferous sediments that accumulate on the seafloor generally have Nd and Sr isotopic

1363 ratios typical of those of ambient seawater. Biogenic phosphate in the form of fish debris

1364 generally forms a component of the sediments. This phosphate has a seawater Nd-Sr isotope

1365 signature (Grandjean et al., 1987; Martin and Haley, 2000). By contrast, the Pb isotope

1366 composition of surface metalliferous sediments changes with increasing distance from a

1367 spreading ridge, from a mainly basaltic signature acquired at the vent site, to a mainly seawater

1368 signature as Fe-rich precipitates in the plume absorb seawater Pb while drifting up to >1000 km

1369 from the ridge (cf. Barrett et al., 1987). During early burial, metalliferous sediments may also

1370 continue to absorb seawater Nd, Sr and Pb present from pore fluids.

1371

1372 High-temperature vent fluids at open-ocean spreading ridges generally have a large positive Eu

1373 anomaly but lack a negative Ce anomaly. Fe-Mn-oxyhydroxide precipitates in the buoyant

1374 plumes above the ridges can, however, show a negative Ce anomaly as well as a positive Eu

1375 anomaly (Sherrell et al., 1999; Edmonds and German, 2004), as can metalliferous precipitates

1376   settling out from these plumes within a few kilometres of the vents (German et al., 1993;

1377   Chavagnac et al., 1995).

1378

1379   Representative REE patterns for metalliferous sediments in the closed basin of the Atlantis II

1380   Deep are shown in Fig. 28, as well as REE patterns of possible source materials such as

1381   seawater, brine and aeolian dust, and εNd values where available. This diagram emphasises the

1382   much higher contents of REE in Saharan dust (marine clays are similar) relative to fluids such as

1383   seawater, brine and even typical black smokers. Even though biogenic carbonate, like seawater,

1384   carries a negative Ce anomaly, biodetrital sediments in the Red Sea lack a Ce anomaly as a

1385   result of their significant content of siliciclastic detritus, which swamps the seawater signal.

1386   Positive Eu anomalies are present in metalliferous sediments from the brine-filled Atlantis II

1387   Deep. They also characterize the upper metre of metalliferous sediment in the brine-free Thetis

1388   Deep (not shown; Pierret at al., 2010). Outside of the axial deeps, positive Eu anomalies are

1389   absent. In a similar fashion, detrital and biodetrital sediments in the Red Sea have distinctly

1390   negative εNd value, whereas metalliferous sediments in the Atlantis II Deep have εNd values

1391   mainly in the -2 to 0 range, and in the Thetis Deep (not shown), two samples have εNd values of

1392   +3.3 and +3.9.

1393

1394   Representative REE patterns for metalliferous sediments, hydrothermal plumes and seawater

1395   in the eastern Pacific Ocean are shown in Fig. 29. Fe-Mn-oxyhydroxide sediments from the

1396   flanks of the EPR, such as those cored on DSDP Leg 92, have the highest REE contents and large

1397   negative Ce anomalies, as well as distinctly negative εNd values of -5.2 to -4.1. Nontronite and

1398   Mn oxide ooze from the near-axial Galapagos hydrothermal mounds have seawater-like REE

1399   patterns but Ce anomaly is less negative. Plume particles from the EPR at 10°N, which are

1400   mainly Fe-oxyhydroxides, also have a seawater-like REE pattern with a moderately negative Ce

1401   anomaly, whereas plume particles from the MAR at 36°N have an additional positive Eu

1402   anomaly. This combination of a negative Ce anomaly and positive Eu anomaly is also shown by

1403   Fe oxides deposited in the Alvin zone, about 2 km from the TAG vent field on the MAR at 26°N.

1404

1405   Figure 30 schematically outlines the variations in Nd and Sr isotopic composition and REE

1406   patterns of sediments deposited in a range of settings, from open-ocean pelagic (siliciclastic-

1407 dominated Nd-Sr; at top of diagram) to hydrothermally dominated on the axes of spreading

1408 ridges (basalt-influenced Nd-Sr; middle of diagram) to biogenic ooze + plume fallout dominated

1409 on the flanks of spreading ridges (seawater-influenced Nd-Sr; base of diagram). The Nd and Sr

1410 isotopic compositions of various possible source materials are given below the respective

1411 horizontal axes of Fig. 30. Metalliferous sediments deposited on the flanks of the East Pacific

1412 Rise, under oxic conditions, are shown by short, light blue bars, whereas those deposited in the

1413 Atlantis II Deep, under anoxic conditions, are shown by inclined red lines.

1414

1415 5.5. Some comments on ancient chemical sediments

1416

1417 The combination of 'opposing' Ce and Eu anomalies is also found in some Palaeozoic Fe-Si-rich

1418 hydrothermal exhalites associated with volcanogenic massive sulphide (VMS) deposits, for

1419 example, in the Cambrian of Newfoundland (Lode et al., 2016), the Ordovician of Norway

1420 (Grenne and Slack, 2005, 2019) and the Ordovician of New Brunswick (Peter and Goodfellow,

1421 1996). By analogy with modern buoyant plumes, 'opposing' Ce and Eu anomalies in ancient

1422 chemical sediments would imply proximity (less than a few km) to high-temperature vents and

1423 possible massive sulphide deposits, which could be used as an exploration tool. However, other

1424 chemical sediments associated with VMS deposits lack such 'opposing' anomalies, instead

1425 having seawater-like patterns, e.g. the Fe-rich umbers that overlie Cretaceous ophiolites in

1426 Japan (Kato, 2005) and Cyprus (Robertson and Fleet, 1976; Josso, 2017). These umbers

1427 presumably were deposited after high-temperature vent fluids had mixed with sufficient cold

1428 seawater to remove any hydrothermal REE signature. In such cases, the Pb isotopic

1429 composition of Fe-rich sediments overlying ophiolites provides a separate means of assessing

1430 the degree of basaltic-hydrothermal input (Barrett, 1980; Gale et al., 1981), and can potentially

1431 be used as an exploration guide to massive sulphide deposits.

1432

1433 Fe-Si-rich sediments form a major component of Precambrian banded iron formations (BIFs).

1434 The origin of these BIFs, some of which formed during extensive periods of mafic volcanism,

1435 particularly in the 3.0 –1.8 Ga period (Isley and Abbott, 1999), has been much debated over the

1436 last half century, and many questions remain concerning the degree of oxidation of the oceans

and the nature of the BIF-precipitating mechanisms during this period (Bekker et al., 2010; Little et al., 2021). The REE patterns of Archean and Palaeoproterozoic BIFs commonly show positive Eu anomalies, but these anomalies are difficult to interpret in terms of distance from a submarine vent source because ocean basins prior to about 1.8 Ga likely were anoxic over much of the water column, and therefore positive Eu anomalies generally would be expected in chemical sediments deposited across the basins (Kato et al., 1998).

The Nd isotope composition of BIFs prior to about 1.8 Ga is likewise difficult to relate to specific vent areas, as oceans at that time generally contained a significant component of dissolved basaltic Nd due to long-term hydrothermal activity. Thus, the εNd values of Fe-rich precipitates in general were elevated relative to those of modern open oceans, reaching values of 0 to +2 (Jacobsen and Pimentel-Klose, 1988; Derry and Jacobsen, 1990; Bau et al., 1997). In the early Palaeoproterozoic, some parts of the deep ocean may have experienced mild oxidation (Little et al., 2021), and by the Late Palaeoproterozoic, oceans may have been characterized by both deeper anoxic water and shallower oxic water (Poulton et al., 2011; Konhauser et al., 2017). Different facies of BIF therefore would be expected to show a range of Eu anomalies (slightly to strongly positive) and Ce anomalies (positive to negative), as discussed by Plavansky et al. (2010). The possibility that coeval basins in different palaeogeographic settings (back-arc, rifted margin, open ocean) had different redox profiles further complicates interpretation of REE data. These factors need to be considered when using Eu anomalies in Precambrian iron formations as an exploration guide for locating high-temperature seafloor vents and associated massive sulphide deposits.

6. Conclusions

Metalliferous deep-sea sediments show a number of chemical features that reflect the nature of the depositional basin (open oxidized oceans versus small, closed, anoxic basins) and the distance from source hydrothermal vents at which chemical precipitates settle to the seafloor. Open-ocean metalliferous sediments related to hydrothermal plumes at a spreading ridge, such as those in the eastern central Pacific, take the form of Fe-Mn-rich oxyhydroxides, whereas

1467 small anoxic basins such as the Red Sea Atlantis II Deep contain a variety of chemical facies that

1468 are enriched in either Fe-oxyhydroxides, Fe-Si clays, base-metal sulphides, Mn

1469 oxides/carbonates, or sulphates. Nd-Sr-Pb isotopic signatures also differ, with closed-basin

1470 sediments preserving a modest but distinct contribution of basaltic Nd, Sr and Pb, whereas

1471 open-ocean sediments show normal seawater Nd and Sr isotopic signatures, although they can

1472 commonly contain a component of basaltic Pb, even at distances of a thousand kilometres from

1473 the hydrothermal source.

1474

1475 The REE patterns of metalliferous sediments in closed basins should retain the positive Eu

1476 anomalies of the high-temperature fluids that enter the basin, owing to the anoxic state of the

1477 pooled brines, which allows Eu to remain in the reduced state and be dispersed laterally. By

1478 contrast, the REE patterns of metalliferous precipitates deposited from non-buoyant plumes in

1479 modern open oceans are seawater-like, with a negative Ce anomaly with no Eu anomaly.

1480

1481 Low-temperature Fe-oxyhydroxide sediments formed on and near sulphide mounds on open-

1482 ocean spreading axes can simultaneously show positive Eu and negative Ce anomalies, implying

1483 precipitation from mixtures of high-temperature vent fluid and normal seawater. Metalliferous

1484 sediments can also form in off-axis settings where low-temperature fluids migrate up through

1485 seafloor sediments and react to deposit Fe-silicates, Fe-oxyhydroxides, and locally Mn-oxides,

1486 e.g., the Galapagos hydrothermal mounds. These off-axis deposits display seawater-like REE

1487 patterns and Nd-Sr isotope signatures, but typically contain some basaltic-hydrothermal Pb.

1488

1489 Metalliferous sediments in closed anoxic basins such as the Atlantis II Deep can host significant

1490 quantities of base and precious metals where the basins are spatially associated with a heat

1491 source that produces hydrothermal activity over thousands of years. In such basins, most of the

1492 hydrothermally supplied metals are deposited within the confines of the basin, largely as

1493 sulphide-rich muds, Fe-oxyhydroxides and Fe-silicates. In open ocean settings, most of the

1494 metals supplied by axial vents are dispersed laterally as Fe-Mn-oxyhydroxide particulates over a

1495 few thousand kilometres by low-density plumes. Although these particulates absorb some

1496 metals and REEs from seawater during transport and early burial, the metalliferous component

1497 of the final sediment on the seafloor is generally minor owing to dilution by large admixtures of

biogenic carbonate and/or silica. However, in those parts of the deep ocean that lie below the CCD, where accumulations rates are very slow, seawater-derived REEs in particular can become sufficiently concentrated as to represent a potential economic resource.

6. Contributions of Authors

TJB: project design, collection of samples from Atlantis II Deep and DSDP Leg 92; writing of bulk of paper and compilation of data. IJ: REE analysis of Atlantis II Deep sediments. MDH: chemical analysis of Leg 92 sediments. MFT: Nd isotope analysis of Atlantis II Deep sediments. IJ, MDH and MFT also contributed to writing of specific sections of the paper. IJ produced the final versions of the figures.

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2409 **Tables in Paper**

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Fig. 1.   Location of study sites. Red-filled circles are main study localities; yellow-filled circles are other key sites providing comparative literature data. NEPR is northern East Pacific Rise, SEPR is southern East Pacific Rise, TAG is Trans-Atlantic Geotraverse hydrothermal field on Mid-Atlantic Ridge. Base map from GEBCO (2020).

Fig. 2.   Location and bathymetry of the Red Sea Atlantis II Deep. (a) Map indicating positions of major deeps along spreading axis of the Red Sea; inset shows bounding tectonic plates and opening directions (modified from Encyclopædia Britannica, 2011). The Atlantis II Deep is marked by the yellow arrow. (b) Bathymetric map of central Red Sea showing Atlantis II Deep and nearby Chain Deeps and Discovery Deep (modified from Augustin et al., 2016); yellow-filled circles locate sediment cores sampled in present study (Table 1); colour codes give depth below sea-level in metres.

Fig. 3.   Schematic cross-section of Atlantis II Deep showing brine layers and geological setting. Note basalt below Deep, flanking Miocene evaporites, and Pliocene–Pleistocene hemipelagic sediments. Compiled from Bäcker (1973), Laurila et al. (2014a) and Schardt (2016). Brine temperatures after Swift et al. (2012).

Fig. 4.   Schematic summary of metalliferous sediment facies in Atlantis II Deep showing generalized column on left side and Southwest Basin column on right side (modified from Laurila (2015), based on Bäcker and Richter (1973)'s classification of lithological units). Core lengths are typically 10–15 m, rarely reaching 20 m. The base of unit SU1 in the general column has an age of ca. 12 ka, yielding high sedimentation rates of >1 m/kyr for overlying sediment units. Most samples in present study are from units CO, SU2 and SAM in the Southwest Basin.

Fig. 5.   Core photographs of metalliferous sediments from the Atlantis II Deep. A selection of units and facies (Fig. 4) are illustrated (core photographs from Laurila et al., 2015). (A) Unit COS: top part mainly green clays; lower part mainly Fe oxyhydroxides. (B) Unit CO: Si-Fe-oxyhydroxides with layers of hydrothermal carbonate and Mn-oxyhydroxide; white layer (arrowed) consists of detrital silicates + biogenic calcite. (C) Unit OAN: red Fe-oxyhydroxide, and grey anhydrite-rich layers and subvertical veins (arrowed). (D) Unit AM with diffuse lamination (unit SU2 occurs below arrowed orange band). Scale bars = 2 cm.

Fig. 6. Bathymetric map and basins of Atlantis II Deep and nearby deeps, showing locations of cores sampled in present study (red-filled circles with core numbers). Contours show depths below sea-level in metres. 2000 m isobath corresponds to top of present-day brine-filled deep. Modified from Anschultz (2015).

Fig. 7. Composition of metalliferous sediments from Atlantis II Deep plotted as molar proportions of Fe–Mn–Al. Shown for comparison are compositions of axial southern EPR (SEPR) metalliferous sediment (Marchig and Erzinger, 1986), Fe-rich SEPR plume particulates (Feely et al., 1996), plume particulates from the northern EPR (NEPR; Feely et al., 1994a, Sherrell et al., 1999), Fe-Mn nodules (Hein et al., 2013), and average Pacific pelagic clay (Cronan, 1976). Geographic locations of data sets are shown in Fig. 1. Note the tight clustering of Atlantis II Deep samples towards the Fe apex, close to composition of SEPR modern plume particulates.

Fig. 8. Composition of metalliferous sediments from the Atlantis II Deep. (a) – (c) Elements associated principally with the siliciclastic fraction: TiO_2, Zr, and $\sum$REE vs. Al_2O_3. (d) Hydrothermally supplied elements: SiO_2 vs. Fe_2O_3. Major elements reported as oxides; total Fe expressed as $Fe_2O_3(t)$. Compositions of nontronite from Galapagos hydrothermal mounds (Barrett and Friedrichsen, 1982) and ideal hematite are shown for comparison.

Fig. 9. Composition of metalliferous sediments from the Atlantis II Deep (dashed lines are estimated trends). Gold is associated with Cu (a), with Zn in many samples (b), and with total S (not shown). Samples with low contents of gold (<0.7 ppm), Zn (< 0.5 wt %), and Cu (<0.2 wt %) are rich in Fe-oxyhydroxides based on chemical data in Supplementary Data Table 1. The Cd-Zn relation in (d) reflects substitution of Cd for Zn in sphalerite.

Fig. 10. REE composition of metalliferous sediments from Core 274, NE margin of the SW Basin, Atlantis II Deep. Data are normalized to Post-Archean Average Australian Shale (PAAS; Taylor and McLennan, 1995). Vent fluids from the TAG area (26°N, Mid-Atlantic Ridge; Fig. 1) are shown for comparison (from Bau and Dulski, 1999). Core 274, which penetrated 11 m of metalliferous sediments, is interpreted to have passed, from top to bottom, through units AM, SU2, CO, SU1, and DOP (cf. Fig. 4; Thisse, 1982).

Fig. 11. REE composition of metalliferous sediments from Atlantis II Deep. (a) – (d) Samples from different parts of SW Basin, which is considered to be the main area of hydrothermal input into the Deep (Laurila et al., 2014a). (e) Samples from various depths within a 'distal' core from West Basin. Note smaller Eu anomaly compared to proximal cores. (f) Effect of detrital aluminosilicate content on bulk-sediment REE patterns: with increasing ∑REE contents, the Eu anomaly decreases. First part of each hyphenated sample number is the core number. Core locations are shown in Fig. 6. REE concentrations normalized to PAAS.

Fig. 12. REE composition of metalliferous sediments from Atlantis II Deep having εNd values of -2.24 to -1.48 (i.e., most of the sample set). This εNd range suggests these sediments contain 20–25 % basaltic-hydrothermal Nd, based on two-component mixing model; other source of Nd in mixing model is terrigenous detritus (see text). All samples have distinct positive Eu anomalies. All samples are from SW Basin, except Core 345 from West Basin (Fig. 6). REE concentrations normalized to PAAS.

Fig. 13. Variation in Atlantis II Deep REE patterns with respect to εNd. (a) REE and Nd isotope variations in Core 274 near eastern margin of SW Basin (Fig. 6); sample at 1.1 m has a higher aluminosilicate content than the two deeper samples. (b) Two most radiogenic εNd samples in present study; samples are also rich in anhydrite or talc. REE concentrations normalized to PAAS.

Fig. 14. Plot of calculated Eu/Eu* versus εNd values for metalliferous sediments from Atlantis II Deep, based on samples from this study and Cocherie et al. (1994). Orange curve shows estimated exponential trend for metalliferous sediments, excluding two samples containing fish debris, and a talc-anhydrite sample (64-3). Horizontal arrows schematically show effect of increasing dissolved basaltic Nd component versus increasing normal seawater component in precipitating fluid. Vertical arrow shows effect of increasing proportion of reduced fluid on Eu anomaly (temperature and extent of basalt-fluid reaction prior to discharge of fluid into brine pool may also play a role in Eu supply). Red-filled circles: this study; red-filled triangles: Cocherie et al. (1994). Also shown are data for two samples of metalliferous sediment containing phosphatic fish debris, and two biodetrital sediments (small blue-filled squares; Cocherie et al., 1994). Blue rectangle is estimated composition of normal Red Sea seawater; εNd range is based on five near-surface samples of biodetrital sediment (-4.9 ± 0.4) from core KS-01 in Shaban Deep (Cocherie et al., 1994). The estimated Eu/Eu* range for normal Red Sea seawater is based on 10 samples of biodetrital

sediments from core 1016 in central Red Sea (Pierret et al., 2010), and on deep oxic seawater from eastern Mediterranean (Censi et al., 2019). Detritus entering the Red Sea (mainly windborne dust) may also affect bulk-sediment εNd and Eu/Eu* values. Over the last 10 kyr, this detritus (represented by grey polygon with 2 sigma error bars) has had a fairly constant εNd value of -5.8 ± 0.8 (Palchan et al., 2013) with a negligible Eu anomaly (Eu/Eu* = 1.0 – 1.3; Greaves et al., 1994; Palchan et al., 2013). Labelled samples: 274-1: contains ca. 75 % siliciclastic component; 64-3: contains ca. 20 % anhydrite; 345-4: large Eu anomaly, low content of base metals, west margin of West Basin. Sample 436-6 (unlabelled, next to 274-1), from center of West Basin, is compositionally similar to 345-5 but has a much smaller Eu anomaly; this may reflect its greater distance from a discharge site along the west margin of the West Basin.

Fig. 15. Bathymetric map of Atlantis II Deep showing calculated basaltic-hydrothermal component (brown-filled circles) and corresponding PAAS-normalized Eu anomalies (Eu/Eu*, red numerals) for metalliferous sediment samples from the present study. Bubble widths are proportional to basaltic-hydrothermal component (legend shows two selected values). Core numbers indicated by the black numerals. Sample depths range from 1 to 10 m. For cores 274 and 345, an average of two samples was used to obtain the values shown on the map (samples 274-1 and 274-4 at depths of 1.0 m and 3.9 m, respectively; and samples 345-4 and 345-5 at depths of 5.1 m and 5.7 m, respectively). Base map modified from Anschutz (2015).

Fig. 16. Map of eastern Pacific Ocean showing locations of DSDP Leg 92 Sites 597–602, East Pacific Rise transect. Also shown are locations of: (a) Leg 85 sites (573, 574) where Eocene–Oligocene basal metalliferous sediments (Fe-Mn oxyhydroxides) were intersected (Jarvis, 1985); (b) surficial metalliferous sediments (Fe-Mn-oxyhydroxides) from crest of East Pacific Rise (EPR) (Bender et al., 1971); (c) Galapagos Mounds Sites 506–508 where Fe-rich silicates (nontronite) form within pelagic sediments 20–30 km south of Galapagos Rift (Honnorez et al., 1983); and (d) Bauer Basin, where Fe-smectite and Fe-Mn-oxyhydroxides occur throughout much of the sediment column (red-filled squares: cores 11 and 14, Sayles and Bischoff, 1973; red-filled circle: DSDP Site 319, Dymond et al., 1976). Base map from GEBCO (2020) with additional annotation.

Fig. 17. Simplified stratigraphic columns for drill holes from East Pacific Rise transect (DSDP Leg 92), showing locations of samples analysed in present study. Site positions are shown in Fig. 16 and listed in Table 1. Stratigraphic columns are from Knüttel (1986). Samples range in age from late Oligocene to Pleistocene. Axis of East Pacific Rise (EPR) lies about 350 km east of Site 601.

Fig. 18. Composition of metalliferous sediments from East Pacific Rise transect (DSDP Leg 92) plotted as molar proportions of Fe–Mn–Al. Shown for comparison are data for axial SEPR metalliferous sediment, high-Fe SEPR plume, plume particulates from NEPR, Pacific Fe-Mn nodules, and average pelagic clay. Note clustering of Leg 92 metalliferous sediment compositions around values for modern SEPR axial sediments. Data sources as in Fig. 7.

Fig. 19. Major-element compositions of metalliferous sediments from East Pacific Rise transect (DSDP Leg 92) on a carbonate-free basis. (a) MnO vs. $Fe_2O_3(t)$. (b) Al_2O_3 vs. $Fe_2O_3(t)$. (c) TiO_2 vs. Al_2O_3. (d) SiO_2 vs. Al_2O_3. Total Fe expressed as $Fe_2O_3(t)$. Three groups of metalliferous sediments can be discerned: orange = samples deposited above lysocline (intermixed with biogenic carbonate ooze prior to chemical leaching to remove carbonate); blue = samples deposited at or below lysocline; green = samples deposited a few metres or less above basaltic basement (all five green samples in Fig. 19 are from Site 597). Comparative literature data: EPR crest, average of 20 samples from five cores on crest of East Pacific Rise (Marchig and Gundlach, 1982); Bauer Deep, open square: average of seven samples from cores 11 and 14 at depths of 0.2–8.8 m (Sayles and Bischoff, 1973; square with X: DSDP Site 319, one sample at 0.2 m depth (Boström et al., 1976).

Fig. 20. Total REE contents of metalliferous sediments from East Pacific Rise transect (DSDP Leg 92) on a carbonate-free basis versus (a) P_2O_5; and (b) $Fe_2O_3(t)$. Orange symbols: typical metalliferous sediments with <2 wt % Al_2O_3; blue symbols: metalliferous sediments deposited at or below lysocline. Latter sediments are enriched in Al_2O_3, Zr and REE due to higher proportions of detrital aluminosilicates. [Note that only three of the five sub-lysocline samples shown in Figs. 19 and 21 were analysed for REE.]

Fig. 21. Selected trace element contents of metalliferous sediments from East Pacific Rise transect (DSDP Leg 92) on a carbonate-free basis. (a) Mo vs. Al_2O_3; (b) Mo vs. depth for Sites 597 and 599; (c) Ba vs. Co; (d) ΣREE vs. Al_2O_3. Orange symbols: metalliferous sediments with <2 wt % Al_2O_3; blue symbols: sediments deposited at or below

lysocline and enriched in terrigenous aluminosilicates; green dots: near-basement sediments containing basaltic detritus (Site 597). In (a), detrital trend is based on average shale composition (Taylor and McLennan, 1995); hydrothermal trend is based on (but extrapolated beyond) the maximum value of 249 ppm Mo and 1.12 % Al_2O_3 reported by Marchig and Gundlach (1982) for carbonate-free metalliferous sediments from crest of East Pacific Rise; hydrogenous trend is based on Pacific Fe-Mn nodules (N symbol; Li and Schoonmaker, 2003). In (b), increase in Mo to values of 500–600 ppm near basaltic basement is attributed to increased hydrothermal contribution, as terrigenous detritus and basaltic debris cannot provide more than several ppm Mo to sediment. In (c), sub-lysocline sediments tend to be enriched in Ba and Co relative to metalliferous sediments due to hydrogenous and detrital components. In (d), most samples lie along a roughly linear trend that is interpreted to result from mixing between rapidly accumulating metalliferous end-member (low Al, low REE) and slowly accumulating detrital + hydrogenous end-member (high Al, high REE).

Fig. 22. REE composition of metalliferous sediments from Sites 599 and 598, East Pacific Rise transect (DSDP Leg 92) on a carbonate-free basis. (a) Site 599; (b) Site 598. Shown for comparison are REE patterns of deep seawater at 18°N, 108°W, 3000 m depth, in east Pacific Ocean (De Baar et al. 1985; deep waters at 26°S, 114°W are very similar: Jeandel et al., 2013), and bone debris and Fe-Mn micronodules from south-central Pacific Ocean (Dubinin and Sval'nov, 2001). Also shown are approximate age ranges (in Ma) of sampled Leg 92 metalliferous sediments. Leg 92 REE patterns shown here are very similar to those reported by Barrett et al. (1986) and Ruhlin and Owen (1986) for different sample suites from Sites 597 to 600, Leg 92. All REE concentrations normalized to PAAS.

Fig. 23. Location and structure of Galapagos hydrothermal mounds. (a) Simplified map of eastern equatorial Pacific Ocean, showing location of Galapagos hydrothermal mounds field on southern flank of Galapagos Rift spreading ridge. Compiled from Van Andel et al. (1971), Pedersen and Furnes (2001), and Scheibner et al. (2013). Location of DSDP Leg 70 Sites 506 to 508, which sampled the Galapagos hydrothermal mounds, is indicated by yellow arrow; other Leg 70 drilling sites are shown as open circles (unlabelled). (b) Schematic cross-section of mound consisting of 20–30 m of interlayered nontronite-rich precipitates and normal calcareous ooze, overlain by thin surficial Mn oxide crusts. Modified from Honnorez et al. (1981).

Fig. 24. REE composition of nontronite and Fe-Mn oxide sediments from Galapagos hydrothermal mounds (Barrett et al., 1988). Arrows show effects of (1) net mass loss during formation of transitional nontronite; and (2) net mass gain during formation of granular nontronite, relative to composition of "incipient nontronite" (nontronite-bearing calcareous pelagic ooze from below the main nontronite interval in Hole 506). Oxygen-isotope data suggest that nontronites formed at 20–50°C (Barrett and Friedrichsen, 1982; McMurtry et al., 1983). REE concentrations normalized to PAAS.

Fig. 25. REE composition of nontronites and residual Fe-oxides from TAG and Alvin areas at 26°N, Mid-Atlantic Ridge (Severmann et al., 2004; location in Fig. 1). REE concentrations normalized to PAAS.

Fig. 26. REE composition of sulphide-silica-sulphate deposits on Southern Explorer Ridge, NE Pacific Ocean (location in Fig. 1). (a) Samples with mixed hydrothermal-seawater REE signal. (b) Samples with mainly seawater REE signal. Data for Southern Explorer Ridge from Barrett et al. (1990). Shown for comparison are REE patterns for deep seawater at 2975 m in eastern Pacific (Jeandel et al., 2013), and Fe-Mn oxide mud from a low-temperature hydrothermal mound near Galapagos Spreading Centre (Barrett et al., 1988). REE concentrations normalized to PAAS.

Fig. 27. Compilation of εNd values for oceanic metalliferous sediments, biodetrital sediments, vent fluids, seawater and basalts. (a) closed-basin settings along axis of Red Sea; (b) and (c) open-ocean settings along spreading axes of eastern Pacific Ocean and Mid-Atlantic Ridge, respectively. Data sources: [1] Scrivner et al. (2004); Tachikawa et al. (2004); [2] Cocherie et al. (1994); [3] this study; [4] Pierrot et al. (2010); [5] Eissen et al. (1989), Volker et al. (1993); [6] Grasse et al. (2012), Jeandel et al. (2013), Molina-Kescher et al. (2014); Tachikawa et al. (2017); [7] O'Nions et al. (1978), Piepgras et al. (1979), Albarède and Goldstein (1992), Ling et al. (1997), van der Flierdt et al. (2004), Amakawa et al. (2017); [8a] O'Nions et al. (1978), Piepgras et al. (1979), Sun et al. (2018); [8b] Halliday et al. (1992); [9] Piepgras and Wasserburg (1985), Hinkley and Tatsumoto (1987); [10] Hegner and Tatsumoto (1987), Hinkley and Tatsumoto (1987), White et al. (1987); [11] van de Flierdt et al. (2016), Tachikawa et al. (2017), Stichel et al. (2018); [12] Chavagnac et al. (2006); [13] Mills et al. (1993); [14] Dias et al. (2008); [15] Chavagnac et al. (2018); [16] Ferreira et al. (2006), Dosso et al. (1999).

Fig. 28. Representative REE patterns and εNd values for typical metalliferous sediment from the Atlantis II Deep (this study; see also Cocherie et al., 1994) and possible source materials in the Red Sea and surrounding region. Sample details, top to bottom: Saharan dust: Greaves (1994); Red Sea sediments: insoluble residue (dust) from biodetrital sample PD55 (15.1 ka), core K23, northern Red Sea (Palchan et al., 2013); Red Sea sediments: biodetrital sample at 15–20 cm, core 1016, central Red Sea (Pierret et al., 2010); Atlantis II Deep: metalliferous sediment 443-2, Table 2 (this paper); MAR smoker fluid: sample 2598 Ti8BS (361°C) from TAG vent field, 26°N on Mid-Atlantic Ridge (Douville et al., 1999); MAR plume particles: sample SAP09-01 from Rainbow plume, 36°N on Mid-Atlantic Ridge (Edmonds and German, 2004); Bannock brine: sample at 3730 m in lower brine (15°C) of Bannock Basin in eastern Mediterranean Sea (Schijf et al., 1995); Mediterranean seawater: sample from 860 m depth (14°C), station S-290, central Mediterranean Sea (Censi et al., 2004).

Fig. 29. Representative REE patterns and eNd values for metalliferous sediments, plume particulates and deep seawater from the eastern Pacific Ocean (and plume particulates from the Mid-Atlantic Ridge, MAR). East Pacific Rise (EPR) Fe-Mn-oxyhydroxide sediments on carbonate-free basis from Leg 92, western flank of the Rise at 19°S (this study; see also Ruhlin and Owen, 1986): (1) sediments deposited above lysocline; (2) sediments deposited below lysocline. Galapagos Hydrothermal Mounds (GHM) granular nontronite and manganiferous mud from Mounds at 1°N on south flank of Galapagos Rift in east Pacific Ocean (Barrett et al., 1988); MAR Fe-oxide sediments from Alvin area, 2 km from TAG sulphide mounds at 26°N on axis of Mid-Atlantic Ridge (Severmann et al., 2004); Deep seawater from VERTEX II site (18°N, 108°W) in east-central Pacific Ocean, 3000 m depth (de Baar et al., 1985); MAR 36°N plume particles: sample SAP09-01 from Rainbow plume, 36°N on the MAR (Edmonds and German, 2004); EPR 10°N plume particles: hydrocast 4, average of two samples (Sherrell et al., 1999). Nd isotopic compositions: DSDP Leg 92 sediments from Halliday et al. (1992); eastern Pacific Ocean deep waters from Grasse et al. (2012); Lacan et al. (2012); Jeandel et al. (2013); Molina-Kescher et al. (2014).

Fig. 30. Schematic trends in Nd and Sr isotopic compositions and REE patterns for metalliferous sediments containing different proportions of three source materials: pelagic shale (terrigenous siliciclastic component), hydrothermal fluid (leached basaltic component), and normal seawater plus biogenic debris (authigenic component). (a) Nd isotopic data for metalliferous sediments from Atlantis II Deep and East Pacific Rise transect (DSDP Leg 92) from present study and Halliday et al. (1992), respectively. (b) Schematic REE patterns, from top to bottom, represent pelagic shale, to which is added a hydrothermal component, then a normal (oxidized) seawater component. Metalliferous precipitates in anoxic closed basins would not develop lower three REE patterns unless hydrological conditions change and brine mixes with normal seawater. (c) Sr isotopic data for the Atlantis II Deep and East Pacific Rise transect (DSDP Leg 92) from Zierenberg and Shanks (1983) and Barrett et al. (1986), respectively. Typical values of potential sources of Nd and Sr to metalliferous sediments are shown on isotopic axes below the two plots. Values are selected from references listed in Table 6 and are meant to be illustrative. Vent fluids, for example, can have εNd values from +3.8 to +9.5 (Piepgras and Wasserburg, 1985; Hinkley and Tatsumoto, 1987; Chavignac et al., 2018), depending on proportion of seawater vs. basaltic Nd in hydrothermal fluid. Range for seawater εNd is based on shallow and deep waters from eastern Mediterranean (Scrivner et al., 2004; Tachikawa et al., 2004). Biogenic range is based on biodetrital sediment from northern Red Sea (Cocherie et al., 1994). "Detrital" refers to terrigenous material supplied by airborne dust and rivers. Nd and Sr isotopic compositions of this material can vary amongst and even within major ocean basins. A-II = Atlantis II Deep.

Barrett et al. Fig.1

Barrett et al. Fig. 2

Barrett et al. Fig. 3

Atlantis II Deep
(General)

Southwest
Basin

AM 3-4m
Amorphous
silica zone

SAM ~4.5m
Sulphidic
amorphous
silica zone

*Lepido-
crocite
layer*

Sulphide layer

SU2 ~4m
Upper
sulphidic zone

OAN 0->8m
Oxidic anhydrite zone

SOAN 2-5m
Sulphidic oxidic
anhy.
zone

∧ *W. Passage*
Ƨ *W. and E. Basin*

∧ *locally*

CO 1-11m
Central oxidic
zone

*CO locally detrital and
with reduced thickness*

COS
0-2.5m
Central oxidic
silica zone

✕ Ƨ ⚡ *W. and
N. Basin*

✕

SU1 2.5-4m
Upper
sulphidic zone

□ *in hill position*
Ƨ *E. Basin*

◉

DOP 1.3-6m
Detrital oxidic
pyritic zone

◉ *~ base Holocene*
■

■ ∧ *N. Passage*

+

Breccia

Amorphous
facies

Anhydrite

Silicate facies

Carbonates

Sulphide facies

Limonite and
limonite-
hematite facies

Manganite facies

Detrital-
microcoquina
facies

◉ abundant diatoms

Ƨ slumping

□ halite phantoms

■ lithified carbonates

⚡ fissures

+ basalt flow

✕ basalt fragments

Barrett et al. Fig. 4

Core 373
460–500 cm

Core 495
560–600 cm

Core 617
358–398 cm

Core 373
10–50 cm

A

B

C

D

COS

CO

OAN

AM

2 cm

Barrett et al. Fig. 5

Barrett et al. Fig. 6

Barrett et al. Fig. 7

(a) $y = 0.052x - 0.011$
$R^2 = 0.751$

(b) $y = 10.6x + 1.1$
$R^2 = 0.663$

(c) $y = 9.12 + 1.24$
$R^2 = 0.806$

(d) *Nontronite*

Hematite

Barrett et al. Fig. 8

(a) $y = 0.0003x + 0.270$
$R^2 = 0.860$

(b) $y = 2.6 \times 10^5 x + 1.46$
$R^2 = 0.885$

(c) $y = 0.0098x - 4.65$
$R^2 = 0.565$

(d) $y = 0.0029x + 1.18$
$R^2 = 0.883$

Barrett et al. Fig. 9

East margin of SW Basin

Sample/PAAS

1.0 m
9.5 m
3.9 m
10.0 m
7.3 m

Black smoker
Diffuse low-T
White smoker

TAG vent fluids all x10

TAG fluids
MAR 26°N

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Sample
number
274-1
274-4
274-8
274-12
274-13
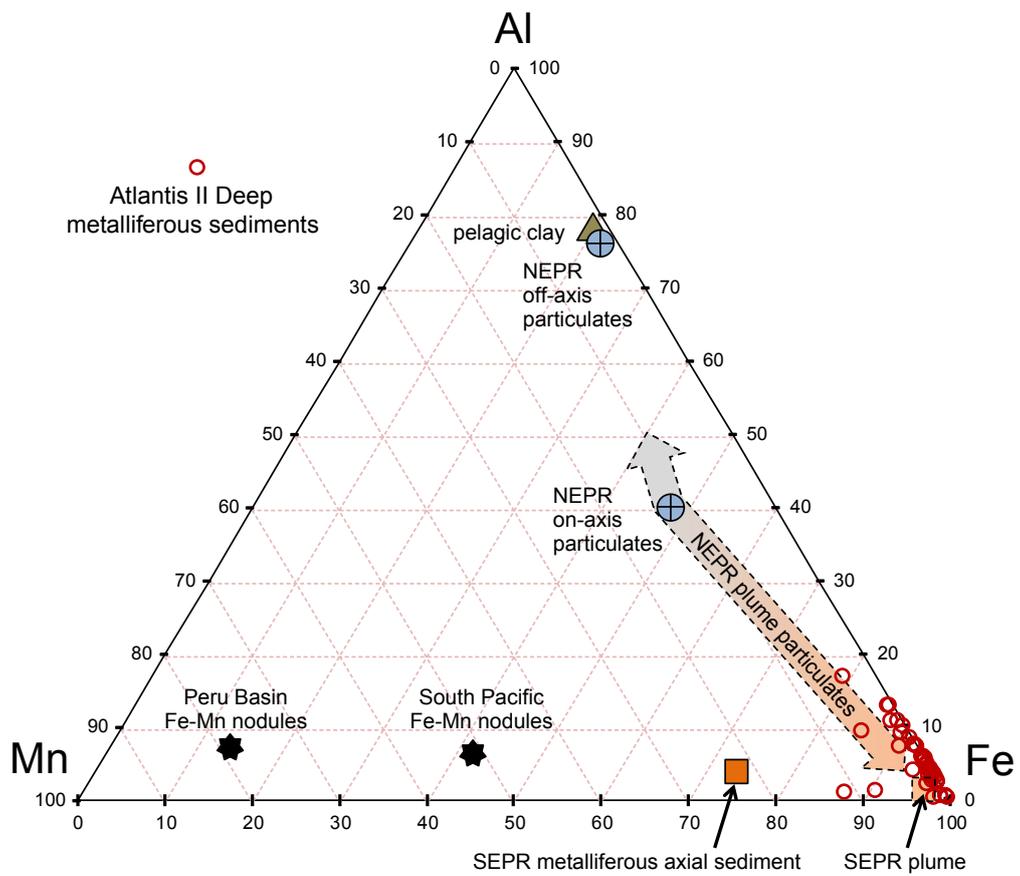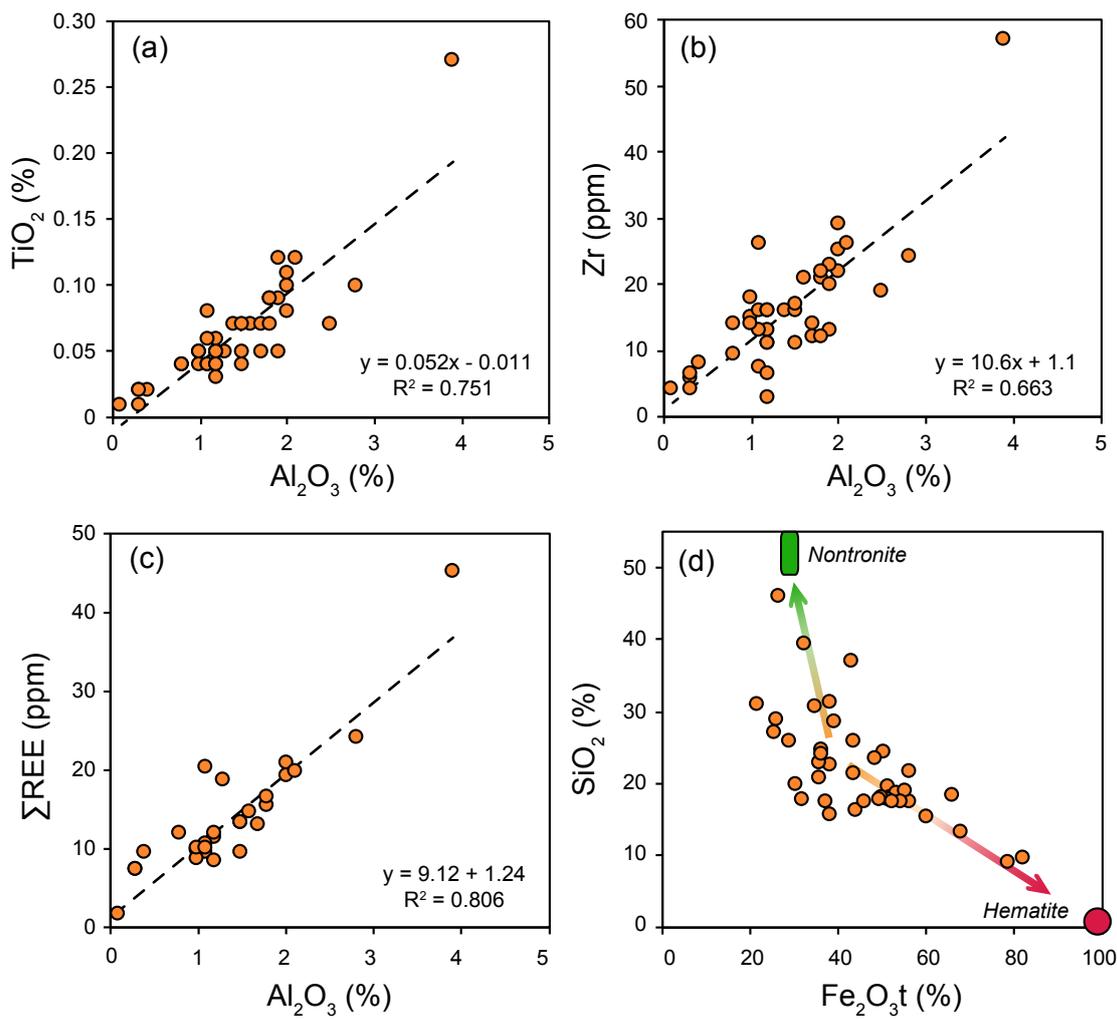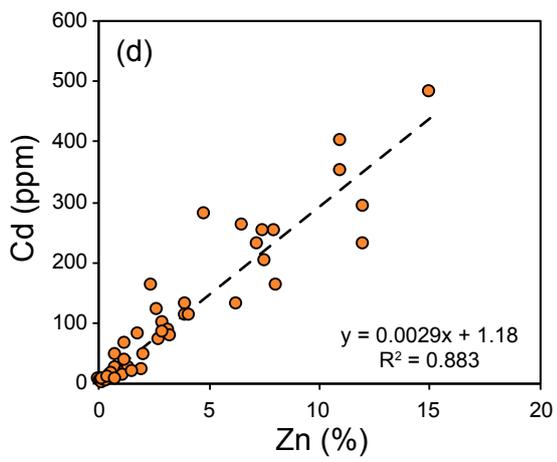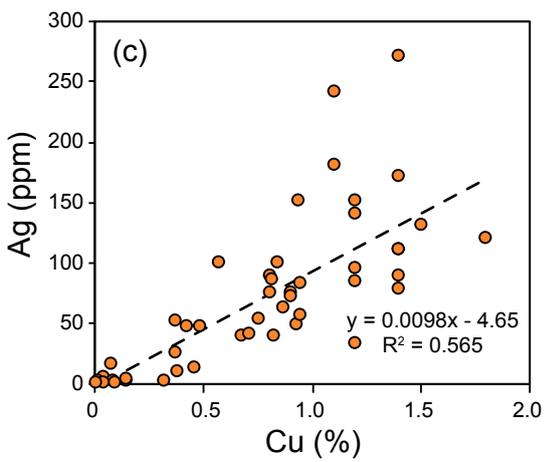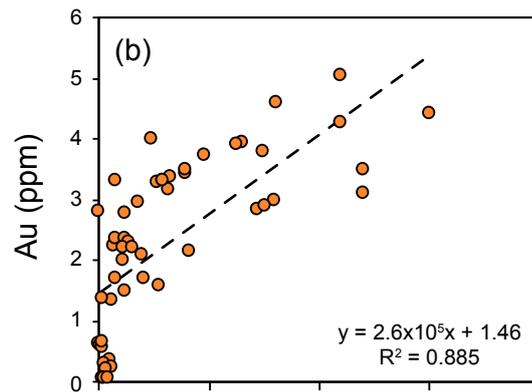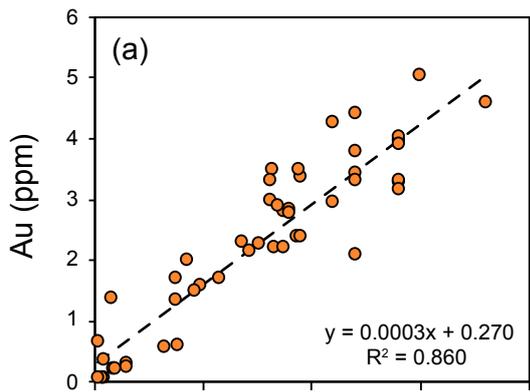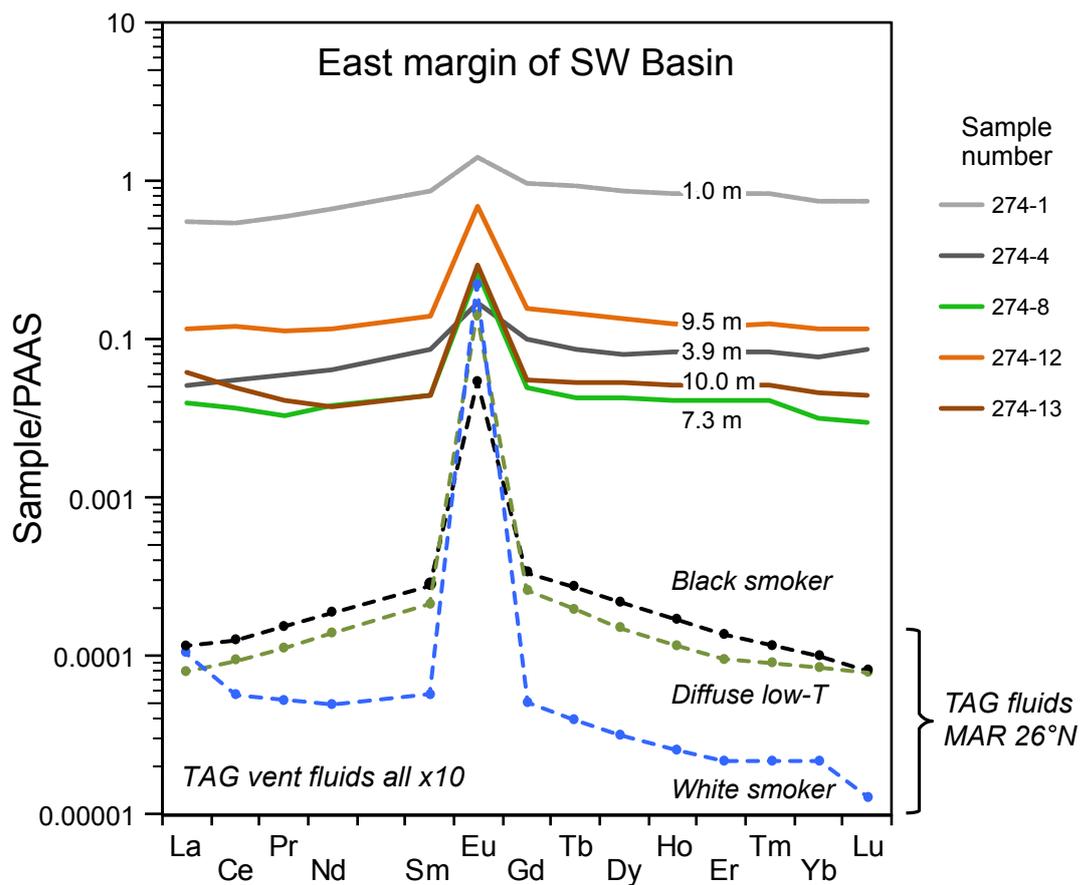
Barrett et al. Fig. 10

Barrett et al. Fig. 11

εNd values for these samples (-1.48 to -2.24) imply a hydrothermal basaltic component of ≈ 20–25%

Barrett et al. Fig. 12

(a) εNd depth variation in core 274

1.0 m, εNd = -2.48
9.5 m, εNd = -1.76
3.9 m, εNd = -2.24

274-1 — — — sulphide-silicate mud
274-4 ——— limonite-rich mud
274-12 ——— silicate-sulphide mud

(b) Highest εNd values in sample set

Calculated hydrothermal
basaltic component ≈ 31–36%

εNd = 0.12
εNd = -0.68

64-3 anhydrite-rich
367-3 talc-rich

Barrett et al. Fig. 13

Barrett et al. Fig. 14

Barrett et al. Fig.15

Barrett et al. Fig.16

DSDP Leg 92 EPR traverse

Barrett et al. Fig.17

Al

0 — 100

10 — 90

20 — 80

Eastern Pacific Leg 92
metalliferous sediments

pelagic clay

NEPR
off-axis
particulates

30 — 70

40 — 60

50 — 50

NEPR
on-axis
particulates

NEPR plume particulates

30

20

Peru Basin
Fe-Mn nodules

South Pacific
Fe-Mn nodules

10

Mn

Fe

100

0   10   20   30   40   50   60   70   80   90   100

0

SEPR metalliferous axial sediment

SEPR plume

Barrett et al. Fig.18

Barrett et al. Fig.19

Barrett et al. Fig. 20

Barrett et al. Fig. 21

(a) Pacific Fe-Mn micronodules

10

1

3.7-8.6 Ma

0.1

Pacific deep
seawater x10^6

599-2-2	599-3-5
599-2-3	599-4-1
599-2-5	599-4-3
599-3-1	
599-3-2	

0.01

DSDP Site 599

Sample/PAAS

(b)

100

Pacific bone debris

≈1-6 Ma

10

≈10-17 Ma

1

deposited
below lysocline
{

598-1-1	598-4-1
598-1-2	598-4-3
598-1-4	598-5-2
598-3-1	598-5-4
598-3-4	

0.1

DSDP Site 598

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Barrett et al. Fig. 22

(a)

COCOS PLATE

Cocos Ridge

Malpelo Ridge

COLOMBIA

Galapagos Rift

506–508

Galapagos Islands

Carnegie Ridge

ECUADOR

SOUTH AMERICAN PLATE

NAZCA PLATE

200 km

(b)

10 m

10 m

25–50 m

Hydrothermal mound

Brown oxidized top 20–40 cm

Mn oxide

8 m

<5% SiO_2

20 m max.

15 m

<50°C

Nontronitic clay

<5% SiO_2

Moat 5 x 25 m

39 m max. drilled into mounds

Calcareous ooze

Calcareous ooze

Basalt

Barrett et al. Fig. 23

(1) *Sediment net mass loss*
(2) *Sediment net mass gain*

Galapagos hydrothermal mounds

- - ● - - Incipient nontronite   ——●—— Transitional nontronite
——○—— Granular nontronite   ——●—— Fe-Mn oxide mud

Sample/PAAS

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Barrett et al. Fig. 24

Mid-Atlantic Ridge

Fe oxides

Nontronite

Legend:
- Alvin residual Fe oxides
- TAG residual Fe oxides
- Alvin nontronite
- TAG nontronite

Y-axis: Sample/PAAS
X-axis: La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Barrett et al. Fig. 25

(a) Southern Explorer Ridge

High-T mound: barite >> sulphide

High-T mound: sulphide >> barite

Deep seawater x 10⁵
(Station GYR 2975 m)

CV-9
P1505-7

(b)

Galapagos: Fe-Mn oxide mud

Silica > sulphide

Silica ≈ sulphide

Sulphide >> silica

Sulphide >> silica > barite ≥ Fe-oxide

P1504-6   P1505-2
P1504-3   D10-10

Sample/PAAS

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Barrett et al. Fig. 26

(a) Red Sea Deeps

Seawater: Eastern Mediterranean	*1*
Biodetrital sediments: Shaban Deep *=brine	*2*
Biodetrital sediments: Atlantis II Deep	*2*
Dominant facies *High REE,P* Metalliferous sediments: Atlantis II Deep	*2,3* *2*
Metalliferous sediments: Thetis Deep *Upper metre*	*4*
Basalt: Atlantis II, Shaban & Nereus Deeps	*5*
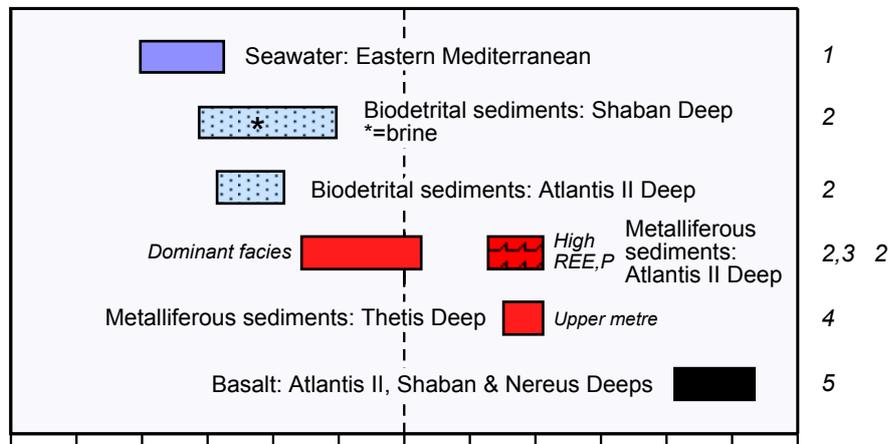
(b) Eastern Pacific Ridges

S. Pacific *E. Pacific* Pacific deep seawater	*6*
Pacific basins Fe-Mn crusts	*7*
EPR & JdeF metalliferous sediments	*8a*
Leg 92 metalliferous sediments, ≈19°S	*8b*
High-T vent fluids: EPR & JdeF	*9*
EPR MORB	*10*

(c) Mid-Atlantic Ridge

to -14 Central Atlantic deep seawater	*11*
Mainly oxyhydroxides Metalliferous sediments: Rainbow 36°N	*12*
Anhydrite & oxidized sulphides Mound sediments: TAG 26°N	*13*
Mound sediments: Lucky Strike 37°N *Barite & sulphides*	*14*
High-T vent fluids: Lucky Strike 37°N	*15*
Basalt: Lucky Strike 37°N	*16*

-12 -10 -8 -6 -4 -2 0 +2 +4 +6 +8 +10 +12

εNd

Barrett et al. Fig. 27

Saharan dust — εNd = -5 to -12

Red Sea sediments — εNd = -4 to -7

Atlantis II Deep metalliferous sediments — εNd = -2 to 0

MAR smoker fluid x10³ — εNd = +8 to +12

MAR 36°N plume particles x10⁶

Bannock brine x10³ — εNd = -4.5

Mediterranean seawater (at 860 m) x10³ — εNd = -4 to -6

Sample/PAAS

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Barrett et al. Fig. 28

Barrett et al. Fig. 29

(a)

εNd

-8 -4 0 +4 +8

εNd

(b) REE patterns

Pelagic shale
∑REE ≈ 100 ppm

Hydrothermal
∑REE ≈ 20 ppm

Deep seawater
∑REE ≈ 20 x 10^{-6} ppm

(c)

^{87}Sr/^{86}Sr

0.703 0.705 0.707 0.709 0.711 0.713

^{87}Sr/^{86}Sr

-8 -4 0 +4 +8

-12 -8 -4 0 +4 +8

3 1 2 4 5

Seawater[1]   Basalt[5]

Detrital[3] Biogenic[2]   Vent fluid[4]

0.703 0.705 0.707 0.709 0.711 0.713

4 3 2 1 5

Basalt[4]   Seawater[1]   Detrital[5]

EPR vents[3]   A-II brine[2]

Barrett et al. Fig. 30

Barrett et al 2021 EarthSciRev TABLE 1 Aug 23 2021

Table 1. Locations of samples from the Atlantis II Deep, the East Pacific Rise transect, the Galapagos hydrothermal mounds, and the Southern Explorer Ridge

Cruise	Core no.	Latitude (°N)	Longitude (°E)	Depth (m)
Atlantis II Deep, central Red Sea (R/V Valdivia cruises)				
VA-1	48	21.3462	38.0842	2179
VA-1	54	21.3437	38.0838	2180
VA-1	64	21.3245	38.0938	2165
VA-1	71	21.3278	38.0922	2162
VA-1	98	21.3287	38.0912	2158
VA-29*	274	21.353	38.082	≈2150
VA-3	345	21.3667	38.0552	2133
VA-3	361	21.3470	38.0812	2170
VA-3	367	21.3607	38.0765	2164
VA-3	369	21.3623	38.0658	2154
VA-3	397	21.3455	38.0962	2078
VA-3	409	21.3390	38.0858	2164
VA-3	416	21.3430	38.0907	2155
VA-3	419	21.3388	38.0848	2162
VA-3	436	21.3813	38.0607	2086
VA-3	443	21.3447	38.0945	2102
East Pacific Rise transect (west of spreading axis, at ca. 19°S)				
DSDP Leg 92	597	-18.8063	-129.7705	4157
DSDP Leg 92	597A	-18.8072	-129.7703	4163
DSDP Leg 92	598	-19.0047	-124.6768	3703
DSDP Leg 92	599, 599B	-19.4515	-119.8813	3644
DSDP Leg 92	600C	-18.9283	-116.8408	3406
DSDP Leg 92	601B	-18.9203	-166.8685	3448
Galapagos Spreading Ridge: hydrothermal mounds on southern flank of ridge				
DSDP Leg 70	506	0.6098	-86.0915	2714
DSDP Leg 70	509B	0.5888	-86.1322	2702
Southern Explorer Ridge: surface samples from axis of ridge				
CASM IV (1)	P1504-3	49.761	-130.259	≈1800
CASM IV (2)	P1504-6	49.761	-130.259	≈1800
CASM IV (3)	P1505-2	49.761	-130.259	≈1800
CASM IV (4)	P1505-7	49.761	-130.259	≈1800
CASM V (5)	CV-9	49.74	-130.27	≈1850
CASM V (6)	D10-10	49.74	-130.27	≈1850

*Location estimated from Bäcker and Richter (1973). CASM samples: (1) sulphides > silica; ≈200 m north of Magic Mountain; (2) sulphides + silica, ≈200 m north of Magic Mountain; (3) sulphides > silica, ≈300 m west of Magic Mountain; (4) sulphides > silica ≈ sulphate, west side of Magic Mountain; (5) silica > sulphate ≈ sulphides, ≈2 km SSW of Magic Mountain; (6) sulphides > silica, ≈2 km SSW of Magic Mountain. The location of the Magic Mountain sulphide deposit is estimated as 49.76°N, 130.26°W based on figure 2 in Deschamps et al. (2013). CASM IV, V = Canadian American Seamount expeditions IV and V. Sample numbers given in second column; prefixes identify the dive/dredge number.

Table 2. Rare-earth element composition of metalliferous sediments from Atlantis II Deep (Red Sea) and hemipelagic sediments from Orca Basin (Gulf of Mexico)

Sample number	Depth (cm)	Sediment unit: facies	Element (ppm)														∑REE	Y
			La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Red Sea Atlantis II Deep																		
48-1	111–114	AM: silicate-sulphide	1.97	3.78	0.396	1.68	0.353	0.157	0.329	0.0509	0.289	0.0593	0.166	0.0244	0.146	0.0226	9.42	1.72
48-2	484–487	CO: hematite-silicate	4.81	7.35	0.699	2.96	0.565	0.300	0.550	0.0847	0.465	0.0951	0.280	0.0410	0.236	0.0343	18.5	2.60
54-2	394–398	CO: silicate-hematite	2.76	6.02	0.615	2.54	0.518	0.332	0.477	0.0757	0.457	0.0915	0.256	0.0368	0.231	0.0341	14.4	2.41
54-3	444–448	CO: anhydrite layer	0.112	0.199	0.0181	0.0696	0.0117	0.0112	0.0120	0.0019	0.0093	0.0018	0.0043	0.0006	0.0042	0.0006	0.456	0.03
64-1	148–152	AM: silicate-sulphide	1.55	3.81	0.406	1.84	0.358	0.174	0.354	0.0540	0.306	0.0680	0.197	0.0285	0.160	0.0264	9.32	1.65
64-2	511–514	AM/SU2: anhydrite layer	0.410	0.643	0.0634	0.228	0.0558	0.0223	0.0480	0.0074	0.0418	0.0082	0.0244	0.0029	0.0177	0.0038	1.62	0.33
64-3	567–569	SOAN: silicate-sulphide-anhydrite	3.77	8.58	0.908	3.74	0.775	0.364	0.739	0.116	0.657	0.132	0.366	0.0539	0.335	0.0502	20.6	3.42
71-1	190–194	AM: silicate-sulphide	2.27	5.42	0.562	2.29	0.471	0.252	0.469	0.0770	0.450	0.0920	0.263	0.0378	0.246	0.0378	12.9	2.02
71-3	967–970	CO: hematite-argillaceous	1.85	3.84	0.381	1.64	0.320	0.179	0.321	0.0484	0.271	0.0577	0.168	0.0226	0.135	0.0196	9.25	1.66
98-1	113–116	AM: silicate-sulphide	1.89	4.32	0.433	1.82	0.376	0.218	0.360	0.0595	0.324	0.0677	0.193	0.0287	0.170	0.0262	10.3	1.86
274-1#	ca. 100	SU2: silicate-sulphide	20.9	42.6	5.18	22.2	4.67	1.50	4.43	0.693	3.95	0.813	2.30	0.332	2.03	0.318	112	18.5
274-4#	ca. 390	CO: limonite-silicate	1.93	4.42	0.527	2.19	0.473	0.182	0.468	0.0650	0.378	0.0823	0.235	0.0333	0.216	0.0368	11.2	2.61
274-8#	ca. 730	CO: silicate-limonite	1.48	2.86	0.291	1.28	0.243	0.283	0.226	0.0328	0.197	0.0402	0.117	0.0170	0.0890	0.0127	7.18	1.05
274-12#	ca. 950	SU1: silicate-sulphide	4.42	9.57	0.986	3.87	0.774	0.737	0.715	0.110	0.617	0.122	0.342	0.0508	0.323	0.0487	22.7	2.91
274-13#	ca. 1000	SU1: silicate-sulphide	2.38	3.93	0.354	1.26	0.242	0.314	0.254	0.0403	0.248	0.0506	0.147	0.0212	0.127	0.0189	9.38	1.39
345-1	182–186	AM: silicate	2.81	4.75	0.486	1.93	0.374	0.197	0.360	0.0574	0.331	0.0694	0.194	0.0282	0.176	0.0279	11.8	1.79
345-3	451–453	CO: limonite	1.76	2.81	0.270	1.10	0.196	0.101	0.219	0.0302	0.190	0.0436	0.130	0.0173	0.108	0.0171	6.99	1.30
345-4	507–510	CO: silicate-hematite	2.24	4.08	0.375	1.49	0.291	0.425	0.286	0.0461	0.252	0.0516	0.151	0.0226	0.131	0.0190	9.85	1.37
345-5	570–574	CO: silicate-hematite-Mn	1.80	4.26	0.396	1.51	0.296	0.230	0.286	0.0413	0.233	0.0482	0.137	0.0194	0.113	0.0178	9.39	1.32
361-1	169–163	AM: silicate	2.80	5.97	0.654	2.90	0.613	0.274	0.580	0.0907	0.513	0.105	0.308	0.0471	0.264	0.0411	15.2	2.72
367-1	24–26	AM: silicate-sulphide	3.47	7.54	0.829	3.55	0.765	0.322	0.713	0.110	0.654	0.130	0.381	0.0571	0.335	0.0509	18.9	3.47
367-3	187–190	AM: silicate-limonite-hematite	3.81	8.78	0.911	3.59	0.670	0.490	0.626	0.0859	0.492	0.100	0.277	0.0384	0.230	0.0353	20.1	2.54
367-4	459–463	SU2: sulphide ooze	2.33	4.89	0.612	2.65	0.533	0.283	0.553	0.0759	0.450	0.101	0.297	0.0406	0.258	0.0434	13.1	2.78
369-1	134–137	AM: silicate	1.51	3.53	0.356	1.60	0.333	0.150	0.312	0.0492	0.297	0.0561	0.170	0.0241	0.146	0.0230	8.55	1.49
369-3	476–485	AM: anhydrite layer	0.488	0.473	0.0334	0.105	0.0270	0.078	0.038	0.0063	0.044	0.0107	0.0378	0.0067	0.0486	0.0089	1.41	0.26
397-2	244–247	AM: silicate	1.75	4.02	0.408	1.80	0.370	0.159	0.357	0.0565	0.326	0.0651	0.188	0.0283	0.167	0.0262	9.73	1.64
397-4	583–585	SU2: silicate-limonite-Mn (within SU2)	7.86	18.8	2.01	8.28	1.76	0.631	1.62	0.260	1.47	0.297	0.830	0.124	0.804	0.120	44.8	6.97
409-1	146–149	AM: silicate-sulphide	2.31	5.30	0.590	2.37	0.518	0.234	0.500	0.0822	0.497	0.102	0.276	0.0405	0.257	0.0414	13.1	2.15
409-3	572–576	CO: silicate-hematite	2.16	4.83	0.499	2.07	0.399	0.260	0.416	0.0621	0.343	0.0780	0.232	0.0319	0.196	0.0321	11.6	2.00
416-1	112–116	AM: silicate	2.97	6.46	0.705	3.15	0.643	0.270	0.607	0.0972	0.518	0.108	0.309	0.0467	0.256	0.0407	16.2	2.73
416-3	553–556	SU2: sulphide-anhydrite	4.92	9.42	0.971	4.32	0.874	0.496	0.863	0.1324	0.730	0.155	0.465	0.0704	0.399	0.0580	23.9	3.91
436-1	216–219	AM: silicate	3.28	7.82	0.908	3.80	0.776	0.325	0.800	0.114	0.661	0.151	0.433	0.0553	0.341	0.0585	19.5	3.66
436-4	760–765	CO: limonite-anhydrite	0.139	0.0749	0.0061	0.0246	0.0058	0.0017	0.0044	0.0006	0.0027	<0.001	<0.002	<0.0004	<0.002	<0.0005	0.260	<0.02
436-6	962–966	CO: hematite-limonite	1.81	3.88	0.439	1.81	0.387	0.119	0.355	0.0579	0.335	0.0695	0.201	0.0296	0.185	0.0285	9.70	1.76
436-7	973–975	CO: limonite-hematite	4.40	9.35	0.943	3.79	0.798	0.259	0.766	0.119	0.684	0.136	0.378	0.0560	0.364	0.0549	22.1	3.80
436-8	994–997	CO?: silicate-sulphide	1.10	2.12	0.212	0.806	0.151	0.0434	0.126	0.0201	0.108	0.0228	0.0697	0.0094	0.0521	0.0073	4.84	0.81
443-1	135–138	AM: silicate	1.50	3.45	0.366	1.50	0.310	0.153	0.299	0.0472	0.278	0.0560	0.162	0.0225	0.146	0.0228	8.31	1.46
443-2	261–264	AM: silicate-limonite	2.24	4.64	0.515	2.25	0.459	0.370	0.437	0.0671	0.378	0.0790	0.224	0.0334	0.194	0.0289	11.9	1.80
443-3	472–475	SU2: sulphide-silicate	3.01	5.21	0.510	1.99	0.385	0.384	0.418	0.0576	0.337	0.0718	0.205	0.0287	0.168	0.0267	12.8	2.22

Table 1. Rare-earth element analyses for metalliferous sediments from the Atlantis II Deep (Red Sea) and Orca Basin (Gulf of Mexico) (continued)

Sample number	Depth (cm)	Sediment unit: facies	Element (ppm)																
			La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REE	Y
Gulf of Mexico Orca Basin																		
87-G-2	4–5 cm	Silty mud, lam. black/grey/red	11.6	23.2	2.59	10.4	1.78	0.396	1.62	0.233	1.33	0.260	0.731	0.111	0.710	0.108	55.1	nd
87-G-2	5–6 cm	Silty mud, lam. black/grey/red	14.5	30.5	3.40	13.7	2.38	0.515	2.12	0.306	1.72	0.349	1.00	0.147	0.941	0.141	71.7	nd
87-G-2	6–7 cm	Silty mud, lam. black/grey/red	11.1	22.6	2.53	10.2	1.78	0.394	1.59	0.228	1.28	0.257	0.724	0.108	0.693	0.108	53.6	nd
Reference material																		
SCo-1	This study	USGS Cody Shale	30.34	59.4	6.57	25.72	4.91	1.17	4.52	0.694	3.98	0.846	2.45	0.356	2.32	0.370	144	21.8
SCo-1	Ref 1	USGS Cody Shale	29.60	60.0	6.22	24.70	4.71	1.16	3.97	nd	3.27	0.660	1.90	nd	1.88	0.290	nd	20.3
SCo-1	Ref 2	USGS Cody Shale	29.50	62.0	6.60	26.00	5.30	1.19	4.60	0.700	4.20	0.970	2.50	0.420	2.27	0.340	nd	26.0

Depth = cm below seafloor. # Location of core 274 estimated from map provided by E. Oudin (pers. comm., 1988). Ref 1 = Jarvis and Jarvis (1985); Ref 2 = Govindarju (1989); nd = not determined; SCo-1 and other determinations include fusion of insoluble residues with lithium metaborate. Gulf of Mexico: lam. = laminated.

Table 3. Nd isotope composition and related data for metalliferous sediments from the Atlantis II Deep, Red Sea

Cruise	Sample number	Depth (cm)	Latitude (°N)	Longitude (°E)	Sediment unit: facies	$^{143}Nd/^{144}Nd$	εNd	Basaltic Nd (%)	Eu_N/Eu_N^*	Fe_2O_3t (wt%)	Al_2O_3 (wt%)	ΣREE (ppm)
		(1)				(2)	(3)	(4)	(5)			
VA-1	48-2	484–487	21.3461	38.0842	CO: hematite-silicate	0.512570 ± 5	-1.48	25.4	2.54	51.2	1.3	18.5
VA-1	54-2	394–398	21.3436	38.0839	CO: hematite-silicate	0.512546 ± 5	-1.95	22.3	3.14	50.5	1.6	14.4
VA-1	64-3 $	567–569	21.3244	38.0939	SOAN: silicate-sulphide-anhydrite	0.512652 ± 5	+0.12	36.1	2.26	30.4	2.0	20.6
VA-1	71-3	967–970	21.3278	38.0922	DOP: hematite-argillaceous	0.512543 ± 9	-2.01	21.9	2.62	65.9	1.1	9.2
VA-3	274-1 #	ca. 100	21.3533	38.0817	SU2: silicate-sulphide	0.512519 ± 5	-2.48	18.8	1.55	nd	6.9 (6)	112
VA-3	274-4 #	ca. 390	21.3533	38.0817	CO: limonite	0.512531 ± 11	-2.24	20.4	1.82	nd	1.2	11.2
VA-3	274-12 #	ca. 950	21.3533	38.0817	SU1: silicate-sulphide	0.512556 ± 10	-1.76	23.6	4.67	nd	nd	22.7
VA-3	345-4	507–510	21.3667	38.0552	CO: silicate-hematite	0.512535 ± 6	-2.17	20.9	6.95	nd	nd	9.9
VA-3	345-5	570–574	21.3667	38.0552	CO: silicate-hematite	0.512556 ± 8	-1.76	23.6	3.73	43.8	0.4	9.4
VA-3	367-3 *	187–190	21.3607	38.0765	AM: silicate-limonite-anhydrite	0.512611 ± 8	-0.68	30.8	3.56	38.0	1.1	20.1
VA-3	397-2	244–247	21.3455	38.0962	AM: silicate	0.512559 ± 5	-1.70	24.0	2.06	48.4	1.0	9.7
VA-3	409-3	572–576	21.3390	38.0858	CO: silicate-hematite	0.512558 ± 6	-1.72	23.9	3.01	56.1	1.2	11.6
VA-3	436-6	962–966	21.3830	38.0607	CO: limonite-hematite	0.512506 ± 11	-2.73	17.1	1.51	67.8	1.1	9.7
VA-3	443-2	261–264	21.3447	38.0945	AM: silicate-limonite	0.512561 ± 11	-1.66	24.3	3.89	nd	nd	11.9

(1) Depth = cm below seafloor. (2) Error is ± 2 standard errors on the 6th decimal place. (3) Relative to CHUR value of 0.512646. (4) Calculated from estimated basaltic and seawater end-members of εNd = 9.7 and εNd = -5.3, respectively. (5) Eu anomaly = Eu_N/Eu_N^*, where $Eu_N^* = (Sm_N*Gd_N)^{0.5}$ and N is the shale-normalized value (PAAS from Taylor and McLennan, 1985). # Location of core 274 estimated from map provided by E. Oudin (pers. comm., 1988). (6) Al_2O_3 estimated as 6.9 % based on Al_2O_3-Zr-Th trends for entire data set (Supplementary Data Table 1). $ Anhydrite-bearing sample. * Talc-bearing sample. nd = not determined.

Table 4. Rare-earth element composition of metalliferous sediments from East Pacific Rise transect, DSDP Leg 92

Sample number	Depth (cm)	Depth below seafloor (m)	Element (ppm)															
			La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REE	Y
597-6-1	75-77	43.76	79	26	13	55	10	1.4	13	2.0	12	2.8	7.8	1.2	7.1	1.0	231	86
597-6-3	74-76	46.75	85	21	15	62	12	3.5	15	2.4	16	3.6	9.9	1.4	8.9	1.3	257	110
597-6-4	74-76	48.25	56	18	12	45	9.4	2.4	10	1.8	11	2.4	6.6	1.0	6.1	0.9	183	62
598-1-1	71-73	0.72	340	180	69	300	64	15	80	13	79	18	51	7.5	49	7.5	1273	640
598-1-2	71-73	2.22	320	110	63	270	54	15	69	11	74	17	47	7.0	44	6.7	1108	600
598-1-4	71-75	5.23	250	81	43	200	40	8.8	53	8.3	54	13	36	5.2	33	5.1	830	480
598-3-1	67-69	16.48	100	43	17	73	15	3.4	19	3.0	20	4.6	13	1.9	12	1.8	327	140
598-3-4	70-74	21.02	90	31	14	61	12	2.8	16	2.5	17	4.1	11	1.7	10	1.6	275	120
598-4-1	15-17	25.56	93	30	14	61	11	2.6	14	2.2	15	3.3	9.3	1.4	9.3	1.4	268	51
598-4-3	25-27	28.66	99	28	17	77	14	3.6	19	2.9	18	4.1	11	1.7	10	1.6	307	120
598-5-2	72-74	37.23	67	20	12	49	9.0	2.1	11	1.8	11	2.5	7.2	1.1	7.4	1.1	202	68
598-5-4	80-82	40.31	76	20	12	55	10	2.3	13	2.0	13	3.0	8.5	1.3	8.4	1.3	226	87
599-2-2	70-74	10.12	50	12	7.4	34	6.4	1.5	9.3	1.4	10	2.6	7.7	1.2	7.5	1.2	152	86
599-2-3	70-74	11.62	63	15	9.5	43	8.0	1.8	12	1.9	13	3.2	9.5	1.5	9.1	1.5	192	110
599-2-5	70-73	14.62	68	16	9.6	42	8.0	1.9	12	1.9	13	3.2	10	1.6	9.6	1.5	198	110
599-3-1	70-74	18.22	66	16	9.6	45	8.3	1.7	13	1.9	13	3.3	10	1.5	9.5	1.4	200	110
599-3-2	70-74	19.72	51	12	7.9	35	6.5	1.8	9.7	1.6	11	2.7	7.8	1.3	7.7	1.2	157	86
599-3-5	70-74	24.22	56	12	7.5	34	6.2	1.3	8.8	1.4	9.8	2.5	7.5	1.2	7.7	1.2	157	81
599-4-1	71-73	27.82	38	8.0	5.6	26	4.7	1.2	7.1	1.1	7.5	1.9	5.7	0.9	5.5	0.8	114	67
599-4-3	71-73	30.82	80	20	11	52	9.5	2.2	14	2.1	14	3.8	11	1.8	11	1.7	234	130
599-4-4	72-74	32.33	47	11	7.0	31	5.9	1.2	8.2	1.3	9.2	2.3	6.8	1.1	6.9	1.1	140	71
599-4-5	72-74	33.82	42	10	6.2	27	5.3	1.1	7.0	1.2	8.1	2.1	6.1	1.0	6.1	1.0	124	61
599B-2-3	70-74	36.02	29	8.7	4.2	20	3.7	0.77	5.3	0.8	5.7	1.5	4.2	0.7	3.8	0.6	89	53
599B-2-4	70-73	37.52	59	14	8.7	38	7.1	1.5	9.5	1.5	10	2.6	7.7	1.2	7.8	1.2	170	84
599B-2-5	74-77	39.06	52	13	7.5	34	6.7	1.9	9.3	1.5	10	2.6	7.6	1.2	7.7	1.2	156	81
599B-2-6	71-74	40.53	51	13	7.2	34	6.8	2.0	9.8	1.6	11	2.9	8.5	1.4	8.3	1.3	159	97
600C-1-4	99-104	5.52	70	19	12	52	10	<0.02	14	2.3	15	3.8	11	1.6	9.9	1.6	222	120
600C-1-6	99-104	8.52	48	10	7.0	33	6.4	1.8	9.7	1.5	10	2.6	7.8	1.2	7.7	1.2	148	94
600C-2-2#	91-96	11.84	6.9	3.9	1.2	6.2	1.3	0.42	2.1	0.4	2.4	0.6	2.0	0.3	2.0	0.3	30	20
601B-1-2	76-81	16.69	65	14	9.3	43	8.2	2.1	12	2.0	13	3.3	9.8	1.6	9.6	1.6	195	110

Note: All data are reported on a carbonate-free basis. Sample number indicates DSDP hole-core-section; depth is sampled interval (cm) in core section. # Contains basaltic material.

Table 5. Summary of REE and Nd-Pb-Sr isotopic features of metalliferous

Basin type	Tectonic setting	Type Example
Closed Basin	Spreading axis	Atlantis II Deep
Closed Basin	Continental slope	Orca Basin
Open Ocean	Spreading axis	East Pacific Rise
Open Ocean	Spreading axis	Mid-Atlantic Ridge
Open Ocean	Spreading axis flank	Galapagos mounds

; sediment types discussed in present paper

Local Setting of Metalliferous Sediments	REE patterns (PAAS-normalized)
Sediments precipitated in sub-oxic to anoxic brine layers (T = 43–68°C) as Fe-oxyhydroxides, Fe-silicates, Mn oxides, metal sulfides, carbonates, sulfates and amorphous compounds.	Mainly flat; moderate to strong positive Eu anomalies; no Ce anomaly, no Y anomaly.
Sediments accumulate in brine pools (T= 5°C) are mainly detrital muds, with some authigenic Fe-Mn and biogenic input.	Mainly flat; no Eu or Ce anomaly.
Fe-Mn oxyhydroxides precipitate from plumes rising above high-T vents and absorb metals, REEs and other cations from both the plume and seawater during lateral dispersion up to a few thousand km from axis.	Patterns slightly LREE-depleted; strong negative Ce anomaly, no Eu anomaly; usually a small positive Y anomaly.
Oxidation of pre-existing sulfide mounds forms Fe-oxyhydroxide-rich sediments that remain in situ or are dispersed by bottom currents up to a few km from mounds. Locally, direct precipitation of Fe-Si-oxyhydroxides and nontronite occurs at low-T vents.	Patterns flat to slighly convex upwards, with moderate to large positive Eu anomaly; often with a small negative Ce anomaly.
Fe-silicate (nontronite)-rich precipitates form as upwelling fluids react with a cover of biogenic sediments at T= 20–50°C. Mn oxides precipitated at surface.	Patterns commonly similar to normal seawater but with a less negative Ce anomaly; some additionally have a small positive Eu anomaly.

Nd isotopes	Pb isotopes
εNd mostly -2.7 to +0.2, suggesting 20–30 % basaltic-hydrothermal Nd; rare sediments with fish teeth have εNd up to +4 and high ∑REE.	Isotope ratios range from near-pelagic-detrital-seawater values to values suggesting up to 30 % basaltic-hydrothermal Pb in sediments.
No data	No data
εNd ranges from -5.2 to -4.1 (DSDP Leg 92 sediments), close to ambient East Pacific seawater values.	Isotope ratios range from near-pelagic-detrital-seawater values to basaltic values (proportion of basaltic component depends partly on distance from paleo-ridge).
εNd ranges from -12.6 to -2.5, Lowest values are close to ambient North Atlantic seawater and pelagic sediments; higher values due to a component of sulfide detritus.	Isotope ratios range from basaltic-hydrothermal (TAG sediments) to values close to seawater and pelagic sediments (low-T Lilliput deposits).
No data	Isotope ratios range from near-basaltic to near-seawater values.

Sr isotopes

Isotope ratios mostly 0.7072 to 0.7080, suggesting 15–30 % basaltic-hydrothermal Sr, with majority of Sr derived from rift-flank Miocene evaporites (=seawater).

No data

Isotope ratios very close to seawater value of 0.7091.

Isotope ratios close to seawater value of 0.7091, but locally down to 0.7082 (due to a small basaltic-hydrothermal component in sediment).

Isotope ratios very close to seawater value of 0.7091.

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Table 6. Compilation of Nd, Pb and Sr isotopic and concentration data for oceanic metalliferous sediments, deep seawater, Atlantis II Deep brine, MOR hydrothermal vent fluids and MOR basalt

	Axial MORB (Global and Red Sea)	High-T vent fluids (Global)	Seawater (Global and Red Sea)	Deep-sea detritus (Red Sea)	Seafloor brine pool (Atlantis II Deep)	Metalliferous sediments (Atlantis II Deep)	Metalliferous sediments (Eastern Pacific Ocean)
Nd content	50.6 µmol/kg (1)	1–10 nmol/kg (9) 1–2 nmol/kg (10)	0.010–0.040 nmol/kg (16a,16b)	ca. 83 µmol/kg (27)	No data	mostly 7–83 µmol/kg (41,36)	290–500 µmol/kg (44)
εNd	+8.0 to +9.8 (2) +6.9 to +8.2 (3) +7.5 to +12.0 (4a)	ca. +9.0 (4b) +5.9 to +7.9 (4c) +7.8 to +9.0 (10)	-9 to -2 (16a) -14 to -8 (16b) -5.0 ± 0.3 (17); -7.0 ± 0.4 (18) -4.9 ± 0.2 (42b)	-5.2 to -4.6 (28) -4.7 to -6.3 (29)	No data [Shaban Deep brine: -4.5 (32)]	-2.7 to +0.1 (present study) -1.8 to -0.3 (42a)	-5.2 to -4.1 (45) -1.0 to -1.6 (46) -0.2 to -4.2 (47) -2.8 to -3.6 (48)
Sr content	1.3–1.9 mmol/kg (5) 1.0 mmol/kg (1)	63–135 µmol/kg (11) 80–312 µmol/kg (12) 45–130 µmol/kg (13)	122 µmol/kg (19) 88–90 µmol/kg (20,21)		400 µmol/kg (33) 514 µmol/kg (34)	228–8440 µmol/kg (34)	4400–4900 µmol/kg (44)
$^{87}Sr/^{86}Sr$	0.7027–0.7031 (2,3)	0.7028–0.7046 (14)	0.70917 (19) 0.7088–0.7090 (22)	0.7075–0.7085 (30)	0.7071–0.7072 (34) 0.7071 (35)	0.7072–0.7077 (34) 0.7073–0.7079 (42a,36)	0.7090–0.7092 (46) 0.7089–0.7091 (44)
Pb content	483 nmol/kg (6) 1450 nmol/kg (1)	60–275 nmol/kg (11) 14–900 nmol/kg (12) 21–265 nmol/kg (13)	0.013 nmol/kg (13) 0.01–0.03 nmol/kg (23)	15–30 µmol/kg (31)	0.48–3.48 µmol/kg (37a) 0.1–1.1 µmol/kg (37b) 0.68 µmol/kg (38); 0.05 µmol/kg (39)	mostly 10–160 µmol/kg (43) mostly 100–11,000 µmol/kg (41)	870–1210 µmol/kg (44)
$^{207}Pb/^{204}Pb$	15.44–15.54 (6,7,8)	15.48 (15a); 15.47–15.51 (15b)	15.7 (24); 15.63 (25); 15.55–15.63 (26)	15.58–15.59 (31)	ca. 15.69 (40); 15.56 (38)	15.53–15.58 (43,36)	15.48–15.58 (44)
$^{206}Pb/^{204}Pb$	18.11–18.67 (6,7,8)	18.30 (15a); 18.44–18.50 (15b)	18.8 (24); 18.91 (25); 18.79–18.82 (26)	18.83–18.99 (31)	ca. 18.72 (40); 18.62 (38)	18.70–18.77 (43,36)	18.41–18.66 (44)

Axial Mid-Ocean Ridge Basalts
(1) Average MORB (Sun and McDonough, 1989)
(2) Red Sea spreading axis: 8 basalts from 6 locations, including 2 in Atlantis II Deep (Volker et al., 1993)
(3) Red Sea: 4 basalts from spreading axis at 18°N (Eissen et al., 1989)
(4a) East Pacific MORB (Hinkley and Tatsumoto, 1987; Hegner and Tatsumoto, 1987; White et al., 1987)
(5) Red Sea: 21 basalts from spreading axis at 18°N (Eissen et al., 1989)
(6) Atlantis II Deep: 2 basalt samples (Dupré et al., 1988)
(7) Atlantis II Deep: 2 basalt samples (Volker et al., 1993)
(8) Atlantis II Deep: 1 basalt sample from hole 226, DSDP Leg 23 (Delevaux and Doe, 1974)

Mid-Ocean Ridge high-T vent fluids
(4b) Southern Juan de Fuca vents (Hinkley and Tatsumoto, 1987)
(4c) EPR 21°N vents, 3 most radiogenic fluids (Piepgras and Wasserburg, 1985)
(9) 27 samples from vents on Mid-Atlantic Ridge, East Pacific Rise, and Lau and Manus back-arc basins (Douville et al., 1999)
(10) 4 high-T vents at 37°N on Mid-Atlantic Ridge: calculated end-member values (Chavagnac et al., 2018)
(11) Juan de Fuca Ridge: 3 vents at 48°N with T = 347-368°C and salinities = 38-77 % of normal seawater (Seyfried et al., 2003)
(12) Eastern Pacific Ocean: 4 vent fields with T = 224-355°C and salinities = 69-118 % of normal seawater (Von Damm, 1990)
(13) Mid-Atlantic Ridge: 5 vent sites in basaltic settings (Douville et al., 2002)
(14) Mid-ocean ridges in eastern Pacific Ocean and Atlantic Ocean: Albarède et al. (1981), Michaud et al. (1984), Edmond et al. (1990)
(15a) Mid-Atlantic Ridge: vent fluids at 26°N (Godfrey et al., 1994)
(15b) East Pacific Rise: vent fluids at 21°N (Chen et al., 1986)

Seawater
(16a) Pacific Ocean deep seawater (>1500 m): Grasse et al. (2012), Jeandel et al. (2013); Molina-Kescher et al. (2014), Tachikawa et al. (2017)
(16b) Atlantic Ocean deep seawater (>1500 m): van de Flierdt et al. (2016), Tachikawa et al. (2017), Stichel et al. (2018)
(17) Scrivner et al. (2004): East Mediterranean shallow water: 0-200 m
(18) Tachikawa et al. (2004): East Mediterranean deep water: average of 11 samples from 857-2257 m
(19) Blanc (1987): modern Red Sea seawater
(20) Pilson (2013, chapter 4): normal seawater
(21) de Villiers (1999): normal seawater, various oceans and depths
(22) Zierenberg and Shanks (1986, 1988): Red Sea: Upper Miocene evaporites (proxy for paleo-seawater)
(23) Bridgestock et al. (2018): Central Atlantic seawater
(24) Inferred from average deep-sea Mn nodules in Pacific Ocean (Reynolds and Dasch, 1971)
(25) Ambient seawater, southern Juan de Fuca ridge (Chen, 1987)
(26) Dupré et al. (1988): Atlantis II Deep: two samples of carbonate sediment (seawater proxy) from core 684, 11.6 m and 13.7 m

Deep-sea detritus in Red Sea
(27) Laurila et al. (2014b): Atlantis II Deep: aluminosilicate component of sediment (avg. Al-rich sediment minus avg. non-detrital component)
(28) Cocherie et al. (1994): Shaban Deep: core KS-01, upper 5 m of biodetrital sediment
(29) Palchan et al. (2013): siliciclastic dust, northern Red Sea, deepwater core KL23: average of 20 samples (age = 5.5 to 20.5 Ka)
(30) Stein et al. (2007): Red Sea: loess dust in seafloor sediments over last 80 ka
(31) Dupré et al. (1988): 2 samples of Recent detrital sediment, ca. 50 km N of Atlantis II Deep; 1 sample of Miocene shale, DSDP Leg 23, hole 227 (4 km E of Atlantis II Deep)

Brines and sediments in Red Sea closed basins
(32) Cocherie et al. (1994): Shaban Deep in northern Red Sea: core KS-01, brine sample
(33) Pierret et al. (2001): Atlantis II Deep, lower brine layer
(34) Anschutz et al. (1995): Atlantis II Deep: core 684, upper 12 m of sediments: interstitial brine and metalliferous solids (measured separately)
(35) Blanc et al. (1995): Atlantis II Deep, lower brine layer
(36) Pierret et al. (2010): Atlantis II Deep: metalliferous sediment from core 1028: 5 samples at depths of 0.2 to 22.2 m
(37) Brooks et al. (1969): brines of Atlantis II Deep (37a) and nearby Discovery Deep (37b)
(38) Delevaux and Doe (1974): Atlantis II Deep: pore-water of metalliferous sediment at 4.5 m depth, hole 226, DSDP Leg 23
(39) Atlantis II Deep, lower brine layer, 2 samples from Southwest and West basins (Anschutz et al., 2000)
(40) Delevaux et al. (1967): Atlantis II Deep brine
(41) Laurila et al. (2014a): Atlantis II Deep: metalliferous sediment samples from 9 cores, salt-free basis (excludes lowest DOP facies)
(42a) Cocherie et al. (1994): Atlantis II Deep: Southwest Basin, core 268, upper 11 m: 5 samples for Nd isotopes and 13 samples for Sr isotopes
(42b) Cocherie et al. (1994): Shaban Deep, northern Red Sea: core KS-01, upper 5 m: average of 5 samples of biodetrital sediment (seawater proxy)
(43) Dupré et al. (1988): Atlantis II Deep: cores 683 & 684: 11 samples of metalliferous sediment at depths of 1-16 m

Metalliferous sediments - Eastern Pacific Ocean
(44) Barrett et al. (1986): Eastern Pacific: DSDP Leg 92 metalliferous sediments: holes 598-601, carbonate-free fraction
(45) Halliday et al. (1992): Eastern Pacific: DSDP Leg 92, hole 598 (bulk sediments)
(46) Sun et al. (2018): Juan de Fuca Ridge: Fe-Mn oxyhydroxides on ridge flank

Barrett et al 2021 EarthSciRev SUPPLEMENTARY DATA TABLE 1

Supplementary Data Table 1. Chemical analyses of metalliferous sediments from the Atlantis II Deep, Red Sea

Sample no. [1]	Depth in core	Lab no.	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$ (t)	MnO	MgO	CaO	K$_2$O	LOI	Total [2]	CO$_2$ (t)	C	S (t)	Na	Cl	Ba	Cu	Zn	Pb	Au	Ag	As	Sb	Bi	Cd	In	Tl	Br	Rb	Cs
	cm		wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
			ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES	ICP-ES					LECO	INAA	calculated	INAA	ICP-ES	INAA	AA	INAA	ICP-MS	INAA	INAA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	INAA	ICP-MS	ICP-MS
274-1	ca. 100	RS-1														11400	17579	570	470	5800	130	0.35	5.2	220	29	<0.5	12	0.11	3.3	24	52	4.4
274-4	ca. 390	RS-2*	15.4	0.06	1.2	8.8	0.47	0.34	14.90	0.18	21.8	63.2				4150	6399	61000		48000		3.73	120	520	95	1.8	280	0.17	27	9	9.1	0.8
274-8	ca. 730	RS-3	9.1	0.02	0.3	78.7	0.21	0.09	0.10	0.05	10.7	99.3				916	1412	1000		670		0.62	1.8	170	11	0.6	4.2	0.08	1.0	3.3	5.7	0.2
274-12	ca. 950	RS-4														4370	6738	7900	14000	27000	860	3.27	78	190	60	0.7	120	0.35	23	4.8	11	0.7
274-13	ca. 1000	RS-5														2090	3223	470	3800	1400	71	0.58	9.7	160	16	0.7	2.2	1.20	2.0	6.6	1.5	0.1
274-15	ca. 1080	RS-6														8770	13523	790	4900	28000	490	1.57	46	170	33	<0.5	72	0.21	6.0	15	39	3.0
48-1	111-114	RS-7	17.3	0.04	1.0	56.4	0.10	0.47	0.62	0.23	15.8	92.0	<0.1	0.4	3.2	10700	16499	360	7600	7200	890	2.24	52	440	30	<0.5	14	0.29	25	13	8.9	0.7
48-2	484-487	RS-8	19.5	0.05	1.3	51.2	0.06	8.59	0.83	0.13	8.3	90.0	<0.1	0.4	3.0	21900	33769	<79	8700	510	250	2.78		350	14					14		
54-1	151-154	RS-9	22.5	0.07	1.4	38.3	0.13	0.93	1.38	0.41	18.5	83.6				19600	30223	360	9000	72000	850	2.83	75	340	43	<0.5	230	0.48	4.5	23	17	2.2
54-2	394-398	RS-10	24.4	0.07	1.6	50.5	0.17	4.51	1.73	0.25	10.4	93.6	0.1	0.6	2.0	10400	16037	660	4300	11000	600	1.99	46	470	33	<0.5	24	0.13	5.8	7.1	12	1.2
64-1	148-152	RS-11	16.3	0.04	1.5	44.1	0.10	1.08	0.78	0.18	23.5	87.6	<0.1	0.3	6.7	10200	15728	980	14000	65000	1100	3.94	110	310	45	0.6	260	0.20	46	9.5	7	0.6
64-3	567-569	RS-12*	19.9	0.10	2.0	30.4	0.41	1.66	8.69	0.40	16.8	80.4	1.1	1.0	7.6	5920	9128	3500	14000	29000	770	3.29	89	170	38	<0.5	99	0.20	13	9.9	19	1.3
71-1	190-194	RS-13	15.7	0.05	1.5	38.1	0.05	1.07	0.75	0.24	23.9	81.4	0.3	0.3	7.1	8670	13369	930	15000	110000	1200	5.03	130	400	54	0.6	400	0.15	40	10	7.9	0.7
71-2	492-497	RS-14	18.0	0.08	2.0	51.9	0.04	5.26	1.24	0.07	12.0	90.6	<0.1	0.4	7.2	6600	10177	350	14000	24000	430	4.00	110	500	60	0.5	160	0.28	15	10	3.2	0.4
71-3	967-970	RS-15	18.4	0.04	1.1	65.9	0.11	0.78	2.18	0.10	4.2	92.8				10600	16345	<85	9300	8200	230	2.36	48	130	14	0.6	47	0.06	7.0	9.2	4.6	0.3
98-1	113-116	RS-16	17.3	0.04	1.1	37.0	0.18	0.62	1.41	0.46	19.5	77.6				37100	57201	590	8100	80000	790	2.97	89	320	44	<0.5	250	0.37	6.9	32	13	1.2
98-2	224-227	RS-17	15.4	0.07	1.7	60.2	1.52	0.83	2.23	0.49	12.5	94.9				4330	6677	1100	9500	12000	440	2.36	82	290	38	0.7	63	0.08	5.0	6.1	46	1.1
98-3	508-511	RS-18	17.6	0.05	1.9	31.9	0.15	0.88	2.44	0.38	23.3	78.6	0.4			7450	11488	<120	12000	150000	1300	4.40	140	300	69	0.5	480	0.13	17	7.3	22	0.9
345-1	182-186	RS-19	18.7	0.04	0.8	53.3	0.97	0.66	1.27	0.56	15.8	92.1	1.9			20500	31610	<79	3700	7600	770	1.70	24	830	20	<0.5	23	0.26	5.1	24	18	1.2
345-2	369-372	RS-20	28.7	0.07	2.5	25.9	0.25	2.37	0.89	0.38	28.3	89.4				15500	23901	490	14000	63000	1500	3.90	170	520	47	0.7	130	0.26	51	21	13	1.0
345-3	451-453	RS-21	9.5	0.01	3.0	82.0	0.69	0.10	0.14	0.18	11.5	104.4				6370	9822	1500	880	3500	61	0.20	1.2	79	6.5	<0.5	3.1	<0.05	6.8	3.3	0.2	0.2
345-4	507-510	RS-22														8910	13739	<100	1500	2600	160	0.29	0.8	370	7.3	<0.5	1.4	0.06	0.4	7.1	5.1	0.4
345-5	570-574	RS-23	21.2	0.02	0.4	43.8	4.14	0.90	1.67	0.41	20.0	92.5	12.4	<0.2	0.2	22700	35003	7400	3200	1700	140	0.55	2.0	200	16	<0.5	0.7	0.52	0.6	16	12	2.0
361-1	169-163	RS-24	25.7	0.09	1.8	43.5	0.09	1.34	1.69	0.44	13.8	88.5	<0.1	0.7	3.4	13900	21433	440	12000	40000	850	3.42	94	270	44	<0.5	110	0.13	11	21	17	1.7
367-1	24-26	RS-25	26.9	0.11	2.0	25.7	0.19	2.64	3.96	0.38	20.5	82.4				19500	30069	<100	8400	76000	690	2.87	100	100	48	0.5	200	0.20	15	31	12	0.9
367-2	117-121	RS-26	46.0	0.12	1.9	26.4	0.10	3.62	1.68	0.40	22.7	102.9				13800	21279	<100	12000	75000	640	3.77	150	63	92	0.6	250	0.18	13	19	11	0.8
367-3	187-190	RS-27	31.2	0.06	1.1	38.0	0.04	9.21	0.99	0.72	13.3	94.6				49900	76945	620	4600	12000	130	1.49	13	200	13	<0.5	19	1.10	1.5	27	7.8	0.8
367-4	459-463	RS-28														23200	35774	8100		120000		3.08	87	680	57	1.1	230	0.19	28	10	15	1.1
369-1	134-137	RS-29	18.8	0.05	1.0	55.5	0.47	0.55	0.65	0.35	15.5	92.9	0.4	0.4	2.1	12900	19891	<64	3700	6400	680	1.33	51	360	18	<0.5	11	0.13	21	15	15	1.1
369-2	413-414	RS-30	30.7	0.07	1.8	35.0	0.90	1.37	1.51	0.52	20.5	92.4				20200	31148	1500	5700	21000	1100	1.68	99	210	36	<0.5	45	0.06	33	16	22	2.0
369-3	476-485	RS-31**	5.2	0.01	0.1	0.1	bd	bd	36.60	0.07	8.8	50.9				818	1261	6900	<100	170	8	0.04	0.5	4.7	0.4	<0.5	0.7	0.49	1.5	<0.5	0.3	0.0
397-1	71-74	RS-32	22.7	0.09	1.9	36.0	0.11	1.13	1.35	0.67	18.5	82.5	<0.1	0.6	4.4	38300	59058	1000	14000	32000	740	3.15	270	280	41	<0.5	87	0.11	21	43	18	1.4
397-2	244-247	RS-33	23.4	0.05	1.0	48.4	0.05	0.83	0.93	0.51	13.8	89.0				26000	40091	260	6800	14000	660	2.29	38	310	27	0.6	24	1.20	11	22	16	1.4
397-3	550-553	RS-34	39.4	0.03	1.2	32.3	0.09	1.21	1.14	0.58	15.2	91.2				19900	30685	<76	8300	11000	750	2.19	38	230	42	<0.5	12	0.08	23	17	25	1.3
397-4	583-585	RS-35	17.4	0.27	3.9	54.5	3.74	1.20	1.21	0.72	13.0	95.9				4180	6445	3200	1500	6100	180	0.24	3.5	750	16	<0.5	15	0.17	3.1	<0.5	29	2.4
409-1	146-149	RS-36	24.5	0.07	1.5	36.3	0.06	1.12	1.24	0.32	21.3	86.4				21100	32536	510	7100	41000	830	2.14	40	240	31	0.6	110	0.24	20	19	10	0.8
409-2	317-321	RS-37	17.4	0.04	1.2	46.2	0.05	0.66	0.65	0.25	23.7	90.2	0.2			9530	14695	<76	8200	40000	1200	3.49	85	430	37	0.5	130	0.21	36	9.3	11	0.8
409-3	572-576	RS-38	21.6	0.05	1.2	56.1	0.33	2.03	1.45	0.22	10.1	93.1				6950	10717	520	9000	12000	520	2.77	71	150	51	0.5	37	0.17	9.0	10	17	0.7
416-1	112-116	RS-39	20.7	0.09	1.8	35.8	0.07	1.38	0.93	0.34	22.9	84.0	0.1	0.5	6.5	8580	13230	<100	11000	110000	1100	4.25	180	240	50	<0.5	350	0.57	15	12	13	1.1
416-2	341-345	RS-40	17.8	0.05	1.2	51.5	0.41	4.23	1.21	0.14	14.1	90.6	1.4	0.3	3.1	14900	22975	<76	9500	33000	140	3.35	56	70	12	<0.5	76	0.14	1.6	10	3.4	0.3
416-3	553-556	RS-41	25.8	0.10	2.8	29.1	0.12	2.48	0.91	0.30	24.0	85.7	<0.1			10800	16653	<100	18000	81000	1200	4.57	120	530	84	0.5	160	0.33	28	23	10	0.7
419-1	149-153	RS-42	18.1	0.04	1.2	49.7	0.06	0.89	0.61	0.29	20.3	91.2	<0.1			6350	9792	310	8100	29000	1200	3.31	74	540	39	0.5	83	0.24	33	8.9	12	0.9
419-2	288-292	RS-43	36.8	0.01	0.1	42.9	0.07	2.28	0.39	2.43	11.4	96.4	<0.1	0.4	4.9	11600	17887	920	150	1600	430	0.64	2.1	240	200	<0.5	4.7	1.10	1.5	11	100	2.3
436-1	216-219	RS-44	28.5	0.12	2.1	39.4	0.24	1.45	2.91	0.87	14.2	89.8				11700	18041	1100	12000	20000	420	2.09	84	190	27	<0.5	21	0.19	19	30	35	2.6
436-2	359-362	RS-45	17.8	0.04	0.8	49.4	0.12	0.56	0.53	0.99	18.2	88.4	<0.1	0.4	1.5	51400	79258	<100	750	2200	440	1.35	16	441	15	<0.5	4.0	0.33	13	45	15	0.9
436-3	671-674	RS-46														24000	37007	<100	8700	16000	1200	2.19	62	379	38	0.5	18	0.10	32	28	31	1.5
436-5	950-953	RS-47	24.0	0.02	0.3	36.5	5.28	1.41	1.95	0.62	23.6	93.7	13.6	<0.2	0.0	40500	62450	<76	940	4000	64	0.19	0.7	23	3.4	<0.5	3.5	0.12	1.2	33	22	2.8
436-6	962-966	RS-48	13.1	0.08	1.1	67.8	0.23	0.37	0.30	0.40	12.0	95.4				2900	4472	<76	400	1900	14	0.05	0.7	645	8	<0.5	4.5	0.18	0.7	1.7	21	2.8
436-7	973-975	RS-49														16600	25597	8700	340	2500	410	0.06		152	12					4.3		
436-8	994-997	RS-50														6700	10331	6800	130	470	55	0.04	0.6	233	5.9	<0.5	1.9	0.10	4.1	0.2		
443-1	135-138	RS-51	17.3	0.05	1.2	52.5	0.20	0.49	0.84	0.38	19.5	92.5				9400	14495	400	12000	7700	1000	3.30	33	494	35	<0.5	4.5	<0.05	11	20	3.9	0.3
443-2	261-264	RS-52														3700	5705	2700	11000	18000	1200	2.94	240	523	140	0.7	80	0.15	27	15	17	1.2
443-3	472-475	RS-53	31.0	0.05	1.7	21.5	0.39	0.23	1.42	0.30	26.1	82.7				8200	12644	9800	9400	120000	1500	3.48	150	1600	51	0.6	290	0.35	69	14	10	1.1

[1] First part of sample number refers to the core number (cruise names and location data given in Table 1).

[2] Totals are the sum of the major elements + LOI. The 2 samples with unusually low totals (51% and 63 %) have the highest contents of anhydrite in the data set. The sample with the highest total (104 %) has the highest Fe content in the data set (the iron occurs as limonite).

Analytical methods are given in the third row.

Note: Se <3 ppm (DL) in all samples.

Note: Hg <2 ppm (DL) in all samples except RS-37 (3 ppm) and RS-41 (7 ppm).

*Anhydrite-bearing sample

**Massive anhydrite

Supplementary Data Table 1.

Sample no. (1)	Depth in core	Lab no.	Cr	Ni	Co	Sc	Sn	W	Mo	Ga	U	Hf	Ta	Th	Nb	Y	Zr
	cm		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
			INAA	ICP-ES	INAA	INAA	ICP-MS	INAA	INAA	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
274-1	ca. 100	RS-1	110	92	44	15	2.4	<1	67	16	7.2	2.30	1.3	4.80	13.0	25.0	93
274-4	ca. 390	RS-2*	31		350	2.0	0.7	29	240	28	5.4	0.29	0.4	0.53	1.6	2.5	13
274-8	ca. 730	RS-3	26		6	0.8	0.5	9	350	6.4	24	0.08	0.3	0.23	0.9	1.2	5.9
274-12	ca. 950	RS-4	35	120	210	2.8	0.8	21	220	35	7.2	0.34	0.2	0.61	2.2	3.3	13
274-13	ca. 1000	RS-5	10	29	22	0.9	4.5	6	400	7.6	23	0.07	<0.2	0.16	1.1	1.6	5.8
274-15	ca. 1080	RS-6	27	46	140	2.4	1.1	66	85	15	7.4	0.55	0.2	0.53	2.2	3.3	23
48-1	111-114	RS-7	22	40	220	1.2	3.8	13	360	14	12	0.31	<0.2	0.21	0.7	1.6	15
48-2	484-487	RS-8	27	59	130	1.5		19	160								
54-1	151-154	RS-9	20	63	110	1.7	17	20	150	21	8.4	0.29	<0.2	0.41	1.3	2.8	16
54-2	394-398	RS-10	27	53	250	2.1	<0.5	43	170	18	9.6	0.41	<0.2	0.48	1.5	3.0	21
64-1	148-152	RS-11	32	61	340	1.3	1.2	17	280	23	16	0.21	<0.2	0.25	0.8	1.8	11
64-3	567-569	RS-12*	29	56	280	2.5	1.5	23	70	18	5.6	0.56	<0.2	0.60	1.9	3.9	25
71-1	190-194	RS-13	33	66	250	1.7	0.6	<1	220	26	12	0.34	<0.2	0.38	1.2	2.2	16
71-2	492-497	RS-14	28	77	280	2.3	0.9	28	290	27	17	0.44	<0.2	0.54	1.7	3.2	22
71-3	967-970	RS-15	30	46	140	1.0	<0.5	15	220	16	14	0.13	0.2	0.23	0.9	1.8	7.3
98-1	113-116	RS-16	10	78	180	1.0	1.0	19	140	20	8.4	0.27	<0.2	0.25	0.8	1.9	13
98-2	224-227	RS-17	41	48	77	1.6	<0.5	20	230	20	20	0.23	0.2	0.42	1.3	2.5	12
98-3	508-511	RS-18	34	67	280	1.2	0.5	19	220	37	8.7	0.22	<0.2	0.27	1.0	1.8	13
345-1	182-186	RS-19	18	32	75	1.3	10	<1	400	11	8.7	0.24	<0.2	0.28	0.8	2.0	14
345-2	369-372	RS-20	28	74	280	2.0	1.6	28	170	36	4.4	0.39	0.2	0.40	1.3	2.5	19
345-3	451-453	RS-21	21	36	28	1.4	<0.5	<1	300	19	23	0.10	0.2	0.17	1.0	1.3	6.3
345-4	507-510	RS-22	10	15	16	1.4	<0.5	<1	320	6.7	20	0.08	<0.2	0.15	1.1	1.4	6.4
345-5	570-574	RS-23	13	<15	21	0.9	1.5	<1	140	8.6	6.1	0.16	<0.2	0.14	0.6	1.9	8.1
361-1	169-163	RS-24	27	35	220	2.0	0.5	19	140	21	11	0.40	<0.2	0.47	1.7	3.2	21
367-1	24-26	RS-25	23	35	390	2.7	0.7	19	100	25	7.7	0.59	<0.2	0.53	1.8	3.7	29
367-2	117-121	RS-26	29	35	210	2.1	0.8	53	82	28	8.4	0.48	0.4	0.51	1.7	5.3	23
367-3	187-190	RS-27	17	14	99	1.7	2.5	80	170	12	14	0.28	<0.2	0.42	1.2	3.1	16
367-4	459-463	RS-28	10		130	2.0	1.2	23	290	33	1.8	0.73	0.5	0.44	1.5	2.0	31
369-1	134-137	RS-29	20	19	210	1.3	1.0	11	240	13	11	0.25	<0.2	0.36	1.0	1.8	14
369-2	413-414	RS-30	24	39	300	1.9	3.5	26	130	28	7.4	0.26	0.3	0.41	1.4	2.4	12
369-3	476-485	RS-31**	<5	<15	2	0.2	0.6	<1	<2	0.7	0.3	0.07	<0.2	<0.02	0.1	0.3	3.3
397-1	71-74	RS-32	21	31	360	1.9	<0.5	26	170	22	8.5	0.46	0.2	0.95	1.8	3.4	20
397-2	244-247	RS-33	16	26	180	1.4	6.7	<1	130	16	9.6	0.39	<0.2	0.30	1.0	2.1	18
397-3	550-553	RS-34	20	18	81	0.9	2.1	66	190	28	9.5	0.09	0.7	0.14	0.6	1.8	6.6
397-4	583-585	RS-35	46	19	23	5.4	0.7	<1	490	10	17	1.30	0.4	1.90	5.1	9.0	57
409-1	146-149	RS-36	18	22	240	1.4	0.7	26	170	20	7.9	0.31	0.3	0.42	1.4	2.6	17
409-2	317-321	RS-37	18	32	270	1.1	0.5	19	290	21	10	0.22	0.4	0.20	0.7	1.5	11
409-3	572-576	RS-38	24	18	180	1.3	0.5	16	200	19	12	0.31	0.2	0.29	1.0	2.5	16
416-1	112-116	RS-39	32	48	300	1.8	1.5	18	140	27	10	0.48	0.3	0.53	1.7	3.4	22
416-2	341-345	RS-40	23	21	97	1.4	<0.5	26	120	17	10	0.32	0.4	0.34	1.2	2.7	16
416-3	553-556	RS-41	27	100	330	2.2	1.5	15	250	51	7.5	0.57	0.7	2.20	9.2	5.8	24
419-1	149-153	RS-42	10	29	260	1.0	0.6	15	240	22	12	0.21	0.4	0.23	0.8	1.7	11
419-2	288-292	RS-43	7	<15	7	0.4	2.6	30	70	5.4	5.0	0.05	<0.2	0.06	0.3	1.5	4.1
436-1	216-219	RS-44	30	18	220	2.5	0.7	17	140	18	10	0.53	0.2	0.82	2.1	4.2	26
436-2	359-362	RS-45	18	8	110	0.9	0.9	14	290	11	9.7	0.18	0.2	0.18	0.6	1.4	9.5
436-3	671-674	RS-46	20	33	99	1.4	<0.5	16	110	34	2.6	0.18	0.2	0.30	0.7	2.0	8.7
436-5	950-953	RS-47	<5	29	24	0.8	<0.5	31	33	4.1	2.5	0.08	0.3	0.12	0.4	1.7	4.2
436-6	962-966	RS-48	36	16	14	1.9	0.5	<1	350	1.9	6.0	0.54	0.2	0.50	1.3	2.5	26
436-7	973-975	RS-49	28	<15	150	3.2		<1	290								
436-8	994-997	RS-50	<5	<15	8	1.5	1.0	<1	300	1.2	25	0.14	<0.2	0.15	0.7	1.2	8.4
443-1	135-138	RS-51	17	17	360	1.6	<0.5	70	330	5	3.8	0.05	<0.2	0.07	0.3	0.4	2.7
443-2	261-264	RS-52	10	28	150	1.9	1.0	22	450	18	17	0.22	0.3	0.38	1.4	2.3	14
443-3	472-475	RS-53	25	46	190	1.8	0.6	18	370	37	11	0.27	<0.2	0.21	0.7	2.4	14

(1) First part of sample number refers to the c
(2) Totals are the sum of the major elements
Analytical methods are given in the third row
Note: Se <3 ppm (DL) in all samples.
Note: Hg <2 ppm (DL) in all samples except R
*Anhydrite-bearing sample
**Massive anhydrite

Supplementary Data Table 2. Chemical analyses of metalliferous sediments from the East Pacific Rise transect (DSDP Leg 92) on a carbonate-free basis

Lab no.	DSDP no.*	Depth**	Depth BSF***	SiO_2	TiO_2	Al_2O_3	$Fe_2O_3(t)$	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Trace elements	Total using Fe_2O_3 measured by ICP	Total using Fe_2O_3 calculated from Fe measured by INAA	Fe	Ba	Cu	Pb	Zn	Au	Ag	As	Sb	Bi	Cd	Tl	In	V
		(cm)	(m)	wt% ICP-ES	wt% ICP-ES	wt% ICP-ES	wt% ICP-ES	wt% ICP-ES	wt% ICP-ES	wt% ICP-ES	wt% ICP-ES	wt% ICP-ES	wt% ICP-ES	wt%	wt%			wt% INAA	ppm INAA	ppm ICP-ES	ppm ICP-ES	ppm INAA	ppb INAA	ppm ICP-MS	ppm INAA	ppm INAA	ppm ICP-MS	ppm ICP-MS	ppm ICP-MS	ppm ICP-MS	ppm ICP-ES
DS-1	597-2-1	76-78	5.37															37.2	2200			1300	9		436	20					
DS-2	597-2-3	75-77	8.36															40.5	2200			1400	5		425	14					
DS-3	597-2-6	68-79	12.84															38.0	2500			1400	4		377	11					
DS-4	597-3-2	78-90	16.54															38.5	4100			1700	45		373	11					
DS-5	597-3-5	76-78	20.97															37.6	2200			1200	32		357	10					
DS-6	597-4-1	69-71	24.50															34.6	2400			1000	7		327	7.7					
DS-7	597-4-3	74-76	27.55															35.1	2600			1100	20		317	7.6					
DS-8	597-4-6	74-76	32.05															33.6	2600			1000	46		356	7.3					
DS-9	597A-5-1	74-76	34.15															33.4	1500			810	60		344	6.6					
DS-10	597A-5-3	75-77	37.16															29.2	1400			1000	<3		310	5.6					
DS-17	597-6-1	75-77	43.76	9.5	0.27	2.97	44.0	15.5	1.15	1.91	0.17	0.39	1.57	20.1	0.680	98.2	100.1	32.1	1300	1200	150	930	7	6.9	369	6.5		3.9	10	0.15	1300
DS-18	597-6-3	74-76	46.75	10.7	0.39	3.44	41.2	15.3	1.06	2.98	0.27	0.46	1.90	19.6	0.696	98.0	100.3	30.4	1500	1300	88	1000	4	21.0	372	8.5		4.6	13	0.16	1200
DS-19	597-6-4	74-76	48.25	14.2	0.48	3.55	41.9	13.7	1.14	1.66	0.20	0.57	1.23	19.0	0.663	98.3	103.0	32.6	1400	1200	56	1200	29	5.2	389	17	1.3	4.5	11	0.12	1200
DS-20	597-6-5	74-76	49.75	12.1	0.47	3.91	39.6	15.2	1.11	2.52	1.63	0.63		19.4	0.150	96.7	98.4	28.9	1400			790	18		366	17					
DS-21	597-6-6	74-76	51.25	9.0	0.44	3.18	44.6	13.9	1.30	1.79	2.12	0.37		19.8	0.177	96.7	99.0	32.8	1500			1100	3		389	18					
DS-22	598-1-1	71-73	0.72	22.6	0.65	7.41	34.9	7.5	1.51	3.20	0.38	0.87	2.98	17.2	1.457	100.6	101.2	24.8	8100	1800	160	820	3	2.0	358	21	2.2	1.3	5.9	0.26	540
DS-23	598-1-2	71-73	2.22	16.5	0.47	6.38	43.1	6.8	1.61	2.50	0.26	0.73	3.02	17.5	1.046	99.9	100.7	30.7	3100	2200	140	1000	10	5.8	440	21	1.9	1.3	6.1	0.31	690
DS-24	598-1-4	71-75	5.23	12.4	0.26	4.68	47.3	6.3	1.54	3.20	0.26	0.39	3.15	18.0	1.368	98.8	101.7	35.1	8300	2000	160	990	16	12	411	20	2.6	1.6	5.3	0.16	680
DS-11	598-2-2	72-76	8.44															34.0	7100			1000	40		304	13					
DS-12	598-2-3	72-76	9.94															39.2	6100			1200	9		365	15					
DS-13	598-2-5	79-83	13.01															39.2	3500			1000	16		392	15					
DS-25	598-3-1	67-69	16.48	7.5	0.17	2.00	58.4	8.6	1.27	0.79	0.10	0.14	1.74	18.8	0.764	100.3	101.5	41.7	2500	1700	140	1100	17	60	414	15	0.6	1.3	5.8	0.24	1000
DS-14	598-3-2	73-77	18.05															40.6	2800			1100	25		414	14					
DS-15	598-3-3	71-75	19.53															39.4	2200			1100	30		423	11					
DS-26	598-3-4	70-74	21.02	6.0	0.11	1.05	51.4	14.5	0.94	1.29	0.06	0.07	1.73	20.2	0.732	98.1	100.6	37.7	2600	1400	120	990	<4	36	409	9.3	1.1	2.2	7.9	0.23	1000
DS-27	598-4-1	15-17	25.56	5.3	0.10	0.95	27.7	17.1	0.90	1.02	0.03	0.03	0.89	20.6	0.509	75.1	99.5	36.4	2100	820	80	1000	5	13	423	9.5	0.8	2.3	12	0.20	620
DS-28	598-4-3	25-27	28.66	5.3	0.10	0.96	45.8	16.2	0.94	1.27	0.04	0.06	1.31	20.8	0.719	93.5	99.2	36.0	1800	1500	140	1000	9	3.1	439	8.8		1.9	13	0.22	1000
DS-29	598-4-5	26-28	31.67	4.6	0.10	0.93	51.8	17.2	0.97	0.78	3.76	0.07		20.5	0.228	100.9	101.5	36.6	2100			920	10		464	9.2					
DS-30	598-5-1	81-83	35.82	5.3	0.09	0.88	50.8	17.7	0.94	0.85	1.71	0.08		20.4	0.247	99.0	99.8	36.1	2300			960	4		444	8.8					
DS-31	598-5-2	72-74	37.23	4.6	0.06	0.67	51.9	16.2	0.92	0.84	<0.03	0.03	1.27	20.4	0.728	97.6	97.5	36.2	2100	1500	130	1000	4	3.3	439	8.6		2.0	10	0.25	1200
DS-32	598-5-4	80-82	40.31	5.7	0.07	0.69	50.0	15.3	0.90	1.19	<0.03	0.05	1.57	19.9	0.719	96.1	100.0	37.7	2700	1400	130	1100	9	2.6	459	8.2		2.4	10	0.32	1100
DS-16	598-5-5	71-73	41.72															36.5	2500			1100	4		434	7.8					
DS-33	598-5-6	71-73	43.22	7.4	0.14	1.58	46.7	14.5	1.29	2.22	1.28	0.10		19.5	0.250	95.0	100.2	36.3	2100			750	11		471	7.5					
DS-34	599-1-1	71-75	0.73	17.9	0.41	7.10	36.7	6.0	1.40	2.40	0.71			18.0	1.147	95.8	101.5	29.6	14000			1000	20		428	20					
DS-35	599-1-5	72-76	6.74	8.4	0.13	1.79	54.1	10.3	1.11	0.41	3.33	0.13		19.9	0.316	99.9	106.4	42.4	3500			860	50		437	15					
DS-36	599-2-2	70-74	10.12	6.6	0.05	0.38	48.0	14.8	0.76	3.89	0.04	0.03	2.99	20.5	0.709	98.7	97.5	32.7	2500	1500	110	890	9	1.8	416	6.1		1.7	11	0.27	1100
DS-37	599-2-3	70-74	11.62	7.0	0.06	0.55	51.1	14.7	0.83	1.03	<0.03	0.03	1.93	20.4	0.779	98.4	97.2	34.9	2800	1500	130	930	6	2.7	443	6.3		1.7	12	0.25	1100
DS-38	599-2-5	70-73	14.62	7.8	0.06	0.59	48.0	14.7	0.81	0.78	0.03	0.03	1.69	20.3	0.714	95.5	96.4	34.2	2300	1400	120	860	7	3.4	414	7.0		1.6	12	0.26	980
DS-39	599-3-1	70-74	18.22	12.5	0.06	0.53	46.3	13.5	0.77	2.18	0.03	0.03	1.90	20.1	0.733	98.6	98.1	32.0	3100	1400	130	870	9	3.9	437	5.6		2.2	13	0.24	990
DS-40	599-3-2	70-74	19.72	8.2	0.05	0.31	49.3	14.7	0.74	0.93	<0.03	0.03	1.52	20.0	0.688	96.5	95.8	34.0	2400	1400	120	840	13	12	452	5.8		1.7	15	0.27	1100
DS-41	599-3-5	70-74	24.22	7.5	0.04	0.32	47.8	14.8	0.70	3.44	0.04	0.03	2.94	20.2	0.717	98.5	97.3	32.6	2100	1500	290	810	9	1.1	437	5.4		2.0	13	0.25	1100
DS-42	599-4-1	71-73	27.82	7.2	0.06	0.32	29.9	16.6	0.67	0.50	<0.03	0.03	1.35	21.1	0.491	78.2	96.8	33.9	2100	840	85	720	15	1.5	433	6.5		1.1	8.9	0.13	640
DS-43	599-4-3	71-73	30.82	9.8	0.06	0.79	48.4	14.0	0.89	0.38	0.03	0.05	1.19	20.3	0.723	96.6	97.5	34.5	2500	1500	140	920	10	7.4	447	6.8		2.1	12	0.31	1000
DS-44	599-4-4	72-74	32.33	7.1	0.05	0.35	42.1	15.8	0.70	2.29	<0.03	0.03	2.03	20.9	0.651	92.0	95.7	32.0	2400	1300	110	780	24	2.7	430	5.4		1.8	13	0.20	960
DS-45	599-4-5	72-74	33.82	7.0	0.05	0.39	34.9	14.9	0.75	1.90	<0.03	0.03	1.57	20.6	0.596	82.7	96.1	33.8	2200	1100	94	830	40	5.5	481	5.8		1.7	9.9	0.20	810
DS-46	599B-2-3	70-74	36.02	8.6	0.08	1.02	50.1	10.9	1.37	0.92	<0.03	0.03	0.54	19.8	0.465	93.8	96.3	36.8	3200	490	53	800	28	3.8	478	7.0	0.6	2.8	15	0.15	370
DS-47	599B-2-4	70-73	37.52	5.6	0.08	0.53	49.2	15.2	0.78	2.20	<0.03	0.03	2.45	20.7	0.729	97.5	98.1	34.8	2600	1500	120	790	9	3.9	503	5.5		2.6	12	0.31	1200
DS-48	599B-2-5	74-77	39.06	7.5	0.19	1.40	45.1	12.7	1.10	4.18	0.05	0.27	3.74	19.4	0.616	96.2	97.5	32.4	1400	1400	120	870	20	1.6	475	12		3.6	9.2	0.31	1000
DS-49	599B-2-6	71-74	40.53	10.2	0.28	1.99	42.2	12.4	1.31	3.94	0.05	0.51	3.73	19.5	0.580	96.7	97.0	29.7	950	1300	100	780	13	18	423	15		3.7	10	0.28	940
DS-52	600C-1-2	94-99	2.47	8.9	0.24	3.24	34.1	5.5	1.01	14.70	1.40	0.22		23.6	0.779	93.7	98.9	27.5	9500			790	33		373	16					
DS-53	600C-1-4	99-104	5.52	6.1	0.10	1.54	38.4	11.2	1.10	0.70	<0.03	0.05	1.30	19.9	0.840	81.2	99.0	39.3	5100	1200	97	890	15	7.3	534	11		2.0	8.6	0.19	860
DS-54	600C-1-6	99-104	8.52	5.4	0.15	0.95	33.7	14.6	0.86	2.87	<0.03	0.03	2.50	20.9	0.571	82.5	95.9	32.9	2200	1000	110	960	22	2.8	489	6.2		4.2	10	0.20	800
DS-55 #	600C-2-2	91-96	11.84	24.5	0.70	4.89	33.5	8.6	2.19	0.82	<0.03	0.39	0.29	18.2	0.194	94.3	97.4	25.6	790	300	46	590	20	4.0	201	12		1.6	2.1	0.15	190
DS-50	601B-1-2	76-81	16.69	5.1	0.10	0.77	51.3	14.7	1.03	0.63	<0.03	0.03	1.79	20.4	0.772	96.6	98.8	37.4	2300	1600	160	1100	9	1.4	536	7.8		4.6	12	0.42	1300
DS-51	601B-1-3	74-79	18.17	4.8	0.10	0.71	45.8	14.5	1.00	4.56	0.04	0.03	3.74	20.1	0.701	96.1	99.3	34.3	1700	1500	150	900	10	9.6	515	9.2		5.2	18	0.33	1200

* Sample number indicates hole-core-section
** Depth in section
*** BSF = below sea floor
\# Contains basaltic material
Note: 4 samples from Sites 599 and 600 yielded $CO_2(t)$, C and $S(t)$ contents of, respectively, ≤ 1.0 %, ≤ 0.2 % and ≤ 0.02 %.
Hg <1 ppm (INAA detection limit) in all samples except DS-32 (3 ppm).
Se <3 ppm (INAA detection limit) in all samples.
Br <1 ppm (INAA detection limit) in all samples except DS-54 (4.0 ppm).
Cs <1 ppm (INAA detection limit) in all samples except DS-2 (5 ppm) and DS-15 (3 ppm).
Ta <1 ppm (INAA detection limit) in all samples except DS-49 (2.0 ppm).

Supplementary Data Table 2. Chemical anal...

Lab no.	DSDP no.*	Depth**	Depth BSF***	Cr	NI	Co	Sc	Sn	Mo	W	Ga	Be	Rb	Sr	Cs	U	Hf	Th	Nb	Y	Y	Zr	Zr	La
		(cm)	(m)	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
				INAA	ICP-ES	INAA	INAA	ICP-MS	INAA	INAA	ICP-MS	ICP-ES	ICP-MS	ICP-ES	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-ES	ICP-MS	ICP-ES	ICP-MS	ICP-MS
DS-1	597-2-1	76-78	5.37	18		130	13		310	18														
DS-2	597-2-3	75-77	8.36	27		130	6.6		350	21														
DS-3	597-2-6	68-79	12.84	29		120	11		93	11														
DS-4	597-3-2	78-90	16.54	34		120	11		110	9														
DS-5	597-3-5	76-78	20.97	33		120	9.1		92	3														
DS-6	597-4-1	69-71	24.50	19		110	5.8		88	8														
DS-7	597-4-3	74-76	27.55	12		120	5.9		95	13														
DS-8	597-4-6	74-76	32.05	24		110	6.9		83	3														
DS-9	597A-5-1	74-76	34.15	13		120	6.3		64	14														
DS-10	597A-5-3	75-77	37.16	27		100	9.1		71	12														
DS-17	597-6-1	75-77	43.76	37	790	110	7.6	27	230	9	23	3.1	7.4	320	0.26	1.9	1.20	0.65	5.4	95	86	95	91	79
DS-18	597-6-3	74-76	46.75	<5	770	120	11	31	510	11	18	2.3	7.5	350	0.20	2.2	0.95	0.50	5.5		110	67	64	85
DS-19	597-6-4	74-76	48.25	<5	710	110	11	16	610	17	16	2.6	11.0	210	0.21	1.8	1.10	0.51	6.7	73	62		160	56
DS-20	597-6-5	74-76	49.75	18		100	9.1		610	18														
DS-21	597-6-6	74-76	51.25	<5		98	8.7		530	63														
DS-22	598-1-1	71-73	0.72	<5	1200	410	41	5.4	170	26	16	2.4	27	240	1.80	2.6	7.90	6.5	32		640		450	
DS-23	598-1-2	71-73	2.22	<5	1200	300	35	9.8	190	22	14	3.0	21	200	1.20	4.0	7.20	3.2	27		600		470	
DS-24	598-1-4	71-75	5.23	<5	670	250	21	31	220	15	16	4.4	11	200	0.74	2.9	3.30	1.9	16		480		250	
DS-11	598-2-2	72-76	8.44	11		140	12		200	23														
DS-12	598-2-3	72-76	9.94	<5		150	13		200	12														
DS-13	598-2-5	79-83	13.01	<5		130	12		180	11														
DS-25	598-3-1	67-69	16.48	<5	510	110	9.7	15	200	5	8.1	3.2	4.1	99	0.34	2.7	2.00	0.87	6.1		140		180	100
DS-14	598-3-2	73-77	18.05	<5		120	9.6		170	19														
DS-15	598-3-3	71-75	19.53	<5		130	5.9		230	9														
DS-26	598-3-4	70-74	21.02	31	650	120	4.8	17	210	12	12	2.7	2.2	150	0.15	2.2	1.00	0.45	5.3		120	99	89	90
DS-27	598-4-1	15-17	25.56	47	450	130	5.4	22	170	10	14	1.6	2.3	79	0.19	2.0	0.97	0.69	4.6		51	98	50	93
DS-28	598-4-3	25-27	28.66	27	840	130	5.6	6.7	130	11	8.5	2.3	2.1	190	0.14	2.1	0.48	0.53	3.7		120	49	43	
DS-29	598-4-5	26-28	31.67	<5		140	5.4		150	5														
DS-30	598-5-1	81-83	35.82	25		120	5.5		150	19														
DS-31	598-5-2	72-74	37.23	11	900	130	4.9	4.0	130	16	7.1	2.0	1.3	120	0.09	1.9	0.91	0.27	3.3	72	68	89	89	67
DS-32	598-5-4	80-82	40.31	<5	840	130	4.8	16.0	130	16	8.6	2.2	2.0	140	0.12	2.2	0.43	0.29	3.0	100	87	42		76
DS-16	598-5-5	71-73	41.72	28		130	6.6		110	15														
DS-33	598-5-6	71-73	43.22	18		120	5.9		120	16														
DS-34	599-1-1	71-75	0.73	<5		310	29		180	23														
DS-35	599-1-5	72-76	6.74	26		140	8.1		260	3														
DS-36	599-2-2	70-74	10.12	<5	560	85	2.4	3.6	110	18	6.8	0.9	1.0	280	0.05	3.4	0.45	0.17	2.2	100	86	52	48	50
DS-37	599-2-3	70-74	11.62	<5	670	93	3.1	5.7	110	14	6.9	1.3	1.2	130	0.07	3.7	0.65	0.25	2.7		110	68	66	63
DS-38	599-2-5	70-73	14.62	<5	570	90	3.5	13	68	18	8.2	1.6	1.4	130	0.09	3.0	0.51	0.23	2.7		110	50	44	68
DS-39	599-3-1	70-74	18.22	<5	550	87	3.5	5.6	56	<1	7.2	1.3	1.4	210	0.07	3.4	0.70	0.23	2.7		110	71	66	66
DS-40	599-3-2	70-74	19.72	16	550	85	2.8	4.0	67	13	7.1	1.0	1.1	170	0.04	3.2	0.54	0.16	2.2	100	86	58	55	51
DS-41	599-3-5	70-74	24.22	<5	530	88	2.8	2.0	65	9	7.1	1.1	1.0	260	0.05	3.8	0.46	0.24	2.1	96	81	52	50	56
DS-42	599-4-1	71-73	27.82	13	320	94	3.2	1.4	67	5	5.9	0.6	0.7	81	0.04	2.9	0.36	0.20	1.4	75	67	36		38
DS-43	599-4-3	71-73	30.82	<5	520	90	4.4	6.6	58	14	6.0	1.9	1.4	70	0.11	2.4	0.45	0.33	3.0		130	44	42	80
DS-44	599-4-4	72-74	32.33	7	550	96	2.5	11	78	13	5.6	0.9	0.9	210	0.04	3.2	0.43	0.15	1.9	81	71	46	43	47
DS-45	599-4-5	72-74	33.82	10	430	92	2.8	2.7	83	9	6.0	1.1	0.8	140	0.04	2.5	0.44	0.15	1.9	76	61	48	41	42
DS-46	599B-2-3	70-74	36.02	20	170	94	3.7	6.2	83	12	4.6	1.1	0.7	54	0.05	1.0	0.43	0.12	1.7	65	53	44		29
DS-47	599B-2-4	70-73	37.52	<5	580	98	3.8	5.1	160	14	6.5	1.0	1.1	190	0.05	3.3	0.60	0.17	2.3	100	84	61	57	59
DS-48	599B-2-5	74-77	39.06	<5	540	81	7.0	3.0	330	15	8.8	0.9	9.1	250	0.16	3.5	0.78	0.18	2.1	94	81	65	60	52
DS-49	599B-2-6	71-74	40.53	<5	620	79	9.1	5.2	360	13	11	0.9	17	230	0.29	4.1	0.90	0.17	2.1		97	64	62	51
DS-52	600C-1-2	94-99	2.47	<5		170	19		250	<2														
DS-53	600C-1-4	99-104	5.52	21	400	120	9.3	1.5	160	5	6.0	1.3	1.5	68	0.15	2.3	1.10	0.54	3.3		120	99	100	70
DS-54	600C-1-6	99-104	8.52	<5	370	79	5.2	2.2	120	11	5.9	0.6	0.7	150	0.04	3.0	0.60	0.18	1.7	100	94	48	47	48
DS-55 #	600C-2-2	91-96	11.84	<5	340	64	18	1.8	140	16	9.6	0.6	12	32	0.11	0.4	0.56	0.24	0.8	25	20	42		7
DS-50	601B-1-2	76-81	16.69	<5	610	83	4.5	3.5	280	16	7.7	0.9	1.2	110	0.07	3.3	0.70	0.25	2.2		110	65	62	65
DS-51	601B-1-3	74-79	18.17	<5	480	79	4.6	2.6	340	14	6.7	0.8	0.8	320	0.05	5.8	0.63	0.16	1.9		100	52	50	52

* Sample number indicates hole-core-section
** Depth in section
*** BSF = below sea floor
# Contains basaltic material
Note: 4 samples from Sites 599 and 600 yielded CO_2(t), C a...
Hg <1 ppm (INAA detection limit) in all samples except DS-...
Se <3 ppm (INAA detection limit) in all samples.
Br <1 ppm (INAA detection limit) in all samples except DS-5...
Cs <1 ppm (INAA detection limit) in all samples except DS-2...
Ta <1 ppm (INAA detection limit) in all samples except DS-4...

Supplementary Data Table 2. Chemical anal

Lab no.	DSDP no.*	Depth**	Depth BSF***	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REE
		(cm)	(m)	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
				ICP-ES	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	
DS-1	597-2-1	76-78	5.37															
DS-2	597-2-3	75-77	8.36															
DS-3	597-2-6	68-79	12.84															
DS-4	597-3-2	78-90	16.54															
DS-5	597-3-5	76-78	20.97															
DS-6	597-4-1	69-71	24.50															
DS-7	597-4-3	74-76	27.55															
DS-8	597-4-6	74-76	32.05															
DS-9	597A-5-1	74-76	34.15															
DS-10	597A-5-3	75-77	37.16															
DS-17	597-6-1	75-77	43.76	80	26	13	55	10	1.4	13	2.0	12.0	2.8	7.8	1.2	7.1	1.0	232
DS-18	597-6-3	74-76	46.75	85	21	15	62	12	3.5	15	2.4	16.0	3.6	9.9	1.4	8.9	1.3	257
DS-19	597-6-4	74-76	48.25	55	18	12	45	9.4	2.4	10	1.8	11.0	2.4	6.6	1.0	6.1	0.9	182
DS-20	597-6-5	74-76	49.75															
DS-21	597-6-6	74-76	51.25															
DS-22	598-1-1	71-73	0.72	340	180	69	300	64	15	80	13.0	79.0	18.0	51.0	7.5	49.0	7.5	1273
DS-23	598-1-2	71-73	2.22	320	110	63	270	54	15	69	11.0	74.0	17.0	47.0	7.0	44.0	6.7	1108
DS-24	598-1-4	71-75	5.23	250	81	43	200	40	8.8	53	8.3	54.0	13.0	36.0	5.2	33.0	5.1	830
DS-11	598-2-2	72-76	8.44															
DS-12	598-2-3	72-76	9.94															
DS-13	598-2-5	79-83	13.01															
DS-25	598-3-1	67-69	16.48	100	43	17	73	15	3.4	19	3.0	20.0	4.6	13.0	1.9	12.0	1.8	327
DS-14	598-3-2	73-77	18.05															
DS-15	598-3-3	71-75	19.53															
DS-26	598-3-4	70-74	21.02	85	31	14	61	12	2.8	16	2.5	17.0	4.1	11.0	1.7	10.0	1.6	270
DS-27	598-4-1	15-17	25.56	50	30	14	61	11	2.6	14	2.2	15.0	3.3	9.3	1.4	9.3	1.4	225
DS-28	598-4-3	25-27	28.66	99	28	17	77	14	3.6	19	2.9	18.0	4.1	11.0	1.7	10.0	1.6	307
DS-29	598-4-5	26-28	31.67															
DS-30	598-5-1	81-83	35.82															
DS-31	598-5-2	72-74	37.23	69	20	12	49	9.0	2.1	11	1.8	11.0	2.5	7.2	1.1	7.4	1.1	204
DS-32	598-5-4	80-82	40.31	72	20	12	55	10	2.3	13	2.0	13.0	3.0	8.5	1.3	8.4	1.3	222
DS-16	598-5-5	71-73	41.72															
DS-33	598-5-6	71-73	43.22															
DS-34	599-1-1	71-75	0.73															
DS-35	599-1-5	72-76	6.74															
DS-36	599-2-2	70-74	10.12	47	12	7.4	34	6.4	1.5	9.3	1.4	10.0	2.6	7.7	1.2	7.5	1.2	149
DS-37	599-2-3	70-74	11.62	61	15	9.5	43	8.0	1.8	12	1.9	13.0	3.2	9.5	1.5	9.1	1.5	190
DS-38	599-2-5	70-73	14.62	59	16	9.6	42	8.0	1.9	12	1.9	13.0	3.2	10.0	1.6	9.6	1.5	189
DS-39	599-3-1	70-74	18.22	61	16	9.6	45	8.3	1.7	13	1.9	13.0	3.3	10.0	1.5	9.5	1.4	195
DS-40	599-3-2	70-74	19.72	48	12	7.9	35	6.5	1.8	9.7	1.6	11.0	2.7	7.8	1.3	7.7	1.2	154
DS-41	599-3-5	70-74	24.22	54	12	7.5	34	6.2	1.3	8.8	1.4	9.8	2.5	7.5	1.2	7.7	1.2	155
DS-42	599-4-1	71-73	27.82	36	8.0	5.6	26	4.7	1.2	7.1	1.1	7.5	1.9	5.7	0.9	5.5	0.8	112
DS-43	599-4-3	71-73	30.82	76	20	11	52	9.5	2.2	14	2.1	14.0	3.8	11.0	1.8	11.0	1.7	230
DS-44	599-4-4	72-74	32.33	45	11	7.0	31	5.9	1.2	8.2	1.3	9.2	2.3	6.8	1.1	6.9	1.1	138
DS-45	599-4-5	72-74	33.82	38	10	6.2	27	5.3	1.1	7.0	1.2	8.1	2.1	6.1	1.0	6.1	1.0	120
DS-46	599B-2-3	70-74	36.02	27	8.7	4.2	20	3.7	0.77	5.3	0.8	5.7	1.5	4.2	0.7	3.8	0.6	87
DS-47	599B-2-4	70-73	37.52	56	14	8.7	38	7.1	1.5	9.5	1.5	10.0	2.6	7.7	1.2	7.8	1.2	167
DS-48	599B-2-5	74-77	39.06	49	13	7.5	34	6.7	1.9	9.3	1.5	10.0	2.6	7.6	1.2	7.7	1.2	153
DS-49	599B-2-6	71-74	40.53	50	13	7.2	34	6.8	2.0	9.8	1.6	11.0	2.9	8.5	1.4	8.3	1.3	158
DS-52	600C-1-2	94-99	2.47															
DS-53	600C-1-4	99-104	5.52	71	19	12	52	10	<0.02	14	2.3	15.0	3.8	11.0	1.6	9.9	1.6	223
DS-54	600C-1-6	99-104	8.52	48	10	7.0	33	6.4	1.8	9.7	1.5	10.0	2.6	7.8	1.2	7.7	1.2	148
DS-55 #	600C-2-2	91-96	11.84	<10	3.9	1.2	6.2	1.3	0.42	2.1	0.4	2.4	0.6	2.0	0.3	2.0	0.3	23
DS-50	601B-1-2	76-81	16.69	63	14	9.3	43	8.2	2.1	12	2.0	13.0	3.3	9.8	1.6	9.6	1.6	193
DS-51	601B-1-3	74-79	18.17	50	9.7	7.0	33	6.7	1.9	10	1.7	12.0	2.9	8.8	1.4	8.9	1.4	155

* Sample number indicates hole-core-section
** Depth in section
*** BSF = below sea floor
# Contains basaltic material
Note: 4 samples from Sites 599 and 600 yielded CO_2(t), C an
Hg <1 ppm (INAA detection limit) in all samples except DS-3
Se <3 ppm (INAA detection limit) in all samples.
Br <1 ppm (INAA detection limit) in all samples except DS-5
Cs <1 ppm (INAA detection limit) in all samples except DS-2
Ta <1 ppm (INAA detection limit) in all samples except DS-4