1 **Chemical and structural control of the partitioning of**

2 **Co, Ce, and Pb in marine ferromanganese oxides**

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ABSTRACT

The oxidation state and mineral phase association of Co, Ce and Pb in hydrogenetic, diagenetic, and hydrothermal marine ferromanganese oxides were characterized by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy and chemical extraction. Cobalt is trivalent and associated exclusively with the Mn oxide component (vernadite). Cerium is tetravalent in all genetic-type oxides (detection limit for Ce(III) ~ 5 at. %), including Fe-rich areas (ferrihydrite) of hydrogenetic oxides, and is associated primarily with vernadite. Thus, the extent of a Ce anomaly does not result from variations in redox conditions, but appears to be kinetically controlled, decreasing when the growth rate increases from hydrogenetic to diagenetic to hydrothermal oxides. Lead is divalent and associated with Mn and Fe oxides in variable proportions. According to EXAFS data, Pb is mostly sorbed on edge sites at chain terminations in Fe oxide and at layer edges in Mn oxide (ES complex), and also on interlayer vacancy sites in Mn oxide (TCS complex). Selective dissolution, spectroscopic data, and electrochemical considerations suggest that the geochemical partitioning in favor of the Mn oxide component decreases from Co to Ce to Pb, and depends on their oxidative scavenging by Mn and Fe oxides.

1. INTRODUCTION

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44   Marine ferromanganese oxides are found in a variety of environments and forms, such as

45   hydrogenetic nodules and crusts on the deep-sea floor, diagenetic precipitates in sediments,

46   hydrothermal deposits near oceanic ridges, and sinking Fe-Mn colloidal particles in the water

47   column (Glasby, 2000). A common trait to all ferromanganese oxides is their enrichment in trace

48   elements relative to seawater. Their ubiquity, abundance, and importance in the cycling of trace

49   elements has aroused the interest of scientists for several decades, in particular with respect to the

50   geochemical partitioning and incorporation mechanisms of trace elements. These questions often

51   have been addressed by interelement correlations using bulk chemical analysis (e.g., Moorby and

52   Cronan, 1981; Calvert and Piper, 1984; Aplin and Cronan, 1985a,b; De Carlo and McMurtry,

53   1992; Wen et al., 1997), and selective dissolution (Moorby and Cronan, 1981; Aplin and Cronan,

54   1985b; Koschinsky and Halbach, 1995; Koschinsky and Hein, 2003). Few studies have used

55   non-invasive spectroscopic methods, although they offer direct, and often unique, access to the

56   problem (e.g., Dillard et al., 1982; Takahashi et al., 2000; Kuhn et al., 2003; Marcus et al.,

57   2004a).

58   In this paper, the oxidation states of Co, Ce, and Pb in hydrogenetic, diagenetic, and

59   hydrothermal ferromanganese oxides were determined by X-ray absorption near-edge structure

60   (XANES) spectroscopy to evaluate the importance of redox reactions in trace element

61   partitioning (Goldberg, 1961, 1965; Goldberg et al., 1963; Piper, 1974; Burns, 1976). Dillard et al.

62   (1982) concluded using X-ray photoelectron spectroscopy (XPS) that cobalt is trivalent in marine

63   ferromanganese oxides, and Takahashi et al. (2000) that cerium is tetravalent using XANES

64   spectroscopy. These two studies were limited to metal-rich hydrogenetic samples. Pb enrichment

65   in ferromanganese oxides has been suggested to result from Pb(II) to Pb(IV) oxidation (Goldberg,

66   1965; Murray and Dillard, 1979), but this hypothesis has received little experimental support

67   (Dillard et al., 1981). The abundances of Co, Ce, and Pb decrease on average from hydrogenetic

68   to diagenetic to hydrothermal deposits (Usui et al., 1997), and the possibility that this evolution is

69   associated with a variation of their oxidation state has not been investigated. Such a relationship

70   would provide insight into chemical processes responsible for the enrichment of redox-sensitive

71   trace elements in ferromanganese oxides. In particular, questions remain as to the reasons for the

72   variability of the Ce anomaly in REE (rare earth elements) patterns, and its possible link to Ce

73   oxidation state.

74   When considering redox reactions in ferromanganese oxides, elemental distribution

75   among Mn and Fe oxides is an important issue. The nature of the trace element host phases were

76   investigated by electron microprobe, micro-XANES spectroscopy (μ-XANES), and Pb L_{III}-edge

77   extended X-ray absorption fine structure (EXAFS) spectroscopy, and the results compared to

78   those from sequential dissolution to assess the usefulness of chemical extraction to speciate trace

79   metals in ferromanganese matrices.

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81   **2. MATERIALS AND METHODS**

82   **2.1. Samples**

83

84   Seventeen samples collected during several research cruises in the Central to NW Pacific

85   Ocean and the Central Indian Ocean were selected for this study (Table 1). They were classified

86   into hydrogenetic (HG), diagenetic (DG), and hydrothermal (HT) origins on the basis of the

87   mineralogy of the Mn oxide, as summarized in Table 1 (Takematsu, 1998). Samples 31GTV2-3

88   and 31GTV6-11 have a mixed hydrogenetic and hydrothermal origin (Kuhn et al., 1998). The

89   two samples had fast growth rates (10-20 mm/Myr) due to the supply of Mn and Fe from

90   hydrothermal plumes, but their trace elements are considered to be derived mainly from seawater.

91   Thus, they are labeled HT + HG in Table 1. Nodule D465 has a hydrogenetic core and a

92   diagenetic rim and the two parts were analyzed separately. Samples containing P-rich layers were

93   disregarded because secondary phosphatization may modify the original distribution of trace

94   elements (Koschinsky et al., 1997). According to this reference, P concentration in phosphatized

95   crusts is higher than 2.5 wt. %, a value well above the P content of our samples (see Results

96   section).

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98   **2.2. Reference materials**

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100   CoO (purity > 99.9 %), orthorhombic PbO (> 99.9 %), Pb_3O_4 (> 99 %), PbO_2 (> 99.9 %),

101    $CeCl_3$ (> 99 %), $Ce(SO_4)_2$ (> 99.5 %), and CeO_2 (> 99.9 %) from Wako Pure Chemical

102   Industries, Ltd., Katayama Chemicals, and Rare Metallic Co., Ltd. were used as references for

103   XANES measurements. Powders were diluted to 0.5 wt. % in boron nitride and pressed into

104   pellets. A $Ce(OH)_4$ gel was prepared by hydrolyzing a $Ce(NH_4)_2(NO_3)_6$ solution at pH 7 in

105   contact with air (Sumaoka et al., 2000). No Ce(IV) reduction occurs at this Eh-pH condition

106   (Brookins, 1988). The $Ce(OH)_4$ gel recovered by filtration was re-suspended in water at pH ~7

107   and adjusted to a 0.5 wt. % Ce concentration for XANES analysis.

108   Ferrihydrite (HFO) and δ-MnO_2 used in Co, Ce, and Pb sorption experiments for XANES

109   measurements were synthesized according to Schwertmann and Cornell (2000) and Murray

110   (1974), respectively. Sorption samples were prepared by adding 10 mL of 17.0 μM Co(II), 7.15

111   μM Ce(III), or 4.83 μM Pb(II) solutions (pH 5) prepared from nitrate salts to 1 mg ferrihydrite or

112   δ-MnO_2 in suspension in synthetic seawater (Nishimura, 1983) at equilibrium with air. Final pH

113   was adjusted to 7.0 (Co), 6.6 (Ce) and 6.5 (Pb) by incremental addition of HCl. The final pH was

114   lower than that of seawater (8.2 $\pm$ 0.1) to prevent metal precipitation. The solid phases were

115   recovered by filtration (0.45 μm; hydrophilic PTFE) after 1 hour of reaction time, washed with

116   bidistilled water (Milli-Q), and packed wet into polyethylene bags for XANES measurements. A

117   Ce-sorbed ferrihydrite sample was equilibrated for 120 hours. The Ce, Co and Pb concentrations

118   in the solid phases are about 0.1 wt. %.

119   A separate series of Pb-sorbed δ-MnO_2 samples were prepared as follows for EXAFS

120   measurements. δ-MnO$_2$ was prepared by reducing at pH 7 a KMnO$_4$ solution with MnCl$_2$

121   (Villalobos et al., 2005). The precipitate was washed, dialyzed, and stored at 5°C in

122   polypropylene containers for several days at the synthesized solid concentration (21.7 g/L).

123   Pb-sorption samples were prepared by addition of a Pb(NO$_3$)$_2$ solution to a δ-MnO$_2$ suspension

124   (2 g/L, 0.1 M NaNO$_3$) that had been pre-equilibrated at the desired pH with an automatic titrator.

125   After allowing several hours for equilibration at constant pH, the sorption sample was filtered on

126   a 0.1 μm cellulose nitrate membrane, washed with Milli-Q water to prevent the precipitation of

127   metal salt, and freeze-dried. We know from previous studies, and from the similarity of our

128   Pb-EXAFS data (see Results section) with those collected on wet pastes (Villalobos et al., 2005)

129   and powders frozen to 10-20 K (Morin et al., 2001), that the binding mechanism of hydrolyzable

130   cations on phyllomanganates is not modified by freeze-drying, probably because they form

131   multidentate inner-sphere complexes (Lanson et al., 2002a; Manceau et al., 2002a). Also, the

132   stability in vacuum of the layer of water in the interlayer of δ-MnO$_2$ and birnessite, which is

133   attested by the persistence of the basal X-ray reflection at ~7 Å, supports the view that data

134   collected on freeze-dried samples are representative of surface complexes at the water-mineral

135   interface. Four samples were prepared at pH 5 and Pb/Mn molar ratios, as measured by

136   inductively coupled plasma-atomic emission spectrometry (ICP-AES), of 0.002 (PbdBi2), 0.044

137   (PbdBi44), 0.112 (PbdBi112), and 0.197 (PbdBi197). One sample was prepared at pH 7 and

138   intermediate surface loading to test the influence of pH on the structure of the Pb surface

139   complex on δ-MnO$_2$. Its EXAFS spectrum was almost identical to the PbdBi44 spectrum (data

140   not shown). The effect of crystallinity was investigated by comparing the data with those for Pb

141   sorbed on well-crystalline hexagonal birnessite at pH 4 and Pb/Mn molar ratio of 0.031 (sample

142   PbBi31 in Lanson et al., 2002a). This reference had been characterized by EXAFS spectroscopy

143   previously (Manceau et al., 2002a), but a higher quality spectrum was recorded for this study.

144

145   **2.3. Chemical compositions**

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147   The Mn, Fe, Co, Ni, Cu, and Zn concentrations in the natural samples were measured by

148   ICP-AES (Yanaco UOP-1S) after acid digestion using HF/HCl/HNO$_3$, and Pb concentration was

149   measured by inductively coupled plasma-mass spectrometry (ICP-MS) (VG PQ-3) using Bi as an

150   internal standard. The precision and accuracy of the analytical values were better than 10 %,

151   based on the analysis of the JMn-1 reference prepared from ferromanganese oxide deposits

152   distributed by the Geological Survey of Japan (GSJ; Terashima et al., 1995). REE abundances

153   were measured by ICP-MS using In and Bi as internal standards (Takahashi et al., 2000).

154   Repeated analyses on JB-1a standard rock prepared by GSJ showed that the precision and

155   accuracy of the REE analyses were generally better than 5 %. REE abundances for D513 are

156   from Ohta et al. (1999), and major and minor (including REE) element concentrations for

157   31GTV2-3 and 31GTV6-11 are from Kuhn et al. (1998). Major elements and Co, Ni, Cu, Zn, Ce,

158   and Pb concentrations in samples CD25, D535, AD14, D465, D514, and FG352 were measured

159   also with an electron probe microanalyzer (EPMA, JXA-8200, JEOL), running at 15 keV

160   acceleration voltage and using a 5 μm-sized beam.

161

162   **2.4. Sequential leaching experiments**

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164   Sequential leaching experiments were performed on powdered samples, following the

165   procedure described in Koschinsky and Hein (2003) and Koschinsky and Halbach (1995). Briefly,

166   0.5 g of powder was mixed with 15 mL of 1 M acetic acid/Na acetate buffer (pH 5) at room

167   temperature for 5 hours. The filtrate (fraction 1) was considered to include exchangeable cations

168   and cations initially present in carbonates. The residue was suspended in 25 mL of Milli-Q water

169   and stirred with 87.5 mL of a 0.1 M hydroxylamine hydrochloride (NH$_3$OHCl) solution (pH 2)

170   for 24 hours. The filtrate at this step (fraction 2) contained cations originally in Mn oxides. The

171   new residue was suspended in 100 mL of Milli-Q water and stirred with 87.5 mL of 0.2 M oxalic

172   acid/ammonium oxalate buffer (pH 3.5) for 12 hours. The filtrate (fraction 3) contained cations

173   originally associated with Fe oxides. The final residue, mainly consisting of silicates and

174   aluminosilicates (fraction 4), was digested for bulk chemical analyses. The Mn, Co, Pb, and Ce

175   concentrations in all filtrates were measured by ICP-MS after dilution by a factor > 100 in 2 %

176   HNO_3, and the Fe concentrations were measured by ICP-AES. For each element, the sum of

177   concentrations from fractions 1 to 4 divided by the bulk concentrations (i.e., recovery of the

178   leaching experiments) was better than 82 %.

179   Re-adsorption of dissolved ions on residual solid phases may occur during sequential

180   leaching experiments (Rendell et al., 1980; Sholkovitz, 1989; Gilmore et al., 2001). The fractions

181   of metals re-adsorbed on Fe oxides and insoluble phases (silicate and aluminosilicates) in the

182   hydroxylamine hydrochloride extraction step were determined using [54]Mn, [58]Co, [139]Ce, and [146]Gd

183   radioisotope tracers (Ambe et al., 1995; Takahashi et al., 1997; Takahashi et al., 1999). Lead

184   radioisotopes were not included in the multitracer solution, and thus Pb was not analyzed. The

185   amounts of re-adsorbed radioisotopes were obtained by measuring the γ-ray spectrum of the

186   filtrate with a Ge solid-state detector. Counting was stopped when the total number of counts was

187   at least 10,000 for each radioisotope. Measurements of the peak area and corrections of the decay

188   of each isotope were carried out by a routine procedure.

189

190   **2.5. XANES and EXAFS measurements and analyses**

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192   Cerium L_{III}-edge and Co K-edge XANES spectra were recorded on beamline BL12C at the

193   KEK Photon Factory in Tsukuba, Japan (Nomura and Koyama, 1996), and Pb-L_{III}-edge XANES

194   spectra on beamline BL01B1 at SPring-8 in Hyogo, Japan (Uruga et al., 1999). The two

195   beamlines have similar layouts. The X-rays were monochromatized with a pair of Si(111)

196   crystals. The beam size at the sample position was about 1×1 mm^2, and its intensity (I_0)

197   monitored with an ionization chamber. The sample was placed at 45 degrees from the incident

198 beam, and the fluorescent X-rays measured with a 19 element Ge solid-state detector. At the Co

199 K-edge, the intensity of the unwanted fluorescence signal from Mn and Fe was reduced by

200 mounting a vanadium filter ($\mu t = 3$ or 6) in front of the detector. Deadtime correction was done

201 by the method of Nomura (1998). Energy was calibrated by assigning the energy of the first peak

202 of CeO_2 at 5730.5 eV (Ce L_{III}-edge), the absorption maximum of CoO (Co K-edge) at 7730.3 eV,

203 and the absorption maximum of PbO_2 (Pb L_{III}-edge) at 13061.5 eV (the first maximum of the

204 derivative of elemental Pb was at 13029 eV). XANES spectra were recorded with a 0.25 to 1 eV

205 step size and 1 to 5 sec counting per step. One to five scans were summed to improve the

206 signal-to-noise ratio, and all spectra were normalized to unit step in the absorption coefficient. No

207 radiation damage was detected during the data acquisition.

208 Bulk XANES measurements were complemented by micro-XANES and X-ray fluorescence

209 (XRF) mapping measurements for the hydrogenetic ferromanganese nodule CD25. The

210 experiments were carried out on beamline 10.3.2 at the Advanced Light Source (ALS), Lawrence

211 Berkeley National Laboratory, USA (Manceau et al., 2002b; Marcus et al., 2004b). The sample

212 was embedded in a high purity resin (Eposet, Maruto Co.,Ltd.), polished on one face, and glued

213 on a glass slide with a wax product (Skywax 415, Maruto Co., Ltd.). After polishing the other

214 face of the sample to a thickness of about 30 μm, the thin section was removed from the glass

215 support by dissolving the wax in *o*-xylene. An area of 1.2×1.1 mm^2 from the free-standing

216 specimen was scanned under a 5×5 μm^2 beam using steps of 5 μm. The distribution of Co and

217 Ce were imaged by recording, for each element, one map above and another below their

218 absorption K edges (7659 and 7759 eV for Co; 5718 and 5730.5 eV for Ce, respectively) and

219 calculating the difference maps. From visual comparison of these elemental distributions, and

220 from the Mn/Fe ratio, specific points-of-interest (POIs) were selected for Co K-edge and Ce

221 L_{III}-edge micro XANES measurements. To avoid the possibility of radiation damage, only one

222 spectrum was collected at each spot, and spectra from nearby spots having similar compositions

223 as seen from the XRF maps were averaged.

224   Fluorescence-yield Pb-EXAFS spectra of the two hydrogenetic samples D1-X1 and D21-m3

225   before treatment and after dissolution of the Mn oxides, as described in section 2.4, were

226   recorded on the FAME (BM 30B) beamline at the European synchrotron radiation facility

227   (ESRF) in Grenoble, France. The white X-ray beam was collimated vertically to 3 mm with a

228   bent Rh-coated Si mirror, monochromatized with a two-crystal Si (220) monochromator, sagitally

229   focused to 300 μm with the second crystal, and vertically focused to 150 μm with a second bent

230   Rh-coated Si mirror downstream of the monochromator (Hazemann et al., 1995; Proux et al.,

231   2006). X-ray fluorescence was detected with a 30-Ge solid-state detector, and the output signal

232   processed with a fast amplifier (0.125 μs shaping time, 300 eV FWHM resolution). Multiple

233   scans were performed to improve statistics. To avoid the possibility of radiation damage, the

234   sample pellet was moved by 0.5 mm after each scan.

235   The EXAFS data analysis was carried out using the codes from the WinXAS package

236   (Ressler, 1998). Phase shifts and amplitude functions for the simulation of data were calculated

237   by FEFF7 (Ankudinov and Rehr, 1997) with quenselite as a structural model (Rouse, 1971). The

238   experimental EXAFS function, $\chi(k)$, was obtained after subtracting the embedded-atom

239   absorption background from the Pb-Lα fluorescence signal normalized to the intensity of the

240   incident beam (I_0), and normalizing the signal by the edge step. EXAFS spectra were Fourier

241   transformed with a Bessel apodization function to real (R) space, and backtransformed to k space

242   for spectral simulation.

243

244   **3. RESULTS**

245

246   **3.1. Chemical composition**

247

248   Abundances of Mn, Fe, Co, Ni, Cu, Zn, and Pb in bulk samples and in the local areas

249   measured by EPMA are listed in Tables 2 and 3. The contents of Co and Pb against the Mn/Fe

250   ratio are plotted in Figure 1. We know from previous studies (e.g., Moorby and Cronan, 1981;

251   Calvert and Piper, 1984; Aplin and Cronan, 1985a,b; De Carlo and McMurtry, 1992; Usui et al.,

252   1997 Wen et al., 1997) that the Mn/Fe ratio increases, and Co and Pb concentrations generally

253   decrease, from hydrogenetic to diagenetic to hydrothermal Mn formations. Aside from samples

254   31GTV2-3 and 31GTV6-11, our data are consistent with this general trend, which confirms that

255   the series of samples includes the three genetic types of ferromanganese oxide. The singularity of

256   the two GTV samples, classified as a mixture of hydrogenetic and hydrothermal oxides, is

257   explained by the incorporation of trace elements from seawater (hydrogenetic characteristic) at a

258   fast growth rate (hydrothermal characteristic) (Kuhn et al., 1998).

259   REE abundances are listed in Table 4, and values normalized to those of the Post-Archean

260   Australian Shale, PAAS (McLennan, 1989) are plotted in Fig. 2a. REE are abundant in

261   hydrogenetic oxides, intermediate in diagenetic oxides, and low in hydrothermal oxides. The Ce

262   anomaly $(Ce/Ce^*)_{SN}$ reported in Table 4 was calculated by defining $(Ce^*)_{SN} = (La^{1/2}Pr^{1/2})_{SN}$

263   (Akagi and Masuda, 1998), where the subscript SN denotes the abundance normalized to PAAS.

264   The Ce anomaly is referred to as positive ($[Ce/Ce^*]_{SN} > 1$) in hydrogenetic and negative

265   ($[Ce/Ce^*]_{SN} < 1$) in hydrothermal oxides. Diagenetic samples have intermediate values that are

266   close to 1. The decrease in REE abundance and inversion of the Ce anomaly along the

267   hydrogenetic - diagenetic - hydrothermal series is consistent with previous studies (e.g., Usui et

268   al., 1997), confirming that the series of samples is representative of the three genetic types of

269   marine ferromanganese oxide.

270

271   **3.2. Sequential dissolution**

272

273   The correlation of Co, Ce and Pb with Fe, and their anti-correlation with Mn in Figure 1 do

274   not necessarily imply that they are chemically bound to or included in the structure of the Fe

275   oxide component (ferrihydrite). To gain further insight, sequential dissolution experiments were

276   conducted on four hydrogenetic samples (D535, AD14, D1-X1, and D21-m3) and two diagenetic

277   samples (FG352 and G181). The extent of Mn, Co, Ce, and Gd re-adsorption on the Fe oxide

278   after dissolution of the Mn oxide component was evaluated with the multitracer technique on

279   D535 and AD14. Mn and Co were marginally readsorbed (< 3 %), but Ce (35 ± 24 %) and Gd

280   (46 ± 21 %) were substantially readsorbed.

281   From 59 % (G181) up to 97 % (D535 and D1-X1) of total Co, and from 71 % (G181) up to

282   95 % (AD14 and D21-m3) of total Mn were leached in fraction 2 (hydroxylamine hydrochloride

283   treatment, Fig. 3), while the ratio of dissolved Fe to total Fe remained low (7 % to 24 %). Thus,

284   Mn oxides were preferentially dissolved over Fe oxides during the second extraction step, and

285   this chemical treatment also released most of Co. The Co-Mn association, confirmed below by

286   EPMA and XANES spectroscopy, indicates that the positive Co-Fe/Mn correlation in Figure 1 is

287   misleading about the nature of the Co host phase. From 75 % (D535) to 99 % (D21-m3) of total

288   Pb was leached out with Fe in fraction 3 (oxalate treatment). The co-extraction of Pb and Fe in

289   ferromanganese oxides has been interpreted as indicating Pb uptake on Fe oxides (e.g.,

290   Koschinsky and Halbach, 1995; 2003). This interpretation should be viewed cautiously, however,

291   because Pb is prone to re-adsorption (Gilmore et al., 2001), and this side-effect is expected to be

292   larger than for REE, such as Ce and Gd (Sholkovitz, 1989). Cerium extraction data are

293   conclusive for D535 and D1-X1 because Ce and Mn were eluviated together: 75 % Ce and 89 %

294   Mn in D535, 62 % Ce and 87 % Mn in D1-X1. In the other samples, Ce was eluviated

295   predominantly with Fe. Thus, re-adsorption of Mn oxide-bound Ce on Fe oxides may artificially

296   enhance the proportion of Ce initially held by the Fe phase. Therefore, Ce is at least partly

297   associated with Mn, and perhaps also with Fe.

298

299   **3.3. Electron microprobe**

300

301   The micrometer-scale variability of the Co, Ce, and Pb correlations with Fe and Mn was

302   examined by analyzing with EPMA the main growth structures of three hydrogenetic samples

303   (CD25, D535, and AD14). Fair to strong correlations were measured between Co and the Mn to

304   Fe ratio: $r^2 = 0.64$ for CD25, $r^2 = 0.76$ for D535, and $r^2 = 0.80$ for AD14 (Fig. 4). In contrast, Pb

305   and Ce lacked clear correlation with Fe and Mn.

306

307   **3.4. Cerium L_{III}-edge XANES**

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309   The excitation energy of an element increases with its oxidation state, due to an increase in

310   binding energy of core electrons and the destabilization of antibonding states as the formal

311   valency of the metal ion increases (Bianconi, 1988). The chemical shift at the Ce L_{III}-edge is

312   illustrated in Figure 5 with $CeCl_3$ as Ce(III) reference, and CeO_2, $Ce(OH)_4$ gel, and $Ce(SO_4)_2$ as

313   Ce(IV) references. The trivalent species has an absorption maximum at 5726.5 eV attributed to a

314   single electronic excitation from the $2p_{3/2}$ to the 5d states. The tetravalent species have two

315   maxima at 5730 and 5738 eV attributed to a double electronic excitation in the final states, owing

316   to a strong hybridization of the 4f states of Ce and the ligand orbitals (Jo and Kotani, 1985;

317   Kotani et al., 1987; Soldatov et al., 1994). The absorbance of CeO_2 and $Ce(OH)_4$ is higher at

318   5730 eV than at 5738 eV, and the two spectra have a shoulder at about 5727 eV. These two

319   features are attributed to many-body effects and to the covalent nature of the Ce-O-Ce bond

320   (Kaindl et al., 1988; Hu et al., 1994; Soldatov et al., 1994; Takahashi et al., 2002a). They are not

321   observed in $Ce(SO_4)_2$ and Ce-sorbed δ-MnO_2 because of the more ionic character of the

322   Ce(IV)-O bond in these compounds (Takahashi et al., 2002a). Apart from D465 (outer), all the

323   sample spectra are similar to those of $Ce(SO_4)_2$ and Ce-sorbed δ-MnO_2, which indicates that Ce

324   is exclusively tetravalent in all genetic-types of ferromanganese oxide. The maximum amount of

325   Ce(III), as estimated from spectral combinations of $CeCl_3$ and $Ce(SO_4)_2$, is 5% for all samples

326   except for D465 (outer).

327   The previous set of bulk XANES spectra was complemented by a micro-XANES spectrum

328   at a Mn-rich spot (spot 1) and an Fe-rich spot (spot 2) of CD25 (Fig. 6). Spot 1 is within the main

329   growth structure, and spot 2 is in the Fe-rich region on the rim of the main growth structure.

330   From the relative intensities of the Mn K_α and Fe K_β signals, the Mn/Fe ratio at spot 1 is about

331   5.6 times higher than that at spot 2. EPMA analysis of spot 2 gave 31 wt. % Fe, 16 wt. % Si, and

332   0.32 wt % Mn. The Fe-Si association may be due to nontronite (Sorem and Fewkes, 1977;

333   Halbach et al., 1988; Takematsu, 1998). Si may be speciated also as amorphous silica (opal).

334   Regardless of the contrasted chemical composition of the two analyzed spots, their XANES

335   spectra were similar and indicative of Ce(IV) only.

336   The nature of the main Ce host phase can be inferred from data on the two sorption

337   references. Figure 5 shows that Ce(III) was oxidized completely to Ce(IV) on δ-MnO_2, but not

338   on ferrihydrite (HFO). The small absorption feature at 5738 eV in the HFO spectra is suggestive

339   of Ce(IV), but this species clearly is minor. Therefore, since Ce is tetravalent in all samples, it

340   should be associated primarily with the Mn oxide component and not, or in subordinate amounts,

341   with the Fe oxide component. This interpretation supposes that ferrihydrite does not oxidize Ce

342   in the physico-chemical conditions of the marine environment, which may not be correct.

343   According to Bau (1999), the ferric oxide reference would have contained more Ce(IV) if

344   sorption had been performed on freshly precipitated colloidal particles rather than on a preformed

345   solid.

346

347   **3.5. Cobalt K-edge XANES**

348

349   Figure 7 shows the Co K-edge XANES spectra of a selection of samples together with those

350   of CoO and Co_2O_3, as references for Co(II) and Co(III), respectively. The chemical shift of the

351   absorption maxima for octahedral Co(II) (7730 eV) and Co(III) (7734 eV) is 4 eV, and can be

352   used to determine the oxidation state of Co in unknown samples (Manceau et al., 1987, 1992a).

353   The sample spectra match the δ-MnO_2 reference, and their edge energy is characteristic of

354   trivalent Co. Two micro-XANES spectra were measured at spots 1 and 2 of CD25 (Fig. 8). From

355   the Co Kα data, the Co concentration is 3.3 times higher at spot 1 than at spot 2. The two point

356   XANES spectra are essentially the same and typical of Co(III). However, a weak shoulder at the

357   energy of the maximum absorbance for the Co(II) species (7729 eV) is apparent on the spot 2

358   spectrum when the spot 1 spectrum is overlaid. The lineshape of the spot 2 spectrum could be

359   reproduced with a linear combination of 80-85 % spot 1 + 10-15 % CoO. This result provides

360   suggestive evidence for some Co-HFO association, but the data are too noisy to draw a definitive

361   conclusion. Therefore, we conclude that Co is trivalent in hydrogenetic (CD25, D465 inner),

362   diagenetic (G181, D465 outer), and hydrothermal (D21-103) Mn oxides. Similarly to Ce, the

363   non-oxidation of Co(II) at the ferrihydrite surface in contact with air, and its oxidation on δ-MnO$_2$

364   (Fig. 7), provide strong evidence for Co association to the Mn oxide component.

365

366   **3.6. Lead L$_{III}$-edge XANES**

367

368   Figure 9a shows the Pb L$_{III}$-edge XANES spectra of a selection of hydrogenetic (CD25,

369   D1-X1, D465 (inner), and D21-m3) and diagenetic (D465 (outer) and G181) ferromanganese

370   oxides, and the two sorption (HFO, δ-MnO$_2$) and the PbO, Pb$_3$O$_4$, and PbO$_2$ references. The

371   spectra from the natural and synthetic samples resemble the PbO spectrum. Since Pb-XANES

372   spectra are essentially featureless, first derivatives are generally plotted to enhance the spectral

373   sensitivity to the electronic structure of Pb (Rao and Wong, 1984; Bargar et al., 1997a; Choi et al.,

374   1999). The 2p to 6s electronic transition at 13.029 keV is possible for the Pb(IV) species owing to

375   its $(5d)^{10}(6s)^0$ configuration, but not for Pb(II), since the two 6s electronic levels are filled in this

376   species. The 2p $\rightarrow$ 6s transition is absent in all spectra from natural and synthetic samples, which

377   indicates that Pb is divalent in marine ferromanganese oxides, and that no oxidation occurred

378   upon Pb sorption on HFO and δ-MnO$_2$, in agreement with previous experimental studies

379   (Manceau, 1992b; Bargar et al., 1998; Matocha et al., 2001; Trivedi et al., 2003; Villalobos et al.,

380 2005). As Pb is dissolved as a divalent species, such as $PbCl_n^{2-n}$ and $PbCO_3^0$, in seawater (Byrne,

381 2002), and as many redox reactions are catalyzed at mineral surfaces (Wehrli, 1990), it has been

382 conjectured that the oxidation of Pb(II) to Pb(IV) is the main enrichment mechanism of Pb in

383 marine ferromanganese oxides (Goldberg, 1965; Hem, 1978; Murray and Dillard, 1979;

384 Nishimura, 1983; Halbach et al., 1988). This hypothesis is not supported by our data.

385   Since Pb is not oxidized by Mn oxides, XANES data do not allow determining whether Pb is

386 associated with the Fe or Mn oxide component. Based on sequential extraction data, Pb is

387 associated with Fe, but this macroscopic technique for determining metal speciation has pitfalls,

388 as mentioned previously. To answer this question, the three hydrogenetic samples AD14, D1-X1

389 and D21-m3 were examined by EXAFS spectroscopy.

390

391 **3.7. Lead L_{III}-edge EXAFS**

392

393 *3.7.1. Pb mineral host*

394

395   The mineralogical nature of the Pb host in AD14, D1-X1 and D21-m3 was determined by

396 recording the EXAFS spectra of the untreated and hydroxylamine hydrochloride treated (fraction

397 2) samples. The spectra can be classified in three groups on the basis of their shape and

398 frequency: AD14, D1-X1 and D21-m3, and the three treated samples (Fig. 10a-e). The spectra

399 within each of the second and third groups are statistically invariant, as illustrated in Figure 10b

400 with D1-X1 and D21-m3. These two spectra could be reconstructed with a linear combination of

401 untreated AD14 and either of the treated samples (Fig. 10f). Consequently, the whole data set

402 forms a binary system which is bounded by AD14 and the Mn-free samples (fraction 2).

403 Comparison of the fraction 2 spectra with Pb-sorbed Fe (oxyhydr)oxides references from a

404 database showed that the treated spectra matched best the ferrihydrite spectrum (PbHFO100), Fig.

405 11a,b). This result is consistent with chemistry and diffraction data, since Fe is speciated as

406   ferrihydrite in these samples.

407   The nature of the Pb host in AD14 was determined by comparing its spectrum with those

408   from the Pb-sorbed δ-MnO_2 references. The PbdBi112 spectrum provided the best match to the

409   data (Fig. 11c,d). The ferromanganese and reference spectra are similar, differing only in the

410   shape of the ascending part of the second oscillation. Qualitatively, one may conclude that Pb has

411   a similar binding environment, and hence likely occupies the same crystallographic sites, in the

412   natural and synthetic phyllomanganates. This interpretation is supported by the Fourier

413   transforms, which show that Pb has a similar local structure in the two solids. Linear

414   combinations of Mn and Fe (oxyhydrox)oxide references verified that Pb is associated only with

415   the Mn oxide phase in AD14, with a detection limit for Pb-ferrihydrite estimated at 10 %. Since

416   AD14 and the fraction 2 spectra are from pure species, the fractional amounts of Fe- and

417   Mn-bound Pb in D1-X1 and D21-m3 can be estimated from their spectral reconstruction with the

418   two single species spectra. The best fits to the D1-X1 and D21-m3 spectra were obtained with 50

419   $\pm$ 10 % Mn-bound Pb and 47 $\pm$ 10 % Fe-bound Pb (Fig. 10f).

420

421   *3.7.2. Uptake mechanism of Pb*

422

423   The nature of the polyhedral connectivity between Pb and the $Fe(O,OH)_6$ octahedra in

424   ferrihydrite was determined by least-squares fitting the reference rather than the sample data

425   because the former had a higher signal-to-noise ratio. The Fourier transform of PbHFO100

426   exhibits a Pb-O peak at $R + \Delta = 1.8$ Å and a Pb-Fe peak at $R + \Delta = 2.9$-3.0 Å, or $R \sim 2.3$ Å and

427   3.3 - 3.4 Å, respectively, after semi-quantitative correction of the phase-shift effect (Manceau et

428   al., 1992b; Ford et al., 1999; Scheinost et al., 2001; Trivedi et al., 2003) (Fig. 11b). More precise

429   interatomic distances were obtained from spectral fits. The best fit structural parameters derived

430   from a two-shell fit model were 2.8 O atoms at 2.36 Å and 1.6 Fe at 3.39 Å (Fig. 12a; Table 5).

431   This model failed to reproduce the wave node at 4.8 Å^{-1} and the shape of the third oscillation at 7

432   Å^{-1}. Splitting the first oxygen shells in two subshells moderately improved the simulation, but

433   splitting the iron shell improved it quite significantly as it halved the goodness-of-fit parameter

434   (Fig. 12b-d, Table 5). An optimal fit to the data was obtained with a four-shell model consisting

435   of about 3 O at 2.38 Å, 1 O at 2.65 Å, 2 Fe at 3.32 Å and 2 Fe at 3.50 Å (Fig. 12d). The Pb-O

436   distances are characteristic of divalent Pb (Manceau et al., 1996), and the Pb-Fe distances of a

437   bidentate edge-sharing complex (ES) between the Pb and Fe coordination polyhedra.

438   In contrast to ferrihydrite, the Pb-metal shell peak is a doublet (Mn1 and Mn2) in the Fourier

439   transform of AD14 (Fig. 11d), which is evidence for at least two Pb-Mn distances. Since the two

440   Pb-Mn peaks are weak, the geometry of the Pb surface complex and nature of the sorption site in

441   AD14 were determined from the analysis of the Pb sorption reference spectra. The five

442   phyllomanganate spectra intersect at the same k values, which signifies that the system is binary

443   (Manceau et al., 1998), and thus that the local structure of Pb varies continuously between two

444   well-defined configurations (Fig. 13a). On the Fourier transforms, the Mn2 peak has a high

445   amplitude and the Mn1 peak a weak amplitude at high surface loading in the δ-MnO$_2$ series, and

446   even more so in well-crystallized birnessite (PbBi31). Decreasing the surface loading down to

447   Pb/Mn = 0.002 (sample PbdBi2) on δ-MnO$_2$ increased the amplitude of the Pb-Mn1 peak and

448   concomitantly decreased that of the Pb-Mn2 peak (Fig. 13b). The dependence of the relative

449   amplitude of the two Pb-Mn peaks on the Pb/Mn ratio and crystallinity demonstrates the presence

450   of two surface complexes having a different affinity for the phyllomanganate surface, as shown

451   previously for Zn on phyllomanganate (Manceau et al., 2002a; Toner et al., 2006) and Cd on

452   goethite (Spadini et al., 1994). When the surface coverage is low and the surface area high (i.e.,

453   δ-MnO$_2$), the short distance Pb species prevails, meaning that it has a high affinity for the mineral

454   surface, while it is outnumbered by the long distance and lower affinity Pb species at high surface

455   coverage.

456   Good spectral agreement between theory and experiment for the δ-MnO$_2$ series was obtained

457   by considering only one shell of oxygens at 2.3 Å and two Mn shells (Mn1 and Mn2) at 3.2 and

458   3.7 Å (Fig. 12; Table 5). The Mn1 shell has been observed previously in δ-MnO_2 and manganite

459   (γ-MnOOH), and was interpreted as an edge-sharing (ES) complex (Matocha et al., 2001; Morin

460   et al., 2001). In ferrihydrite, in which the ES complex also occurs, the Pb-Fe interaction is about

461   0.1 Å larger (i.e., 3.3 Å) than the Pb-Mn interaction in δ-MnO_2, a value that matches the

462   difference in effective ionic radii between Mn(IV) and Fe(III) (0.53 vs 0.64 Å). Since δ-MnO_2

463   has a layered structure and its crystallites have a small lateral extension (i.e., low crystallinity),

464   the ES complex is located probably at layer edges and is presumably tridentate (Fig. 14). The

465   Mn2 shell has been reported previously in well-crystallized birnessite and attributed to a

466   tridentate corner-sharing complex (TCS) in the interlayer (Manceau et al., 1999; 2002a; Morin et

467   al., 1999; Matocha et al., 2001). This structural interpretation was confirmed subsequently by

468   electron and X-ray diffraction (Drits et al., 2002; Lanson et al., 2002a). At this interlayer position,

469   the Pb atoms are bonded to three O atoms from a vacant octahedral site of the Mn oxide layer,

470   thus helping to balance the charge deficiency of the layer created by Mn(IV) vacancy sites (Fig.

471   14).

472   Consideration of a Mn3 shell at 4.09 Å in PbBi31 better replicated the data than the single

473   Mn2 shell model, in particular in the $9 < k < 11$ Å^{-1} interval (Fig. 12k, Table 5). This second shell

474   was not resolved in our previous study (Manceau et al., 2002a) because the EXAFS data were

475   limited to $k < 10$ Å^{-1}. The magnitude of the distance separation between the Mn2 and Mn3 shells

476   (4.09 - 3.70 = 0.39 Å) is similar to that in quenselite (3.96-[(3.57+3.43)/2] = 0.46 Å;

477    $PbMnO_2OH$) (Rouse, 1971) and, by analogy with the structure of this mineral, the six nearest

478   Pb-Mn distances from the TCS complex likely are unequal. The incoherency of the Pb-Mn

479   distances in Pb-sorbed birnessite explains the apparent loss of coordination since an effective

480   number of $N = 1.0 + 0.8 = 1.8$ Mn atoms are detected instead of a crystallographic number of CN

481    $= 6$ (Fig. 11).

482   Another distinction among the reference spectra is a 0.04 Å reduction of the average Pb-O

483   distance in PbBi31 and PbdBi197 relative to PbdBi2, PbdBi44, and PbdBi35 (Table 5). Since the

484   first group of samples has a higher ES/TCS ratio, the ES complex presumably has a longer

485   average Pb-O distance than the TCS complex. This increase in distance can be explained by the

486   higher electrostatic repulsion between Pb(II) and Mn(IV) at the edge-sharing site (shorter Pb-Mn

487   distance) than at the corner-sharing site (longer Pb-Mn distance). This effect was detected

488   because the proportion of TCS complex is low at low surface coverage.

489   Finally, the proportion of ES and TCS complexes in AD14 was estimated from the effective

490   number of Pb-Mn1 and Pb-Mn2 pairs ($N = 0.2$ and 0.6, respectively; Table 5) and the

491   crystallographic number of nearest Mn neighbors at site TCS ($CN = 6$) and ES ($CN = 2$) (Fig. 14).

492   According to this calculation, Pb is evenly distributed over the two sites.

493

494   **4. DISCUSSION**

495

496   **4.1. Ce anomaly**

497

498   Cerium L_{III}-edge XANES data showed that Ce is exclusively tetravalent in all samples,

499   regardless of genetic origin. In general, Ce oxidation is considered to be responsible for the

500   positive Ce anomaly in REE patterns of ferromanganese oxides (e.g., Takahashi et al., 2000).

501   The rationale is that Ce(IV) is taken up preferentially over Ce(III) by solid phases in contact with

502   seawater because Ce(IV) is much less soluble than Ce(III). This explanation does not seem to be

503   valid for diagenetic and hydrothermal ferromanganese oxides because they have a negative, or at

504   best moderately positive, Ce anomaly when the data are normalized to PAAS (shale), as is often

505   observed (Fig. 2a). Figure 2b shows that this discrepancy disappears when the REE

506   concentrations in the solid phase are normalized to their abundances in deep seawater (Piepgras

507   and Jacobsen, 1992). In doing this, the Ce anomalies are all positive, which agrees with the

508   dominance of Ce(IV) in all samples (Fig. 2b). The reason is that REE in deep seawater, where

509   hydrogenetic nodules occur, are more strongly depleted in Ce than the more reducing interstitial

510   and hydrothermal waters, where the two other types of ferromanganese oxides occur. Also, Ce

511   normalization by PAAS is unsuitable because Ce is not removed by the same geochemical

512   processes in shales and marine nodules.

513   If we assume that Ce(III) in ferromanganese oxides is in equilibrium with Ce(III) in water,

514   and that Ce(III) is the only soluble species, then the normalized abundance of Ce(III) in the solid

515   phase, denoted Ce*, can be obtained from the interpolation of the normalized abundances for La

516   and Pr: $(Ce*)_{SW} = (La^{1/2}Pr^{1/2})_{SW}$, where SW stands for normalization by REE abundances in

517   seawater. The $(Ce*/Ce_{total})_{SW}$ ratio calculated for FG352 is 15 %, and could be detected by

518   XANES spectroscopy. This ratio is a maximum value among the samples examined, because this

519   sample has the lowest Ce anomaly in the dataset (Fig. 2b). The $CeCl_3 : Ce(SO_4)_2$ spectrum in

520   Figure 5 shows that 10 % of Ce(III) in a mixed-valence sample manifests itself in the appearance

521   of a shoulder at 5724 eV. None of the sample spectra have such a shoulder including FG352.

522   Also, the maximum of the 1st derivative of this composite spectrum is at 5724.4 eV, while this

523   maximum is between 5726 and 5727 eV in the sample spectra and Ce(IV) references. This

524   analysis confirms the lack of detectable Ce(III) in ferromanganese oxides, even in a sample

525   having a weak Ce anomaly. Therefore, Ce(III) is completely oxidized to Ce(IV) in

526   ferromanganese oxides, and the magnitude of the positive Ce anomaly is not related to a

527   variation of redox conditions, but probably to kinetic factors, as discussed below.

528

529   **4.2. Ce and Co incorporation in ferromanganese oxides**

530

531   Homogeneous precipitation and formation of Ce oxide in marine sediments have been

532   proposed for Ce(IV) removal from seawater (e.g., De Carlo and McMurtry, 1992; Ohta et al.,

533   1999; Haley et al., 2004). This mechanism can be dismissed because none of the XANES spectra

534   of the samples resemble those of CeO_2 and $Ce(OH)_4$. Therefore, oxidative sorption of dissolved

535   Ce(III) likely is the main pathway of Ce incorporation in ferromanganese oxides. Since Ce(IV) is

536   sparingly soluble (De Baar et al., 1988; Byrne, 2002), the sorbate remains at the surface of the

537   Fe-Mn oxide after oxidation took place, leading progressively to Ce enrichment. Based on the

538   low amount of Ce in seawater and the nanometer size of the ferrihydrite and manganese particles

539   (Villalobos et al., 2006), saturation of reactive surface sites by Ce(IV) is unlikely to occur. Also,

540   the exposed surface is progressively buried during the growth of the ferromanganese oxide. This

541   process controls the Ce enrichment, and prevents poisoning of the surface, as observed in the

542   laboratory at high sorbate - metal sorbent ratio (Manceau et al., 1997). Therefore, Ce enrichment

543   must be controlled by the growth rate of the ferromanganese oxide, as suggested for Co (Halbach

544   et al., 1983; Mannheim and Lane-Bostwick, 1988; Takematsu et al., 1989). Consistent with this

545   interpretation, the growth rate of ferromanganese oxides increases in the order hydrogenetic <

546   diagenetic < hydrothermal oxides (Dymond et al., 1984), while the degree of Ce anomaly (and

547   REE content) decreases in the reverse order. The fact that the Fe/Mn ratio varies with the Ce

548   anomaly does not mean that Ce is associated with the Fe oxide component.

549   This geochemical interpretation of the Ce partitioning at the Mn oxide - water interface can

550   be extended to cobalt, since this element is divalent in seawater (Byrne, 2002), oxidized to

551   Co(III) by Mn oxides (Murray and Dillard, 1979), sparingly soluble in its oxidized form,

552   systematically present as Co(III) in the three genetic-type oxides, and less abundant in fast

553   growing ferromanganese oxides (Halbach et al., 1983; Mannheim and Lane-Bostwick, 1988).

554   Co(III) is substituted isomorphically for Mn in the manganese layer (Manceau et al., 1987, 1997),

555   and the steric match between Co(III) (0.54 Å) and Mn(IV) (0.53 Å) is believed to be responsible

556   for the selective enrichment of cobalt in manganese oxides (Burns, 1976). The nature of the Ce

557   incorporation site in phyllomanganates is unknown. With a size of 0.80 Å in octahedral

558   coordination, Ce(IV) is too big to occupy Mn layer site, but may reside in the interlayer on top of

559   vacant Mn layers sites commonly observed in metal-containing birnessite (Drits et al., 2002;

560   Lanson et al., 2002a; Manceau et al., 2002a).

561

562   **4.3. Pb surface complexation on ferrihydrite**

563

564   EXAFS results show that Pb forms the same type of surface complex on marine ferrihydrite

565   as in the laboratory. Pb sorption on synthetic ferrihydrite at pH 6.5 was modeled by Manceau et al.

566   (1992b) by two nearest oxygen subshells at 2.22 and 2.42 Å, and two next-nearest iron subshells

567   of 0.3 Fe at 3.29 Å and 0.4 Fe at 3.45 Å. The two Pb-O (2.38 and 2.65 Å) and Pb-Fe (3.32 and

568   3.50 Å) distances reported here are similar to those inferred in our past spectroscopic study. The

569   new values are more accurate because the Pb-EXAFS spectrum from the previous study had a

570   lower signal-to-noise ratio and k range. The Pb-O distances are similar to those in β-PbO (2.21

571   and 2.49 Å; Leciejewicz, 1961) and, by analogy with the coordination of Pb(II) in this compound,

572   lead atoms are assumed to be at the apex of a distorted pyramid. The Pb-Fe distances are

573   interpreted by the formation of an ES surface complex, and their bimodal distribution as the

574   consequence of the split of the Pb-O distances in the first shell. Similar geometry was reported

575   for lead sorption on goethite and hematite (Bargar et al., 1997b, 1998). The formation of an ES

576   complex on synthetic ferrihydrite was confirmed by Scheinost et al. (2001), who reported an Fe

577   coordination about Pb of one at a distance of 3.32 Å at pH 5.0. In this last study, the local

578   structure of Pb was invariant with the reaction time (up to 2 months), ferrihydrite morphology

579   (with and without freeze-drying), metal competition (Cu^{2+}), and fulvic acid concentration.

580   Similarly, Trivedi et al. (2003) reported an average Pb-Fe distance of 3.34 Å on ferrihydrite at pH

581   5.5 and 6.5. While the resolution in interatomic distance was lower in the studies of Scheinost et

582   al. (2001) and Trivedi et al. (2003), all of the above results collectively support the formation of

583   edge-sharing lead complex on ferrihydrite, regardless of its origin and formation conditions. In

584   particular, there is no spectroscopic evidence for the existence of Pb-Cl pairs in natural samples

585   and, hence, for the formation of a Pb-Cl-Fe ternary surface complex, despite the high activity of

586   chlorine (0.54 M) in seawater. This finding was predicted from laboratory studies (Balistrieri and

587   Murray, 1982; Bargar et al., 1998).

588

589   **4.4. Pb surface complexation on phyllomanganate**

590

591   Two short distance Pb-Mn pairs were identified, one at 3.2 Å and another at 3.7 Å,

592   corresponding to ES and TCS complexes, respectively. The ES complex occurs at layer edges

593   (Morin et al., 2001) and the TCS complex in the interlayer (Manceau et al., 1999, 2002; Morin et

594   al., 1999; Matocha et al., 2001). The detection of the ES complex at low Pb loading in δ-MnO$_2$

595   indicates that it has a high affinity for the phyllomanganate surface. This complex likely occurs

596   in PbBi31, but its fractional amount relative to the TCS complex is negligible because PbBi31

597   contains 15 times more Pb than PbdBi2, and its particles have a larger lateral size (i.e., better

598   crystallinity). Their lateral dimension, as estimated by X-ray diffraction from the size of coherent

599   scattering domains (CSD), is ~ 200 Å (Lanson et al., 2002a) compared to 60 Å for δ-MnO$_2$

600   (Villalobos et al., 2003), consistent with Brunauer-Emmett-Teller (BET) measurements, showing

601   that the well-crystallized birnessite particles have an external (N$_2$) specific surface area of 27

602   m^2/g (Manceau and Charlet, 1992) vs. 120-150 m^2/g for δ-MnO$_2$ (Villalobos et al., 2003).

603   The higher affinity of lead for lateral sites cannot be explained by a higher number of

604   Pb-O-Mn bonds at these sites since in the proposed structural model (Fig. 14) lead is coordinated

605   to three surface oxygens on both interlayer and external sites (i.e., formation of a tridentate

606   complex on both sites). The reason may be electrostatic in nature. Because the three oxygens

607   from a vacant octahedral site are doubly coordinated to layer Mn, the total charge deficit at a

608   TCS site is $3x[(-2) + 2x(4^+/6)] = -2$ v.u. Thus, sorption of two protons or one Pb^{2+} at a TCS site

609   compensates the charge deficit on either side of a Mn(IV) vacancy (Silvester et al., 1997). In

610   contrast, the ES site has two oxygens singly coordinated to bulk Mn atoms and one doubly

611   coordinated (Fig. 14). The total charge at an ES site is $2x[(-2) + (4^+/6)] + [(-2) + 2x(4^+/6)] = -3.3$

612   v.u. Its charge compensation requires the sorption of one Pb^{2+} and one or two protons. Then, the

613   high reactivity of lateral sites towards metal sorption can be viewed as the consequence of the

614   lamellar structure of δ-MnO_2 and the nanometer size of the particles (high external to internal

615   surface ratio). One may argue that basal sites should be preferred over lateral sites since

616   conjoined edges have significantly more Pb^{2+}-Mn^{4+} repulsion (shorter Pb-Mn distance) than TCS

617   sites. However, lateral sites have less steric restriction than basal sites because two of the three

618   surface oxygens are singly coordinated in the first case, whilst they are all doubly coordinated in

619   the second.

620

621   **4.5. Evaluation of the formation of DCS complexes at layer edges**

622

623   The progressive reduction in amplitude of the TCS Pb-Mn peak (d(Pb-Mn2) = 3.7 Å) with

624   decreasing Pb/Mn ratio (Fig. 13b) is interpreted as the preponderance of a high surface-affinity

625   ES complex (d(Pb-Mn1) = 3.2 Å) at low surface coverage. This evolution also has been

626   interpreted by the existence of a double-corner sharing (DCS) complex on layer edges with a

627   Pb-Mn distance of 3.50-3.55 Å (Villalobos et al., 2005). In this alternative model, the TCS and

628   DCS sites were supposed to be occupied concurrently and independently of the Pb/Mn ratio,

629   meaning that Pb had the same affinity for external (DCS) and internal (TCS) sites. As explained

630   below, this structural interpretation is problematic.

631   In the DCS+TCS model of Villalobos et al. (2005), the data were fit with the following

632   assumptions. First, Pb forms a DCS complex ($CN = 2$) at layer edges and a TCS complex ($CN =$

633   6) in interlayers. This predetermined structural model was used in the spectral simulations to

634   constrain the EXAFS numbers (N) of Mn neighbors at each site to the Pb occupancy (f_{ext} and f_{int},

635   with $f_{ext} + f_{int} = 1$), such that $N(DCS) = 2 \times f_{ext}$ and $N(TCS) = 6 \times f_{int}$. For example, if Pb was

636   evenly distributed among the two sorption sites, then $N(DCS) = 2 \times 0.5 = 1.0$, and $N(TCS) = 6 \times$

637   0.5 = 3. Second, the structural disorder is anharmonic in the O shell (N(EXAFS) < CN) and

638   harmonic in the Mn shells (N(EXAFS) = CN). This assumption is incorrect for the immense

639   majority of Pb compounds, including sorption complexes (Manceau et al., 1996; Bargar et al.,

640   1997a). In practice, this model reproduced the data fairly well (Fig. 12j), but with generally

641   meaningless values (e.g., σ = 0.16 Å) for the Debye-Waller parameter (the harmonic model

642   becomes questionable when σ is higher than ~0.10 Å ; Teo, 1986; Crozier, 1997). With one

643   exception this disorder parameter was arbitrarily fixed to a lower value for the more distant TCS

644   shell than for the DCS shell, as if the structural disorder in solid matter could decrease with radial

645   distance. Still another problem with the DCS+TCS model is the unrealistically large interval of

646   variation of the energy threshold parameter (-21 $\leq$ ΔE_0 $\leq$ -13 eV). In a binary system, this

647   parameter should be constant, both for physical reasons and to decrease the degree of freedom

648   (Schlegel et al., 2001), otherwise non-linear least-squares fits converge to local minima and,

649   hence, to erroneous structural solution.

650   Consequently, the physical and mathematical problems with the DCS+TCS model are

651   believed to be the reasons for the misidentification of the ES complex at 3.2 Å as a DCS complex

652   at 3.50-3.55 Å. To test this hypothesis, the PbBi31 spectrum was fit successively with the TCS

653   (Fig. 12i) and the DCS+TCS (Fig. 12j) models. This sample contains major TCS and minor ES

654   complexes because it has 15 times more Pb than PbdBi2, and its particles have a large lateral

655   dimension. The TCS model (R = 3.72 Å, N = 1.3, σ^2 = 0.008 Å^2) and the DCS + TCS model (R =

656   3.46 Å, N = 1.0, σ^2 = 0.014 Å^2 + R = 3.70 Å, N = 3.0, σ^2 = 0.014 Å^2) equally reproduced the data

657   (Rp = 24, Table 5), and accounted for the major spectral features. This apparently anomalous

658   result has a simple explanation.

659   Consider an EXAFS signal consisting of waves from two shells as in the DCS+TCS model,

660   with the shells differing only in distance and coordination number. A simplified representation of

661   this signal is given by

662    $$\chi = A(k)\exp(2ikR + \delta(k))(1 + a\exp(2ik\Delta r))$$

663   where A and δ are the usual single-scattering EXAFS terms, a is the ratio of amplitudes of the

664   two shells, R the distance for the stronger shell (TCS), and Δr the distance difference. In our case,

665    $a = 1/3$ since $f_{ext} = f_{int}$, $R = 3.70$ Å, and $\Delta r = -0.24$ Å. For these values, the phase difference $2k\Delta r$

666   is π at $k = 6.5$ Å^{-1} and, the two waves interfere destructively over most of the data range (Fig. 15).

667   This makes the coordination number appear small, and the FT peak low in amplitude. However, it

668   is not obvious that the sum of the two waves really looks like a single wave. We can show that it

669   does by considering the phase difference between the combined signal (DCS + TCS model) and

670   that from a single wave (TCS model) with distance R:

671    $$\Delta\phi = \arg(1 + a\exp(2ik\Delta r))$$

672   If we draw an Argand diagram (phasor plot), we see that as a function of k, this phase difference

673   oscillates between limits of $\pm\sin^{-1}a$, which is about 19° (0.34 rad) here. The extrema occur

674   when $2k\Delta r = \pi \pm (\pi/2 - \sin^{-1}a)$. In our case, $\Delta R = 0.24$ Å, so these points occur at $k = 4$ and 9.1

675   Å^{-1}, approximately bracketing the range where the signal is largest. Thus, within that range, there

676   is an approximately linear phase difference between the DCS + TCS and TCS-only signals,

677   which can be compensated for in the data fitting by adjusting the assumed distance (i.e., 3.70 vs.

678   3.72 Å) and energy origin (i.e., $\Delta E_0 = -7$ vs -5 eV, Table 5). The above argument even accounts

679   for the distance in the TCS model fit (3.72 Å) being greater than the greater of the two distances

680   in the DCS + TCS model (3.70 Å). The phase difference $\Delta\phi$ is negative for $k < \pi/(2\Delta R)$, zero at k

681    $=\pi/(2\Delta R)$, where the shells are exactly out of phase, and positive for $k > \pi/(2\Delta R)$, which is the

682   effect provided by a distance increase over R, plus a small adjustment of the energy origin ΔE_0.

683   Similarly, the amplitude can be shown to be approximately (within the goodness of the fit to

684   TCS-only) described by a change of mean-square relative deviation (i.e., σ value). We see that

685   unless the data are taken over a large k-range and fit to very good models, it can be impossible to

686   tell the difference between a single shell (TCS model) and a pair of shells (DCS + TCS model) of

687   different coordination numbers and distances. Here, the correct model (ES + TCS) was

688   determined by varying experimentally the Pb/Mn ratio over two orders of magnitude (0.002

689   <Pb/Mn < 0.197 in the δ-MnO$_2$ series) compared to a factor of 5 (0.035 ≤ Pb/Mn ≤ 0.174) in

690   Villalobos et al. (2005), and by constraining the variation range of the fit parameters to physically

691   meaningful values.

692

693   **4.6. Pb partitioning among Mn and Fe oxide**

694

695   With a Mn/Fe weight ratio of 1.04 (Table 2) and a Mn-bound to Fe-bound lead ratio of

696   approximately 1, lead is unfractionated between the two oxides in D21-m3. In contrast, it is

697   moderately partitioned in the Mn oxide in D1-X1 (Mn/Fe = 0.3; Mn-bound/Fe-bound ≈ 1), and

698   strongly partitioned in AD14 (Mn/Fe = 1.1; Mn-bound/Fe-bound > 9). The sorption of Pb on

699   both Fe and Mn oxide in D21-m3 and D1-X1 can be explained by the fact that conjoined edge

700   sites also exist at chain terminations in ferrihydrite (Drits et al., 1993) which also have a high

701   affinity for cations (Spadini et al., 1994). Therefore, tridentate sites at chain terminations in Fe

702   oxide and at layer edges in Mn oxide may sorb lead equally in marine ferromanganese oxides.

703   The similarity of the O-O conjoined edge distances for FeO$_6$ octahedra (2.59 Å; Szytula et al.,

704   1968) and MnO$_6$ octahedra (2.62 Å; Lanson et al., 2002b) also explains the ability of the two

705   oxides to complex Pb(II) adions in tridentate edge-sharing geometries. Fe oxides may also bind

706   metal adions in bidentate edge-sharing geometries (i.e., sharing of only one edge with a single

707   octahedron), but apparently the energy stabilization gained from forming multiple edge bonds to

708   the Fe oxide surface is higher (Spadini et al., 2003). In summary, from a structural standpoint,

709   lead may sorb on either oxide, and its strong partitioning in AD14 does not have a simple

710   structural explanation.

711   It has been suggested that lead is associated with the Fe oxide component in marine

712   ferromanganese oxides because Pb is speciated as neutral or negatively charged moieties, such as

713    $Pb(CO_3)_n^{(2-2n)-}$ (n>1), and because Fe oxides have a net positive charge and Mn oxides a net

714   negative charge at circumneutral pH (Stumm, 1993; Koschinsky and Halbach, 1995; Langmuir,

715   1997; Koschinsky and Hein, 2003). This electrostatic explanation to geochemical partitioning on

716   Fe oxide is satisfying for anionic species, such as AsO_3^{3-} and AsO_4^{3-} (e.g., Smedley and

717   Kinniburgh, 2002; Koschinsky and Hein, 2003), but not for Pb because cationic moieties (Pb^{2+},

718    $PbCl^+$, and $PbOH^+$) co-exist with neutral and negative species in seawater according to chemical

719   equilibrium calculations. Three explanations can be proposed for Pb sorption on Fe and Mn

720   oxides in seawater. First, cationic lead species preferentially sorb on Mn oxide and anionic lead

721   species on Fe oxide. Second, sorption of cationic Pb species on Mn oxide shifts chemical

722   equilibrium in direction of the dissociation of anionic Pb complexes, thus leading to Pb

723   enrichment on Mn oxide. Third, the chemical (i.e., binding) component of the free energy for

724   tridentate Pb(II) sorption to octahedral edges on both oxides is much larger than the electrostatic

725   component. In this case a charged adion is sorbed specifically regardless of the sign of the surface

726   charge (Anderson and Rubin, 1981). Since Pb can be taken up by Mn and Fe oxides in the marine

727   environment, the Pb – Fe/Mn correlation in Fig. 1b does not mean that Pb is chemically bound to

728   the Fe oxide component, but that its enrichment depends on the growth rate of the

729   ferromanganese oxide, as for Ce and Co.

730   Independent of the geochemical partitioning of Pb between Mn and Fe oxide, both oxides

731   have strong binding sites that must be able to retain Pb over long periods of time because

732   ferromanganese deposits have a slow growth rate (mm/Myr) (e.g., Halbach et al., 1983; Halbach

733   et al., 1988; Takematsu, 1998). Knowing the molecular mechanism of Pb sequestration in these

734   deposits is essential to understand its marine geochemistry, and in particular its enrichment by up

735   to a factor of 200 relative to its crustal abundance (8.0 mg/kg; Faure, 1998) and 7×10^8 relative

736   to seawater concentration (1.3×10^{-11} M; Schaule and Patterson, 1981). This knowledge is also

737   important for environmental contamination issues because ferrihydrite and vernadite (the generic

738   term for natural turbostratic phyllomanganate; Manceau et al., 2006) are ubiquitous in soils and

739   continental sediments (Chukhrov and Gorshkov, 1981; Dixon and Skinner, 1992; Davison, 1993;

740   Manceau et al., 2003, 2005; Vodyanitskii and Sivtsov, 2004; Hochella et al., 2005a), and because

741   the lead-ferrihydrite / lead-vernadite co-association (D21-m3, D1-XA) and the lead-vernadite

742   partitioning (AD14) described here are common (Mckenzie, 1989; Hudson-Edwards, 2000;

743   Latrille et al., 2001; Liu et al., 2002; Cornu et al., 2005; Hochella et al., 2005b). Therefore, this

744   work provides context for further studies on the sequestration mechanism of Pb at Earth's

745   surface.

746

747   **4.7. Redox reactions of Ce, Co, and Pb sorbed on ferromanganese oxides**

748

749   Although Co and Ce have similar geochemical behavior in the marine environment (Addy,

750   1979; Ohta et al., 1999), some differences exist that are related to their redox properties. Ce and

751   Co are both readily oxidized by manganates, but while Ce may be oxidized also by Fe

752   oxyhydroxides (e.g., Bau, 1999; Kawabe et al., 1999), Co is not (e.g., Coughlin and Stone, 1995;

753   Angove et al., 1999; Jeon et al., 2003; Pozas et al., 2004). The redox potential of the

754   Ce(III)/CeO$_2$ couple in seawater is about Eh = 178-237 mV (pε = 3-4; De Baar et al., 1988). The

755   redox potential of the Co^{2+}/CoOOH couple at pH 8, Co$^{2+}_{(aq)}$ = 2.0 × 10^{-11} M (the dissolved Co

756   concentration in seawater; Martin et al., 1989), and E^0 = 1.48 V (Moffett and Ho, 1996), is 689

757   mV. Thus, Ce(III) is easily oxidized in seawater, even by dissolved oxygen (De Baar et al., 1988),

758   whereas Co(II) is only oxidized by MnO$_2$ (Murray and Dillard, 1979; Manceau et al., 1997).

759   Thermodynamic considerations also help understand the lack of oxidation of Pb(II) to

760   Pb(IV) in marine ferromanganese oxides. The potential of the Pb^{2+}/PbO$_2$ couple is 837 mV,

761   based on Brookins' data (1988) and a Pb$_{(aq)}$ concentration in seawater of 1.3 × 10^{-11} M (Schaule

762   and Patterson, 1981). This value is greater than the potential of H$_2$O/O$_2$ at P$_{O2}$ = 1 atm and pH 8

763   (756 mV), meaning that Pb(II) cannot be oxidized to Pb(IV) in homogeneous condition within

764 the stability field of water. Catalytic Pb(II) oxidation at the phyllomanganate surface could occur

765 (Murray and Dillard, 1979), but XANES and EXAFS spectroscopic data show that it does not

766 (Matocha et al., 2001; Manceau et al., 2002a; Takahashi et al., 2002b; Villalobos et al., 2005).

767 According to thermodynamic calculations, Pb(II) oxidation could be mediated by hausmannite

768 (Mn_3O_4; Hem, 1978), but this mixed-valence Mn oxide with a spinel structure has never been

769 identified in marine ferromanganese oxides.

770   Thus, it can be argued that the partitioning of the three redox-sensitive trace metals depends

771 on their redox potential. Since Co(II) is oxidized exclusively by Mn(III) and Mn(IV), and is

772 present as Co(III) in marine ferromanganese oxides, then this element can be anticipated to be

773 strictly associated with Mn oxides, as is shown by ample experimental evidence. Ce, which is

774 immobilized also in its oxidized form, probably is associated predominantly with Mn oxides

775 because Mn(IV) is a strong oxidant at pH 8.3. However, Ce(IV) - Fe oxide associations may also

776 occur, as Ce(III) can be oxidized by oxygen and freshly precipitated Fe oxides (Bau, 1999). This

777 association is not widespread because it is inhibited kinetically by the slow rate of Ce(III) to

778 Ce(IV) oxidation by O_2 and Fe(III). Of the three trace metals studied here, Pb probably has the

779 lowest affinity for Mn oxides, since it is always divalent. This hypothesis is supported by EXAFS

780 data, which show that Pb is associated partly with Fe in two of the three samples examined, and

781 re-adsorbed on the Fe component when the Mn component is dissolved. The lesser affinity of Ce

782 and Pb for the Mn oxide component compared to Co likely accounts for the weak Ce - Mn/Fe and

783 Pb - Mn/Fe correlations measured by EPMA (Fig. 4). Consistent with our hypothesis, the

784 correlation between Co and Mn/Fe is strong.

785

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1131

1132   **FIGURE CAPTIONS**

1133

1134   Fig. 1. Co (a) and Pb (b) abundances as a function of the Mn/Fe ratio for the series of

1135   ferromanganese oxides studied here and by Usui et al. (1997). Concentrations are from bulk

1136   and average EPMA analyses

1137   Fig. 2. REE patterns for the three genetic-type ferromanganese oxides. (a) Data normalized to

1138   PAAS; (b) Data normalized to the average REE abundances in deep seawater (Piepgras and

1139   Jacobsen, 1992).

1140   Fig. 3. Results from sequential dissolution of D535, AD14, D1-X1, and D21-m3 (hydrogenetic),

1141   and FG352 and G181 (diagenetic) ferromanganese oxides. Metal speciation has been

1142   operationally defined by Koschinsky and Halbach (1995) and Koschinsky and Hein (2003)

1143   as follows. Fraction 1: exchangeable cations and Ca carbonate fraction; Fraction 2: Mn oxide

1144   fraction; Fraction 3: Fe oxyhydroxide fraction; Fraction 4: residual fraction, mainly

1145   consisting of silicates and aluminosilicates.

1146   Fig. 4. Co, Ce, and Pb abundances against Mn/Fe ratio in CD25, D535, and AD14. Data from

1147   electron microprobe analyses. Numbers in parenthesis are correlation coefficients (r^2).

1148   Fig. 5. Cerium L_{III}-edge XANES spectra of a selection of ferromanganese oxides and references.

1149   Ce-sorption reaction times are one hour on δ-MnO_2 and HFO-1 and 120 hours on HFO-2.

1150   An overlay plot of the $CeCl_3$ spectrum is represented in dotted line for comparison. In some

1151   spectra, the position of the maximum of the 1st derivative is indicated by an arrow. CeO_2 and

1152 $Ce(OH)_4$ have a shoulder at 5727 eV pointed out by an asterisk.

1153   Fig. 6. Cerium L_{III}-edge micro XANES spectra at spot 1 in the growth structure and at spot 2 in

1154   the Fe-rich area of CD25. The locations of the analyzed spots are indicated by a cross in the

1155   X-ray fluorescence maps.

1156   Fig. 7. Cobalt K-edge XANES spectra of a selection of ferromanganese oxides and references.

1157   Fig. 8. Cobalt K-edge micro XANES spectra at spots 1 and 2 on the X-ray fluorescence map

1158   presented in Figure 7. The difference spectrum suggests that 10-15 % of Co is divalent at

1159   spot 2.

1160   Fig. 9. (a) Lead L_{III}-edge XANES spectra of hydrogenetic and diagenetic ferromanganese oxides

1161   and reference compounds. (b) First derivative of some XANES spectra.

1162   Fig. 10. Pb L_3-edge EXAFS spectra of untreated (D1-X1, AD14 and D21-m3) and

1163   hydroxylamine-treated (D1-X1-Fe, AD14-Fe and D21-m3-Fe) hydrogenetic ferromanganese

1164   oxides (a-e). The D21-m3 spectrum was best simulated (Sum-sq = 0.039) with a mixture of

1165   AD14 and D21-m3-Fe, in proportions of 50 and 47 %, respectively. Precision: 10 % of total

1166   Pb (f).

1167   Fig. 11. Pb L_3-edge EXAFS spectra (a,c) and Fourier transforms (b,d) of hydroxylamine-treated

1168   D21-m3 (D21-m3-Fe) and untreated AD14 compared to Pb-sorbed ferrihydrite (PbHFO100,

1169   pH 6.5) and Pb-sorbed δ-MnO_2 (Pbd112, pH 5) references. The numbers after the code

1170   names are the Pb to sorbent metal (Fe or Mn) mole ratio in parts per thousand.

1171   Fig. 12. Model fits of the Pb-EXAFS data for lead sorbed on ferrihydrite (PbHFO), δ-MnO_2

1172   (PbdBi) and well-crystallized birnessite (PbBi). The data are in dashed lines, and the models

1173   in solid lines, and the best-fit parameters for each model are listed in Table 5. The

1174   contributions from the Pb-O, Pb-Fe (ferrihydrite), and Pb-Mn (δ-MnO_2 and birnessite)

1175   nearest shells have been filtered by Fourier transformation.

1176   Fig. 13. Pb L_3-edge EXAFS spectra (a) and Fourier transforms (b) of Pb sorbed on δ-MnO_2

1177   (PbdBi series) and well-crystallized birnessite (PbBi) at different Pb/Mn ratio.

1178   Fig. 14. Structural model for the uptake mechanism of Pb on Mn^{3+}-free phyllomanganate. TCS

1179   and DES are triple-corner and double-edge sharing complexes. At low surface loading, Pb

1180   occupies both lateral (DES) and basal (TCS) sites of the MnO_2 layer. On the lateral site, the

1181   base of the Pb pyramid is formed by two conjoined edges from two neighboring Mn(IV)

1182   octahedra (tridendate edge-sharing complex). On the basal site, the base of the Pb pyramid is

1183   formed by the face of a vacant Mn(IV) layer octahedron and, therefore, is parallel to the

1184 layer plane (tridendate corner-sharing complex).

1185 Fig. 15. Electronic waves from the two Mn shells at $R = 3.46$ ($N = 1.0$, $\sigma^2 = 0.014$ $Å^2$) and $R =$

1186 3.70 Å ($N = 3.0$, $\sigma^2 = 0.014$ $Å^2$) for PbBi31 in the model fit of Pb-sorbed phyllomanganate

1187 proposed by Villalobos et al. (2005). The two waves are out-of-phase at 6.5 $Å^{-1}$ ($\Delta E_0 = 0$

1188 eV).

1189   **Electronic Annex captions**

1190

1191 **Fig. EA-1.** X-ray diffraction patterns of hydrogenetic samples. F = feldspar (mostly albite), FeOx

1192 = poorly crystallized Fe oxyhydroxide, Gt = goethite, P = phyllosilicate, Ph = phillipsite, Qtz =

1193 quartz. The 7 Å and 10 Å phyllomanganates are one-water (7 Å) and two-water (10 Å) layer

1194 hydrates of vernadite. Hydrogenetic Mn oxides have low Mn/Fe ratios (Table 2) and weak basal

1195 reflections. Recording conditions for all patterns: Cu Kα radiation, angular range = 5 - 80 °2θ,

1196 step size = 0.04 °2θ, counting time = 40 s/pt.

1197

1198 **Fig. EA-2.** X-ray diffraction patterns of diagenetic samples. Diagenetic and hydrothermal Mn

1199 oxides (Fig. EA-3) have high Mn/Fe ratios and intense basal reflections.

1200

1201 **Fig. EA-3.** X-ray diffraction patterns of hydrothermal and mixed hydrogenetic-hydrothermal

1202 samples. C = calcite, H = halite, T = todorokite.

1203

Table 1. List of the samples of ferromanganese oxides studied in this work.

Sample name	Sampling site			Cruise name	Type of deposition	Mineralogy of of Mn oxides[a]
	Latitude	Longitude	Depth (m)			
D535	13º00.6'S	159º17.6'W	5222	Hakurei-maru GH83-3	HG	Fe-vernadite
CD25	16º26.0'N	169º32.3'W	2320	Farnella FN-86-HW	HG	Fe-vernadite
AD14	14º11.8'N	167º24.4'E	1617	Hakurei-maru 96S	HG	Fe-vernadite
D1-X1	32º04.5'N	138º31.5'E	2600	Moana Wave MW9503	HG	Fe-vernadite
D21-m3	31º23.5'N	138º45.3'E	1110	Moana Wave MW9503	HG	Fe-vernadite
D465, inner	09º03.4'N	174º04.1'W	5968	Hakurei-maru GH80-5	HG	Fe-vernadite
D465, outer	09º03.4'N	174º04.1'W	5968	Hakurei-maru GH80-5	DG	10Å-vernadite
D513	01º05.2'S	166º10.0'W	5341	Hakurei-maru GH82-4	DG	10Å-vernadite
D514	00º45.9'S	166º07.0'W	5200	Hakurei-maru GH82-4	DG	10Å-vernadite
FG352	03º15.8'N	169º41.1'W	5370	Hakurei-maru GH81-4	DG	10Å-vernadite
G181	07º01.4'N	171º59.7'W	5660	Hakurei-maru GH76-1	DG	10Å-vernadite
B6	30º17.8'N	172º10.5'W	5350	Hakurei-maru GH80-1	DG	10Å-vernadite
F243-1	07º40.2'N	172º56.3'W	5907	Hakurei-maru GH80-1	DG	10Å-vernadite
D11-X9	32º00.1'N	139º10.1'E	1575	Moana Wave MW9503	HT	10Å+7Å-vernadite + todorokite
D12-X2	31º58.0'N	139º04.2'E	1590	Moana Wave MW9503	HT	Hexagonal birnessite
D21-103	31º23.5'N	138º45.3'E	1110	Moana Wave MW9503	HT	10Å+7Å-vernadite +ctodorokite
31GTV2-3	25º24.0'S	69º45.4'E	2800	SO92 Sonne	HG + HT	Fe-vernadite
31GTV6-11	25º24.0'S	69º45.4'E	2800	SO92 Sonne	HG + HT	Fe-vernadite

[a] Turbostratic (i.e., c-disordered) phyllomanganates found in marine ferromanganese oxides have been named δ-MnO$_2$, buserite and birnessite in the literature on the basis of the intensity and position of basal reflections by XRD. Today, it appears that there is no fundamental structural difference between all these phyllomanganate varieties. As discussed in Manceau et al. (2006), the use of the generic term vernadite, which dates back to long before the three others (Betekhtin, 1940), is preferred to describe natural turbostratic phyllomanganates. In sample D12-X2, the phyllomanganate layers are stacked regularly with an hexagonal sequence as in synthetic HBi

(Silvester et al., 1997). Diffraction patterns are presented in Electronic Annex.

Table 2. Bulk chemical analyses.

	Mn	Fe	Mn/Fe	Co	Cu	Ni	Zn	Pb
	(wt.%)		(wt. ratio)			(mg/kg)		
D535	12.8	12.7	1.01	4750	1020	2820	465	714
CD25	13.1	12.1	1.08	6350	513	1690	741	1170
AD14	13.4	11.7	1.15	8370	904	3450	1420	1640
D1-X1	5.57	17.1	0.326	830	276	870	441	1650
D21-m3	14.4	13.9	1.04	2450	177	1460	401	1870
G181	29.4	4.68	6.28	1630	11500	8550	1340	162
B6	25.6	5.30	4.83	1140	18800	14300	1310	234
F243-1	26.8	4.20	6.38	1540	12800	10900	1680	211
D513	24.9	5.99	4.16	717	18200	14400	1330	182
D514	20.8	9.30	2.24	1750	9650	10400	908	448
FG352	25.9	6.07	4.27	1320	19200	13300	1170	259
D11-X9	41.6	0.420	99.0	d.l.	13.4	61.0	73.0	35.0
D12-X2	44.2	0.080	553	46.0	4.6	119	54.5	56.0
D21-103	43.2	d.l.	-	176	62.5	295	26.0	34.0
31GTV2-3 [a]	12.4	17.2	0.721	755	563	1200	518	408
31GTV6-11[a]	15.4	19.8	0.778	966	713	1730	541	315

[a] Data from Kuhn et al. (1998).

d.l.: below detection limit.

Table 3. Electron microprobe analyses (wt.%) in main growth structures.

Sample name	Mn	Fe	Mn/Fe	Al	Si	P	Ti	Co	Ce	Pb	N (number of analyzed points); observed minor phase
D535	20.5-34.4	10.4-22.2	0.92-3.29	0.353-2.10	0.244-2.61	0.109-0.266	0.713-1.15	0.228-1.33	0.134-0.294	0.001-0.169	N=30; Opal with high Fe content.
	27.9	16.4	1.81	0.69	0.645	0.217	0.904	0.679	0.208	0.087	
	(3.6)	(3.1)	(0.64)	(0.42)	(0.674)	(0.045)	(0.123)	(0.428)	(0.041)	(0.044)	
CD25	15.5-36.3	9.35-27.8	0.570-3.82	0.044-0.654	0.167-4.40	0.150-0.379	0.829-2.88	0.243-1.32	0.028-0.825	d.l.-0.393	N=90; Opal with high Fe content and particle with high contents of Fe and Ti.
	26.0	16.5	1.75	0.244	0.919	0.248	1.44	0.648	0.167	0.154	
	(4.5)	(4.5)	(0.67)	(0.147)	(1.13)	(0.055)	(0.45)	(0.352)	(0.093)	(0.104)	
AD14	19.1-39.4	6.47-30.2	0.635-5.81	0.073-0.422	0.043-0.816	0.211-1.88	0.412-1.20	0.168-2.32	0.076-0.260	0.137-0.392	N=60; Phosphate and Fe precipitate (Mn/Fe is around 0.07).
	29.5	16.7	2.64	0.151	0.268	0.561	0.735	0.867	0.152	0.263	
	(6.2)	(8.5)	(1.86)	(0.057)	(0.193)	(0.430)	(0.251)	(0.758)	(0.046)	(0.071)	
D465, inner	18.9-38.2	2.27-15.5	1.27-16.3	0.822-3.96	0.135-2.03	0.047-0.270	0.210-1.07	0.060-0.404	d.l.-0.138	0.019-0.126	N=30
	28.6	9.45	3.96	2.47	0.566	0.141	0.705	0.260	0.077	0.058	
	(4.9)	(3.28)	(3.37)	(0.734)	(0.352)	(0.050)	(0.258)	(0.077)	(0.039)	(0.025)	
D465, outer	16.1-39.7	0.173-18.5	0.955-217	0.755-4.01	0.021-1.30	0.017-0.264	d.l.-0.837	0.001-0.350	d.l.-0.129	d.l.-0.113	N=30
	25.4	8.54	26.4	2.33	0.633	0.135	0.415	0.191	0.059	0.046	
	(8.1)	(6.19)	(51.0)	(0.70)	(0.358)	(0.084)	(0.289)	(0.095)	(0.039)	(0.036)	

D514	23.3-42.8	1.47-3.30	9.14-27.6	0.604-2.24	0.461-1.82	0.036-0.072	0.067-0.749	0.092-0.308	0.111-0.182	n.m.	N=7
	36.3	2.49	15.9	1.54	1.09	0.059	0.265	0.175	0.140		
	(7.1)	(0.60)	(6.59)	(0.66)	(0.50)	(0.013)	(0.289)	(0.095)	(0.027)		
FG352	21.4-46.3	0.103-8.20	3.72-447	0.124-3.38	0.041-3.60	0.021-0.162	0.007-0.453	0.050-0.207	0.052-0.204	n.m.	N=7
	35.8	3.34	100	1.46	1.23	0.076	0.148	0.136	0.119		
	(9.1)	(2.87)	(177)	(1.07)	(1.26)	(0.051)	(0.166)	(0.057)	(0.055)		

First row = range of concentrations, second row = average values, third row (in parenthese) = standard deviations of the measured values. In some cases, the standard deviation exceeds the average value due to chemical heterogeneity. d.l.: below detection limit; n.m.: not measured.

Table 4. Bulk REE abundances (mg/kg)

Sample name	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(Ce/Ce*)$_{SN}$ [d]
D535 [a]	130	177	1230	41.3	164	38.3	8.97	40.3	5.90	33.8	6.89	20.2	2.88	19.3	2.95	3.31
CD25 [a]	188	303	844	70.8	283	62.2	15.1	64.9	9.43	58.0	11.5	32.1	4.39	27.3	4.16	1.33
AD14 [a]	131	167	573	28.4	124	25.9	6.58	30.2	4.57	29.2	6.63	20.4	2.90	18.9	3.01	1.91
D1-X1	59.6	203	1130	41.1	168	35.1	8.69	31.8	4.89	23.5	3.94	10.5	1.41	9.23	1.39	2.85
D21-m3	207	304	621	60.3	260	56.5	13.9	61.6	9.68	54.5	10.7	30.3	4.15	25.5	3.90	1.05
D465, inner	115	150	916	33.3	139	30.2	7.38	31.9	5.07	31.0	5.73	18.2	2.59	17.7	2.74	2.98
D465, outer	59.0	63.0	178	18.4	76.7	19.4	4.80	19.2	3.32	18.1	3.41	9.67	1.44	9.51	1.34	1.20
G181	41.4	44.0	91.4	13.6	58.4	14.6	4.13	14.0	2.34	13.2	2.48	6.87	1.01	6.48	0.982	0.860
B6	81.6	68.5	81.7	18.3	79.5	18.8	5.33	19.3	3.22	18.8	3.65	10.7	1.51	9.89	1.53	0.531
F243-1	37.4	36.7	84.8	11.4	49.3	12.6	3.58	12.7	2.14	11.9	2.30	6.44	0.960	6.15	0.939	0.953
D513 [b]	64.2	64.4	114	17.2	75.0	17.4	4.21	17.6	2.88	16.5	3.19	9.86	1.31	8.52	1.29	0.790
D514	86.9	103	262	25.6	106	24.3	5.82	25.5	3.85	22.4	4.25	12.0	1.68	11.2	1.64	1.17
FG352	66.9	70.9	64.4	15.4	65.7	15.1	3.43	15.1	2.52	14.1	2.87	9.04	1.21	8.65	1.17	0.448
D11-X9	32.2	4.64	5.14	0.753	3.43	0.776	0.810	1.41	0.261	2.34	0.744	2.85	0.462	3.36	0.617	0.632
D12-X2	12.9	4.24	6.59	0.791	3.68	0.773	0.180	1.08	0.180	1.38	0.370	1.32	0.211	1.60	0.269	0.827
D21-103	1.80	0.661	0.213	0.0839	0.454	0.0590	0.0207	0.103	0.0160	0.133	0.0393	0.127	0.0204	0.152	0.0259	0.208
GTV2-3 [c]	189	276	320	61.9	241	48.2	12.2	55.3	7.96	46.8	9.21	25.1	3.68	22.0	3.36	0.563
GTV6-11 [c]	186	289	253	60.9	238	48.5	12.1	54.2	7.89	46.8	9.33	25.6	3.74	22.7	3.60	0.439

[a] Data from Takahashi et al. (2000) except for Y.

[b] Average values of six analyses reported in Ohta et al. (1999).

[c] Data from Kuhn et al. (1998).

[d] (Ce/Ce*)$_{SN}$ = the degree of Ce anomaly normalized to PAAS (McLennan, 1989).

Table 5. Pb-EXAFS for Pb sorbed phyllomanganates and hydrous ferric oxide

Sample	Fit Model	O shell			Me[a] shell			ΔE_0 (eV)	Rp
		R (Å)	N^b	σ^2 (Å²)	R (Å)	N^b	σ^2 (Å²)		
PbBi31	Two-shell fit	2.30	1.6	0.011	3.72	1.3	0.008	-5	24
	Three-shell fit	2.29	1.7	0.012	3.70	1.0	0.008[c]	-9	14
					4.09	0.8	0.008[c]		
	Three-shell fit[d]	2.29	1.7	0.011	3.46	1[e]	0.014	-7	24
					3.70	3[e]	0.014		
PbdBi197	Two-shell fit	2.29	2.3	0.012	3.68	0.8	0.008	-9	15
PbdBi112	Three-shell fit	2.33	2.2	0.012	3.23	0.2	0.008[c]	-9	12
					3.73	0.6	0.008[c]		
PbdBi44	Three-shell fit	2.33	2.3	0.012	3.23	0.3	0.008[c]	-9	15
					3.73	0.5	0.008[c]		
PbdBi2	Three-shell fit	2.34	2.2	0.012	3.25	0.3	0.007[c]	-9	15
					3.76	0.5	0.007[c]		
PbHFO100	Two-shell fit	2.36	2.8	0.013	3.39	1.6	0.014	-4	32
	Three-shell fit	2.37	2.9	0.013[c]	3.41	1.6	0.014	-2	26
		2.66	1.2	0.013[c]					
	Three-shell fit	2.36	2.9	0.013	3.26	1.9	0.014[c]	-5	17
					3.44	2.7	0.014[c]		
	Four-shell fit	2.38	3.3	0.014[c]	3.32	1.9	0.014[c]	-1	9
		2.65	1.3	0.014[c]	3.50	2.5	0.014[c]		

EXAFS parameters were optimized by minimizing the Rp value defined as sum$\{|k^3\chi_{exp} - k^3\chi_{fit}|\}$/sum$\{|k^3\chi_{exp}|\}$. The R+$\Delta$ intervals for the Fourier backtransforms were [1.1-4.2] Å for PbBi31, [1.1-3.9] Å for PbdBi197-5 and PbdBi35-7, [1.1-3.8] Å for PbdBi44-5 and PbdBi2-5, and [1.1-3.7] Å for PbHFO100.

[a] Me = Mn for Mn compounds, and Me = Fe for HFO.

[b] effective coordination numbers. The Pb full coordination is lost due to anharmonic structural disorder.

[c] σ parameters constrained to the same value for the two sub-shells. $S_0^2 = 0.85$.

[d] Same model fit as Villalobos et al. (2005)

[e] Parameters fixed to the same values as in Villalobos et al. (2005)
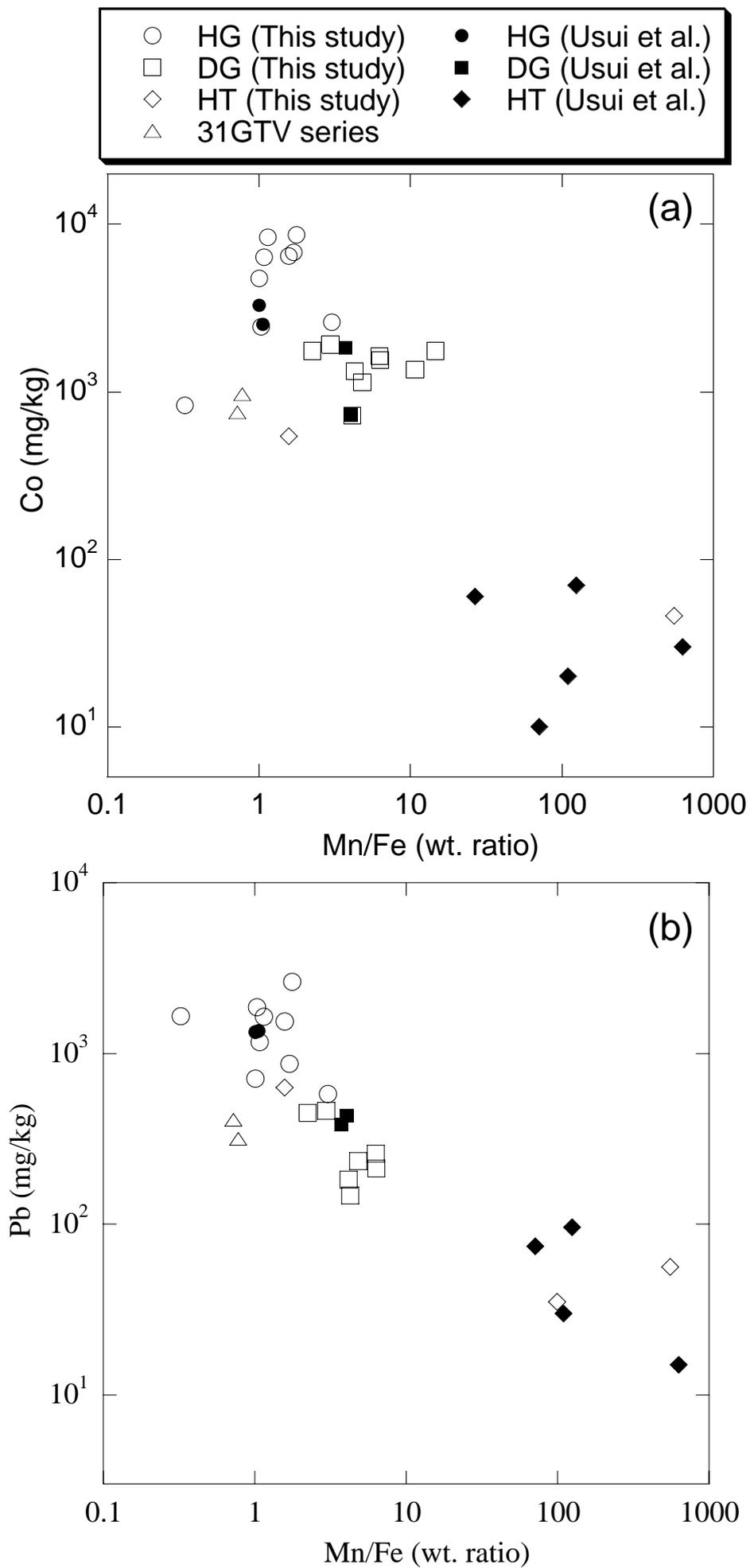
Fig.1

Fig.2a

Fig.2b

Fig.3

Fig. 4

Ce on HFO-2

Ce on HFO-1

CeCl₃

CeCl₃:Ce(SO₄)₂
= 1:9

CeO₂

Ce(OH)₄

Ce(SO₄)₂

Ce on δ-MnO₂

AD14

D535

CD25

D465 (inner)

D465 (outer)

FG352

G181

31GTV2-3

31GTV6-11

D11-X9

Absorption

Energy (eV)

Fig.5

Mn K$_\alpha$ mapping

Co K$_\alpha$ mapping

Fe K$_\beta$ mapping

Spot 2 (Fe-rich area)

Ce L$_\alpha$ mapping

Spot 1 (Mn oxides)

0.3 mm

0.8 mm

Absorption

Spot 2

Spot 1

5710 5720 5730 5740 5750 5760

Energy (eV)

Fig.6

Co on HFO

Co on δ-MnO$_2$

D21-103

G181

D465 (outer)

D465 (inner)

CD25

Co$_2$O$_3$

CoO

Absorbance

7700   7720   7740   7760

Energy (eV)

Fig.7

Fig.8

Fig.9

a

D1-X1
AD14
Sum-Sq = 1.2 10⁻¹

b

D1-X1
D21-m3
Sum-Sq = 2.1 10⁻²

c

D1-X1
D1-X1-Fe
Sum-Sq = 8.2 10⁻²

d

D21-m3
D21-m3-Fe
Sum-Sq = 8.6 10⁻²

e

AD14
AD14-Fe
Sum-Sq = 2.1 10⁻¹

f

D21-m3
Sum-Sq = 3.9 10⁻²
0.50 AD14 + 0.47 D21-m3-Fe

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Fig. 14

Fig. 15