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1 Zr, Hf AND REE DISTRIBUTION IN RIVER WATER UNDER DIFFERENT IONIC STRENGTH
2 CONDITIONS

3
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17

18 **Abstract**

19 The Platani River flowing in south-central Sicily, interacting with evaporite rocks, generates a wide
20 range of ionic strength in the water catchment from 0.1 to 5.0 mol kg⁻¹. We sampled 38 river sites
21 and analysed the composition for the dissolved fraction filtered through 0.45 µm, the truly dissolved
22 fraction obtained through ultrafiltration (10 KDa) and the relative included colloidal fraction.

23 This study was focused on the recognition of Zr, Hf and REE behaviour under changing ionic
24 strength conditions, since this is one of parameters responsible for colloid stability in natural waters.

25 In turn, this phenomenon leads to REE release from the colloidal fraction and their scavenging onto
26 surfaces of suspended particles or sediment, or their complexation with dissolved ligands.
27 Our results indicated that in both dissolved and ultra-filtrated fractions REE increases either in the
28 middle (Sm – Dy) or in the heavier (Ho – Lu) part of the PAAS-normalised distribution, while the
29 Zr/Hf ratio value ranges from sub-chondritic to super-chondritic.
30 Scanning Electron Microscopic and Energy Dispersive X-ray Spectrometric (SEM-EDS) analyses
31 and dissolved Mg, Al and Fe concentrations suggested that the studied colloids consist of
32 aggregations of Al-oxyhydroxides, carbonate nanoparticles and clays where organic traces were not
33 found. The studied colloids showed greater affinity with dissolved Zr than Hf determining Zr/Hf
34 values larger than the chondritic values. The largest Zr/Hf values were found in colloidal fractions
35 from waters with ionic strength larger than 0.6 mol kg⁻¹. These Zr/Hf values up to 280 (w/w) are
36 provided by the faster removal of Hf relative to Zr from coagulating colloids and its preferential
37 scavenging onto authigenic Fe-oxyhydroxides in bottom sediment. Further studies are needed to
38 clarify if this suggested process can represent a suitable starting point for the Zr-Hf decoupling
39 observed in seawater.

40

41 **1. INTRODUCTION**

42 Elements' transport from continent to seawater represents the main part of their exogenous cycle.
43 Rare Earth Elements (REE) transport was investigated in a large number of scientific studies
44 throughout the last 40 years (Elderfield and Greaves, 1982; Elderfield, 1988; Elderfield et al., 1990).
45 These studies highlighted some REE characteristics occurring during aqueous processes including the
46 large REE affinity towards solid surfaces and the related tendency of these elements to partition
47 along the REE series. Accordingly, REE removal from the dissolved phase during reactions between
48 suspended solids and colloids is one of the most common processes occurring in natural waters
49 (Goldstein and Jacobsen, 1988; Sholkovitz and Elderfield, 1988; Elderfield et al., 1990; Sholkovitz et

50 al., 1994; Sholkovitz, 1992; 1995; Lawrence and Kamber, 2006; Rousseau et al., 2015; Merschel et
51 al., 2017).

52 This sensitivity towards surfaces of different natures during interface processes was also recognised
53 in natural waters for Zr and Hf (Schmidt et al., 2014; Inguaggiato et al., 2015; 2016; Censi et al.,
54 2015; 2017). This sensitivity determined the decoupling of these elements that run relative to their
55 strong geochemical coherence evidenced during the crystallisation of rock-forming minerals (Bau,
56 1996).

57 Studies focused on the REE distribution in rivers showed the importance of estuaries as areas where
58 the largest difference between geochemical behaviour of these elements in continental and seawater
59 was emphasised throughout interface processes. The same effort for Zr and Hf consisted of some
60 studies in rivers (Godfrey et al., 2008; Pokrovsky et al., 2010; 2014) and seawater (McKlively and
61 Orians, 1993; 1998; Godfrey et al., 1996; Firdaus et al., 2008; 2011; Frank, 2011).

62 REE studies demonstrated that the transport of metal ions occurs in colloids from continental waters
63 (Sholkovitz, 1993; 1995; Lawrence and Kamber, 2006; Cidu and Frau, 2009; Cidu et al., 2013; Tepe
64 and Bau, 2014; Johannesson et al., 2017; Merschel et al., 2017 and references therein). Accordingly,
65 changes of ionic strength in estuaries were demonstrated to play a key role in determining the REE
66 partitioning among dissolved phase, suspended particles and sediments and then influencing the REE
67 transport from continents to the sea (Sholkovitz, 1995 and references therein; Elbaz-Poulichet and
68 Dupuy, 1999; Sholkovitz and Szymczak, 2000; Nozaki et al., 2000; Hannigan and Sholkovitz, 2001;
69 Barroux et al., 2006; Censi et al., 2007; 2010; Kulaksiz and Bau, 2007; 2011; Godfrey et al., 2008;
70 Johannesson et al., 2017). On the other hand, the mixing of water masses and the regime of coastal
71 currents can disturb the geochemical REE effect simply due to the contribution of ionic strength in
72 estuaries.

73 The above-mentioned examples addressed to the Zr-Hf distribution in natural waters highlighted the
74 large difference between the geochemical coherence of these twin elements in rocks and partially in

75 continental waters compared to the strong fractionation reported in seawater. The extent of this
76 difference suggested several possible explanations of this finding, such as the incongruent weathering
77 of zircon bearing rocks, Zr-Hf hydrothermal input in seawater, or Zr-Hf involvement in the
78 biogeochemical cycles along the water column (Bau and Koschinsky, 2006; Frank, 2011).

79 In this study, our objective was to determine whether Zr-Hf decoupling under the effect of ionic
80 strength may represent the starting point of large observed differences in Zr-Hf fractionation
81 occurring in seawater relative to continental water. In turn, changes of ionic strength in waters could
82 influence the Zr/Hf and REE signature of authigenic minerals and sediment fraction (Inguaggiato et
83 al., 2018; Zuddas et al., 2018). In order to investigate this item, we have to investigate how aqueous
84 Zr, Hf and REE distribution can react to severe changes of ionic strength along a small river far from
85 its estuary. In the studied waters, the limited pH and Eh changes observed should have lower effects
86 than the variation of ionic strength on the distribution of Zr, Hf and REE among colloids, truly
87 dissolved fractions and river sediment. The location of the selected Platani river catchment is South-
88 Central Sicily, where some of the largest Messinian evaporite deposits crop out in the Mediterranean
89 (Rouchy and Caruso, 2006). The weathering of these deposits drives the high salt content of river
90 waters, determining the required change of ionic strength spanning between 0.11 and 5.15 mol kg⁻¹.

91 The size of the selected river and the turbulence of its waters causes the resuspension of the finest
92 sediment fraction that in turn represents the main component of the suspended river load. So, the
93 assessment of the effect of this suspended load on the distribution of aqueous Zr, Hf and REE can be
94 considered negligible, with a result quite similar to that induced by partitioning with sediment. Our
95 focus on the “coarse” colloidal fraction with molecular weight cut-offs between 10 KDa and 450 nm
96 should allow to investigate its resistance to salt-induced coagulation, its organic and/or inorganic
97 nature in a river system dominated by weathering of soluble sediments.

98

99 2. STUDIED AREA

100 South-central Sicily, i.e. the Caltanissetta basin (see Fig. 1), is a NE-SW elongated area about 140 km
101 large, characterised by widespread evaporite outcrops belonging to the Gessoso-solfifera formation.
102 These sediments were deposited as a consequence of the progressive lack of communication between
103 the current Mediterranean Sea and the ocean during the Messinian Salinity Crisis (Hsu et al. 1973).
104 The Caltanissetta basin is included between the northernmost Appenino-Maghrebide range and the
105 easternmost Iblean plateau. The evaporite succession is preceded by diatomites (locally called
106 Tripoli). Diatomites are followed by the lowermost evaporitic unit consists of limestones (locally
107 called “Calcare di Base”) followed by laminated gypsum (balatino) and selenite, often embedded
108 with gypsum marls and locally topped by salt deposits. Immediately above the Calcare di Base, a
109 sulphur-bearing limestone locally called “Calcare Solfifero” occurs, consisting of microcrystalline
110 calcite, celestine, aragonite and native sulphur (Dessau et al. 1962). Here, starting from the Roman
111 period, sulphur extraction procedures were carried out, initially by hand. The uppermost evaporite
112 unit consists of laminar, massive and clastic gypsum with marly to clay intercalations followed by a
113 transgressive conglomerate locally called “Arenazzolo” (Manzi et al. 2009). The Messinian Salinity
114 Crisis was ended by the deposition of the Trubi formation consisting of foraminiferal marls
115 corresponding to the reopening of water communication between the evaporitic basin and the open
116 ocean (Rouchy et al. 2001).

117 The mining exploitation in the Bosco-San Cataldo area began with a sulphur mine between 1930 and
118 1938. During the exploitation of the sulphur deposit, large landfills were produced close to the
119 mining area. These consisted of wastes formed by detritus of “Calcare solfifero” hosting the sulphur
120 deposit that was roasted to extract sulphur. These materials consist of carbonates (mainly calcite,
121 aragonite and sometimes strontianite) and variable amounts of celestine and gypsum. In 1954, the
122 discovery in the same area of a large kainite deposit led to the conversion of the progressively
123 declining sulphur mine to a more promising salt mine. The kainite exploitation and related industrial

124 activities involved the accumulation of a large salt landfill up to 1988, when mining activity was
125 interrupted. Now, the studied area shows a characteristic white deposit of salt wastes whose
126 occurrence strongly influences the composition of the surface waters belonging to the Platani river
127 catchment.

128 The Platani River has the second widest drainage basin in south-central Sicily (1,785 km²) and flows
129 through the western part of the Caltanissetta basin (Fig. 1) where wide evaporitic sequences crop out.
130 In particular, the Stincone-Salito flow rate is close to about 1 m³ sec⁻¹.

131

132 **3. MATERIALS AND METHODS**

133 Samples of 38 river waters were collected along the Platani catchment, starting from the Bosco-San
134 Cataldo mining area. The weathering of these landfills by rainwater has promoted salinization of the
135 higher course of the Platani River, creating the conditions for investigating trace element
136 fractionation between the dissolved pool (consisting of colloids and the truly dissolved fraction) and
137 river sediments in a wide range of ionic strength conditions (Censi et al., 2016). Many water samples
138 were collected along the tributaries of the Platani River; these are creeks rather than rivers and are
139 characterised by limited water depth and turbulent water flows. Therefore, the large suspended
140 particles (larger than 450 nm) were mainly considered as a result of the resuspension of the riverbed
141 sediments and their composition was not investigated in this study. The studied area along the River
142 Platani, its location in South-Central Sicily and the Bosco-S. Cataldo abandoned mining site are
143 reported in Fig. 1.

144 The field work was carried out during several seasons from 2014 to 2016: December 2014, January
145 2015, May 2015, April 2016 and October 2016. The Eh, pH, temperature and conductivity of the
146 studied waters were measured directly in the field with an ORION 250+ meter. Eh measurements
147 were carried out with an Eh oxytrode Pt probe (Hamilton™) using a reference standard solution
148 buffer at 0.475±0.005 V. The accuracy of determinations was ±0.01 V for Eh, ±0.1 for pH, ±0.1°C

149 for temperature, and 1% for EC. The major anions were analysed using a Dionex ICS 1100
150 chromatograph on filtered and acidified (HNO₃) samples with a Dionex CS-12A column for cations
151 and on filtered and acidified (HNO₃) samples with a Dionex AS14A column for anions. Alkalinity
152 was determined in the field by titration with HCl 0.1 M. At each sampling site, three litres of water
153 were collected:

154 Two litres were immediately filtered on-field through 450 nm sterile filter membrane
155 (CHM™ cellulose acetate filter) and represented the dissolved fraction (DF). Then, DF was stored in
156 a previous acid-cleaned polyethylene bottle for subsequently separating the colloidal (CF) from the
157 truly dissolved (TDF) fraction by ultrafiltration. The ultrafiltration procedure was carried out was
158 carried out in the lab with a VIVAFLOW 50R® (Sartorius Stedim Biotech GmbH) cross-flow
159 filtration cassette manifold (molecular weight cut-off 10 KDa) with a 50 cm² filter surface area and
160 filters made by regenerated cellulose. In detail, the choice of collecting the 10 KDa colloid fraction
161 was made since this coarser fraction usually concentrates Zr, REE and other trace elements relative to
162 the “light” 1 KDa fraction where transition metals are usually associated (Lyven et al., 2003). During
163 the cross-flow filtration, concentration factors (C_f) > 10 were found to be suitable for the
164 determination of the colloidal fraction. C_f values were assessed according to the equation:

$$165 \quad C_f = \frac{(Volume_{TDF} + Volume_{CF})}{(Volume_{CF})} \quad (1)$$

166 (Larsson et al., 2002; Guo and Santschi, 2007). After their collection, TDF was added with 1% ultra-
167 pure HNO₃ solution to attain pH ≈ 2 and then stored for trace element analysis.

168 Another litre of water was collected, acidified with 1% ultra-pure HNO₃ solution to attain pH ≈ 2,
169 and then stored in a polyethylene bottle. This is hereafter defined as the dissolved fraction (DF).

170 Without further treatment, Fe and Mn concentrations were analysed in this fraction.

171 As follows, Zr, Hf and REE in DF and TDF solutions were enriched according to the method
172 reported by Raso et al. (2013). Then, an NH₄OH (25%) solution was added to attain pH 8 in the

173 aqueous phase and an excess of FeCl₃ (1%) solution was added there to induce the precipitation of
 174 solid Fe(OH)₃. REE, Zr and Hf were scavenged onto the surface of the crystallising Fe(OH)₃ and
 175 could be separated from the remaining liquid. In order to be sure that the crystallisation of Fe-
 176 hydroxide was complete, the solution was left in a closed flask for 48 h and then Fe hydroxide was
 177 collected onto a membrane filter (Millipore™ manifold filter diameter 47 mm, pore size 450 nm). Fe
 178 hydroxide was dissolved in 3 M HCl. The obtained solution was diluted 1:3 and analysed by
 179 quadrupole-ICP-MS (Agilent 7500cc) with an external calibration procedure. The overall
 180 concentration factor of investigated elements was approximately 33-fold. The assessment of the
 181 analytical precision in the determination of REE, Zr and Hf concentrations was hard to carry out
 182 since, to the author's knowledge, aqueous standard reference materials with referenced
 183 concentrations of these elements are not available. Hence, following the procedure of Raso et al.
 184 (2013), three aliquots (one litre each) of NASS-6 (distributed by the National Research Council of
 185 Canada) were treated as water samples according to the above-mentioned procedure and the obtained
 186 concentrations were compared with those previously reported in the literature (Jochum et al., 2006;
 187 2008). The results of this procedure are reported in Table S1 of the supplementary on-line material.
 188 REE concentrations were normalised to PAAS (Post Archean Australian Shale) as defined by Taylor
 189 and McLennan (1995). Features of shale-normalised patterns were depicted in terms of ratio between
 190 heavy REE (HREE) and light REE (LREE) according to the equation:

$$191 \quad \frac{HREE}{LREE} = \frac{([Ho]+[Er]+[Tm]+[Yb]+[Lu])/5}{([La]+[Ce]+[Pr]+[Nd])/4} \quad (2).$$

192 The extent of enrichment in intermediate REE (MREE) were calculated in terms of geochemical
 193 anomaly according to the equation:

$$194 \quad \frac{MREE}{MREE^*} = \frac{\frac{2x([Sm]+[Eu]+[Gd]+[Tb]+[Dy])}{5}}{\frac{[La]+[Ce]+[Pr]+[Nd]}{4} + \frac{[Ho]+[Er]+[Tm]+[Yb]+[Lu]}{5}} \quad (3).$$

195 In order to assess possible interferences of BaO^+ on Eu^+ mass, the entire calibration procedure was
196 performed with calibration solutions having a Ba/Eu weight ratio of 10000. Furthermore, during the
197 entire analytical session, in order to evaluate the accuracy of analysis, certified reference waters
198 (Spectrapure Standards, Norway) containing both elements at 2 different concentrations: 0.5 ppb of
199 Eu and 50 ppb of Ba in SPSSW1, 2.5 ppb of Eu and 250 ppb of Ba in SPSSW2 were repeatedly
200 analysed and the results were always within $\pm 10\%$ for both elements.

201 Following the procedures of Schlosser and Croot (2008) and Kulaksiz and Bau (2013), Zr, Hf and
202 REE concentrations in CF were assessed as difference between their dissolved and truly dissolved
203 concentrations.

204 All chemicals used during laboratory manipulations were of ultra-pure grade. Ultra-pure water
205 (resistivity of $18.2 \Omega \text{ cm}$) was obtained from an EASY pure II purification system (Thermo, Italy).
206 Nitric acid 65% (w/w), ammonia and hydrochloric acid were purchased from VWR International.
207 Working standard solutions for the studied elements were prepared on a daily basis by stepwise
208 dilution of the single-element stock standard solutions provided from CPI International ($1000 \pm 5 \mu\text{g}$
209 ml^{-1}) in 1 M HCl medium.

210 All labware was made of polyethylene, polypropylene or Teflon and the calibration of all volumetric
211 equipment was performed. A calibrated E42-B balance (Gibertini, Italy) was used to weight all
212 samples and standards. pH measurements were carried out with a HI 991300 pH meter (Hanna
213 Instruments, Italy).

214 CF samples for SEM observations were obtained according to two different methods. During the first
215 method, 10 ml of collected colloid suspension from selected samples were collected in a 20 ml
216 Falcon vial and ultracentrifuged (20000 rpm for 5 min). Then, the aqueous supernatant was removed
217 and 500 μl of the remaining fully enriched colloidal suspension was transferred onto an aluminium
218 stub previously coated with a graphite disk sticker. Then, the stub was heated at 50°C for 20 minutes
219 to evaporate any water residue. In the second approach, CF samples were ultracentrifuged at 10,000

220 rpm for 10 min. Then, 500 μ l of the colloid fraction were transferred on the graphite-coated
221 aluminium stub and dried at 60°C for 30 min. Both of these methods produced the same effects. The
222 aluminium stub was gold coated and SEM observation and EDS analyses were carried out using a
223 LEO 1430 SEM (Carl Zeiss, Cambridge, UK) equipped with an EDS OXFORD INCA energy-
224 dispersive spectrometric microanalysis system. Quantitative analyses were carried out with 15 kV
225 accelerating voltage, 600 pA beam current and 1 μ m beam diameter. Correction of matrix effects was
226 routinely applied. EDS calibration for quantitative analyses was carried out using natural mineral and
227 glass standards.

228 In order to analyse traces of REE, Zr and Hf in bottom sediments, seven samples were selected.
229 Sample analyses were carried out with sequential extractions using the method proposed by
230 Koschinsky and Halbach (1995). The sequential leaching procedure was used to analyse the
231 concentrations in four different sediment fractions. The procedures are as follows:

232 • Labile fraction: an aliquot of 1 g of powdered sample was added to 30 ml of an acetic acid
233 solution (1 M), buffered with Na acetate, at room temperature for 5 hours. The solution was
234 filtered through a 450 nm membrane filter, the residual sediment was washed and the filtered
235 solution was brought up to a final volume of 50 ml.

236 • Easily reducible fraction: 175 ml of a prepared solution of 0.1 M hydroxylamine
237 hydrochloride (pH 2) was added to the residue of step 1 and stirred for 24 hours at 25°C. The
238 final solution was treated as step 1 and the final volume of the filtrate was 200 ml.

239 • Moderately reducible fraction: the solid residue of step 2 was treated with 175 ml 0.2 M
240 oxalic acid, buffered with ammonia oxalate (3.5 pH) and the mixture was stirred at 25°C for
241 12 hours.

242 • Residual-silicate fraction: The final residue of the previous steps was totally digested in
243 Teflon bombs at 180°C for 12 hours, with a solution of 3 ml of 48% HF, 3 ml of 37% HCl

244 and 1 ml of 65% HNO₃. After digestion, the solution was filtered and Millipore water was
245 added up to a final volume of 50 ml.

246 According to Koschinsky and Halbach (1995), the leaching solution from the first sediment fraction
247 represents the release of labile bound trace elements and those coming from carbonate minerals. The
248 solution from the second sediment fraction represents the release of trace elements from Mn-bearing
249 phases, probably Mn-oxyhydroxides. The large geochemical coherence between V and Fe suggests
250 that the solution from the third sediment fraction can represent the release of trace elements from Fe-
251 bearing phases. The significant occurrence of Be, Ti, Cr, Co, Ni, Cu, Zr and others in the solution
252 from the fourth fraction is consistent with its origin from the detritic contribution.

253 An analytical check of data quality was carried out by measuring the Zr, Hf and REE concentrations
254 in five aliquots of MAG-1 (marine sediment reference standard distributed by the United States
255 Geological Survey), only for the total digestion procedure, since the certification of trace element
256 concentrations for MAG-1 is not given for sequential extractions, to our knowledge. The analysis of
257 MAG-1 is reported in Table S1 of the supplementary on-line material and compared with reference
258 data.

259 The obtained solutions from each procedure were suitably diluted and analysed by quadrupole-ICP-
260 MS (Agilent 7500cc) with an external calibration procedure. All reagents used in the procedures were
261 at least of analytical grade purity.

262

263 **4. RESULTS**

264 The chemical-physical parameters, major and selected minor element concentrations of the studied
265 waters are reported in Table S3 of supplementary on-line material. The ionic strength (μ) and the Eh
266 values cover a wide range from 0.11 to 5.15 mol kg⁻¹ and -0.04 to 0.20 V, respectively. Sample
267 waters are characterized by a wide spectrum of major elements composition related to the nature of
268 evaporitic rocks outcropping in the catchment area (See Table S2 of supplementary on-line material).

269

270 **4.1 Dissolved fraction <450 nm (DF)**

271 The concentrations of Zr, Hf, Y and Ho measured in DF are provided in Table S4 of the
272 supplementary on-line material. Zirconium and Hf concentrations ranged between 52 and 2529 pmol
273 kg⁻¹ and between 0 and 49 pmol kg⁻¹, respectively. Zr/Hf weight ratios were between 50 and 350,
274 although many Zr/Hf values close to the chondritic signature (70.4 ±5.7, Jochum et al., 1986) were
275 measured in samples collected in the middle and lower river paths of the Platani River. Figure 2
276 shows that Zr and Hf concentrations describe two different linear trends in DF samples. Zr and Hf
277 concentrations measured in waters collected close to the Bosco-San Cataldo mine (samples from PL1
278 to PL7) fell along a trend line with a slope of 208, whereas other samples fell along a trend line with
279 a slope close to 51. Figure 3A shows that Zr/Hf values in DF samples progressively increased with
280 the ionic strength, starting from slight subchondritic to chondritic values found in samples with $\mu \leq 1$
281 mol kg⁻¹. Similar results were also observed for the Y/Ho ratio. Figure 3B shows that subchondritic
282 and chondritic Y/Ho values are found in DF samples with a low ionic strength, whereas Y/Ho
283 progressively increased with the ionic strength up to superchondritic terms.

284 The REE concentration in waters range from 0.3 and 49.1 nmol kg⁻¹ with higher REE values
285 occurring along the middle river path. The values of Y/Ho weight ratio are distributed between 25.3
286 to 90.0. In other places along the river, Y/Ho values were close to the chondritic range of values (52
287 ± 5; Jochum et al., 1986). Figure 3C shows that the overall REE concentration in DF described an
288 exponential array with the largest REE concentrations being observed in the lowest ionic strength
289 river waters.

290 The shale-normalised REE patterns of DF samples showed two different features. The first, hereafter
291 defined as a Type I pattern, was characterised by an ascending feature determined by a progressive
292 increase in normalised concentrations along the REE series, whereas the second, defined as a Type II
293 pattern, showed a characteristic MREE enrichment relative to LREE and HREE. Only in two samples

294 were La enrichments shown and some evidence of Ce anomalies observed. Positive Gd anomalies
295 were shown in some river waters from the middle river path (Fig. 4).

296

297 **4.2 Colloidal fraction (10 KDa < CF <450 nm)**

298 The concentrations of Zr, Hf and REE measured in CF are reported in Table S5 of the supplementary
299 on-line material. Zirconium and Hf concentrations were in the range of 54.2-855.9 pmol kg⁻¹ and 0.1-
300 2.5 pmol kg⁻¹, respectively. As a consequence, Zr/Hf values fell within a range of values from 82.3
301 and 525.4. At the same time, Y and Ho concentrations ranged between 23.1 and 230.5 pmol kg⁻¹ and
302 from 0.6 and 3.9 pmol kg⁻¹, respectively. The related values of the Y/Ho ratio fall between 24.6 and
303 63.1. The REE concentration in CF was between 109.8 and 810.7 pmol kg⁻¹. Figure 3D shows that
304 the Zr/Hf values in CF progressively increase with increasing ionic strength with the highest value
305 found at about 3.2 mol kg⁻¹. Figure 3E shows that the Y/Ho ratio in CF progressively decreased, with
306 increasing ionic strength from slightly superchondritic to chondritic values towards subchondritic
307 ratios. Figure 3F shows a possible decrease of the overall REE concentration in CF with increasing
308 ionic strength.

309 Figure 5A showed the features of shale-normalised REE patterns. These are characterised by Ce/Ce*
310 values ranging from 0.6 to 2.5, Gd/Gd* values between 1.0 and 3.4 and a slight MREE enrichment in
311 some samples with MREE/MREE* ranging from 0.6 and 1.8 (Table 1). As a consequence, some
312 similarity can be found between the normalised trends in CF shale-normalised Type II patterns.

313 Comparing the feature of shale-normalised patterns from Fig. 5A with those calculated for the
314 corresponding DF samples (Fig. 5C), the observed Gd/Gd* > 1 values in CF may be responsible of
315 the same features observed in DF.

316 The SEM images were carried out on CF samples (Fig. 6A-C) and on suspended solids after filtration
317 at 450 nm (Fig. 6B-D). Figure 6A shows aggregates of grouped nanospheres with a diameter ranging
318 from about 200 to about 400 nm onto the substratum. Microspheres with similar Ca-Mg carbonatic

319 composition (Fig. 6E) also occurs in suspended fraction (Fig. 6B). EDS analyses carried out on
320 nanoaggregates of crystals collected from CF samples (Fig. 6C) suggest their clayey nature (Fig. 6F).
321 On the contrary, the composition of substratum of colloids shows an Al-Mg-K rich composition (Fig.
322 6G). These features are observed in almost all the studied samples irrespective of the ionic strength.
323 Fig. 7 shows the texture of colloids concentrated from the PL-26 water sample. According to the X-
324 ray maps of Al and Mg, these materials mainly consisted of Al- and Mg-bearing products. On the
325 contrary, Si was mainly clustered on the left side of the aggregates, together with Ca-bearing
326 materials. Fe was scattered everywhere, suggesting the coating nature of Fe-bearing products.

327

328 **4.3 Truly dissolved fraction (TDF < 10 KDa)**

329 The concentrations of Zr, Hf and REE measured in TDF from the studied water samples are reported
330 in Table S5 of the supplementary on-line material. The Zr concentration was between 37.3 and 259.8
331 pmol kg^{-1} , whereas the Hf content ranged between 0.6 and 1.7 pmol kg^{-1} . The related Zr/Hf values
332 fell between 66.5 and 275.9, with higher values measured in high ionic strength samples. The Y and
333 Ho concentrations in TDF (6.7 and 303.7 pmol kg^{-1} , 0.6 and 3.0 pmol kg^{-1} , respectively) were lower
334 than those found in CF. The Y/Ho weighted ratio values ranged from 44.8 and 101.2, similar to those
335 found in DF and CF. Figure 3D, E and F show that the Zr/Hf, Y/Ho and REE concentrations in TDF
336 progressively increased with the ionic strength.

337 The shale-normalised REE patterns in TDF of some samples were different relative to those observed
338 in CF (Fig. 5B) since they often showed negative Ce anomaly values (Table 1) and more pronounced
339 ascending behaviour along the REE series, than those observed in the Type I pattern of DF samples.
340 Only two samples show the abovementioned MREE enrichment. and neither Ce nor Gd anomalies
341 were reported. The latter finding confirms that the observed $\text{Gd/Gd}^* > 1$ values in DF (Fig. 5C) are
342 determined by the colloidal fraction occurring in the dissolved pool.

343 Figure 5D summarises the features of shale-normalised REE patterns in DF, CF e TDF. TDF are
344 characterised by MREE depleted patterns ($MREE/MREE^* \leq 1$) and large HREE/LREE fractionation.
345 CF shows moderately MREE enriched patterns associated to the lesser extent of HREE/LREE
346 fractionation than TDF. On the contrary, DF samples are distributed along a curved array and show
347 the largest observed MREE/MREE* features.

348

349 **4.4 Sediment**

350 The mineralogical composition of the sediments showed gypsum, calcite, dolomite, celestine,
351 boehmite and rare strontianite in the coarse ($> 2 \mu\text{m}$) fraction, whereas montmorillonite and kaolinite
352 occurred in the fine ($< 2 \mu\text{m}$) fraction (Fig. 8). A similar composition was observed in suspended
353 particulates ($> 450 \text{ nm}$) where the X-ray maps obtained by EDS analyses showed that the finest
354 particles were formed of Si-Al bearing clays, whereas Ca, Mg-carbonates and gypsum occurred
355 among the coarser subangular fragments of suspended solids (Fig. 9).

356 The concentrations of Zr, Hf and REE measured in different extracted sediment fractions from the
357 collected samples are reported in Table S6 of the supplementary on-line material. Zirconium
358 concentrations ranged between 0.1 and $0.2 \mu\text{mol kg}^{-1}$ whereas Hf around $0.01 \mu\text{mol kg}^{-1}$ in the first
359 sediment fraction. Here, REE concentrations ranged from 27.5 and $41.8 \mu\text{mol kg}^{-1}$. Zirconium
360 concentrations ranged from 0.01 and $0.1 \mu\text{mol kg}^{-1}$ whereas Hf was between 0.00 and $0.001 \mu\text{mol kg}^{-1}$
361 ¹ in the second sediment fraction. In these solids, REE concentrations ranged from 1.8 and $4.1 \mu\text{mol}$
362 kg^{-1} . In the third sediment fraction, Zr concentrations were between 1.1 and $7.0 \mu\text{mol kg}^{-1}$ whereas Hf
363 was between 0.01 and $0.12 \mu\text{mol kg}^{-1}$. The REE content of these materials was 3.6 to $22.9 \mu\text{mol kg}^{-1}$.
364 In the detritic component represented by the fourth sediment fraction, the largest trace element
365 concentrations are shown: the Zr content was between 164.5 and $1532 \mu\text{mol kg}^{-1}$ whereas Hf ranged
366 from 2.3 to $20.1 \mu\text{mol kg}^{-1}$. The REE concentrations ranged between 19.8 and $533.8 \mu\text{mol kg}^{-1}$.
367 Related Zr/Hf values fell within the following ranges for the first fraction (43.5 - 117.7), second

368 fraction (92.7-170.9), third fraction (51.1-86.1) and fourth fraction (71.6-79.9). Figure 10 shows that
369 the Zr and Hf concentrations in the studied fractions fell along the same a linear trend characterised
370 by a chondritic slope.

371 Y/Ho values were clustered around the chondritic range of values or slight higher in the third and
372 fourth sediment fractions, whereas slight superchondritic values were found in the first and second
373 fractions. The shale-normalised REE patterns of sediment fractions showed MREE enrichments in
374 the first and third fractions and were almost flat in shape in the second and fourth fractions (Fig. 11).
375 In the second fraction, almost all the studied samples showed a positive Eu anomaly that was also
376 recognised in the fourth sediment fraction. The flat behaviour of the REE patterns in the fourth
377 fraction was also observed in evaporite outcroppings in the surroundings. Although the features of
378 the shale-normalised patterns in the sediment fractions were similar, the HREE/LREE fractionation
379 in the first (and partially in the fourth) fraction was lower than those observed in second and third
380 fractions (Fig. 11). All the samples were free from positive Ce anomalies. In the second fraction, the
381 shape of the shale-normalised patterns was flatter, with a lesser extent of MREE enrichment. Instead,
382 there were strong positive Eu anomalies ranging from 1.40 and 3.73. In the third sediment fraction,
383 Ce/Ce* values were close to 1 and no significant Ce anomalies were observed. In the fourth fraction,
384 positive Ce anomalies were shown ($1.11 \leq \text{Ce/Ce}^* \leq 2.12$), sometimes with positive Eu anomalies
385 attaining 5.32.

386

387 **5. Discussion**

388 **5.1 Nature of colloids in studied waters**

389 The lack of organic SEM observations carried out on the separated colloidal fraction suggests the
390 mainly inorganic nature of the 10 KDa colloidal fraction that consists of nanoparticles aggregated of
391 Al-oxyhydroxides, clay minerals and carbonate (Fig. 6). The occurrence of colloidal nanoaggregates
392 also under high ionic strength conditions can be explained with pseudohydrophilic behaviour of Al-

393 oxyhydroxides (Volkova et al., 2017). In these waters, the apparent lack of organic colloids is
394 probably determined either by their coagulation under high ionic strength conditions, or by the
395 fractionation of a humic-like fine colloidal fraction in TDF rather than in the 10 KDa coarse fraction
396 (Liu et al., 2016).

397

398 **5.2 Zr, Hf and REE distribution between colloids and truly dissolved fraction**

399 Zr/Hf values larger than the chondritic signature calculated for studied colloids suggest a larger
400 affinity of aqueous Zr rather than Hf species towards colloid surfaces. This hypothesis is rather
401 strange considering that usually the higher Hf affinity than Zr towards available surfaces was
402 observed during interface processes driven by coulombic interactions (Koschinsky and Hein, 2003;
403 Godfrey et al., 2008; Bau and Alexander, 2009; Schmidt et al., 2014; Censi et al., 2017). In natural
404 waters, the dissolved Zr and Hf speciation is usually determined by hydroxyl-complexes, at least if an
405 ionic strength less than 2 mol kg^{-1} occurs (Aja et al., 1995; Veyland et al., 1998; Byrne, 2002; Ekberg
406 et al., 2004; Qiu et al., 2009; Wang and Lee, 2016). Under these conditions, $(\text{Zr}(\text{H}_2\text{O})_4(\text{OH})_4)$ and
407 $(\text{Hf}(\text{H}_2\text{O})_3(\text{OH})_5)^-$ complexes seem to be the most stable Zr and Hf species under alkaline conditions
408 (Jahn et al., 2015) and the preferential Hf scavenging relative to Zr would occur onto positively
409 charged surfaces. Colloid nanoaggregates recognised in studied waters consist of Al-oxyhydroxides
410 having a zero-point charge between 5.7 to about 10 in pH scale, depending from the mineralogy Al-
411 bearing solid formed by diaspore or boehmite and gibbsite, respectively (Stumm, 1992; Kosmulski,
412 2002; 2016; Mui et al., 2016). Therefore, if diaspore is the most abundant phase in Al-oxyhydroxide
413 nanoaggregates, its surface would have a negative charge at the measured pH values and the
414 preferential Hf scavenging relative to Zr would not occur. So, if the recognised relationship between
415 pH values and Zr/Hf ratio in CF materials (Fig. 12) represents a confirmation that the interactions
416 between the Zr-Hf complexes and nanoaggregate surface have a coulombic nature (Smith, 1999), it

417 also suggests that the extent of Zr-Hf decoupling may be also influenced by the mineralogy of Al-
418 oxyhydroxides.

419 The shale-normalised REE patterns of the studied colloids are characterised by LREE depletion
420 similar to those recognised in previous studies (Sholkovitz, 1992; 1995; Bertine and VernonClark,
421 1996; Pokrovsky et al., 2005). Probably, in studied colloids the LREE depletion is consistent with
422 the presence of detritic dolomite eroded from marine evaporites that usually shows LREE-depleted
423 shale-normalised patterns (Meyer et al., 2012). Otherwise, since the shale-normalised REE patterns
424 in TDF are affected by LREE depletion, this phenomenon could be a consequence of preferential
425 LREE sequestration onto Fe-oxyhydroxides, as modelled by Schijf et al. (2015). This is probably
426 disseminated onto surfaces of nanoaggregates as indicated by the Fe distribution shown by the X-ray
427 map (Fig. 7) and by the observed X-ray lines of Fe in the EDS spectra (Fig. 6).

428 The concurrent effect of changes in REE concentration and Zr/Hf ratio in DF of studied waters is
429 reported in Fig. 13A where allows to depict a hyperbolic array. This evidence suggests that the
430 changes of REE concentration and Zr/Hf values are determined by the combination of two opposite
431 circumstances. The first one (EM-1) characterised by high REE concentrations and chondritic to
432 subchondritic Zr/Hf values. The second one (EM-2) where high Zr/Hf values are coupled to low REE
433 concentrations. The companion plot constructed reporting Zr/Hf values vs. 1/[REE] shows a linear
434 array (Fig. 13B) confirming that shown in Fig. 13A effectively represents a mixing hyperbola
435 (Langmuir et al., 1978; Albarede, 1996 for a comprehensive review). Only high ionic strength waters
436 collected close to the Bosco-San Cataldo mine fell outside the trend in the companion plot (Fig.
437 13B).

438 Similar features observed in Fig. 13A are also shown in Fig. 14. Here, the largest Al, Fe and REE
439 concentrations in DF are found in samples with ionic strength less than 0.5 mol kg^{-1} , whereas lower
440 concentrations of the aforementioned metal ions are found in waters with $\mu > 1 \text{ mol kg}^{-1}$. Taking into
441 account that the largest colloid content in DF should occur under low ionic strength conditions

442 (Sholkovitz, 1993; 1995; Merschel et al., 2017 and references therein) and metal ions should mainly
443 occur as aqueous specie in TDF under high ionic strength waters, this distribution easily mirrors the
444 Al, Fe and REE distribution between CF and TDF. Accordingly, the distribution of REE and Zr/Hf
445 values in Fig. 12A could be influenced by the fractionation of these metal ions between CF and TDF.

446

447 **5.3 The role of sediment fractions on the composition of river waters**

448 The Zr/Hf signature in DF is not driven only by interactions between TDF and CF. The surface of
449 suspended solids and sediment represents suitable interfaces where Zr and Hf can decouple each
450 other. Zr/Hf values in the 1st sediment fraction decrease up to subchondritic values as pH is 8 (Fig.
451 15A). At the same time, Fig. 15B shows that the same Zr/Hf values are related to the dolomite
452 saturation index. Then, considering that the 1st sediment fraction is considered representative of the
453 leaching of labile phases and carbonates (Koschinsky and Halbach, 1995; Koschinsky and Hein,
454 2003; Bau and Koschinsky, 2006), the considered change from superchondritic to subchondritic
455 values of Zr/Hf values can be influenced by the change of surface charge from positive to negative of
456 dolomite that occurs at pH = 8 (Pokrovsky et al., 1999).

457 Type 1 patterns are shown in both the DF of high ionic strength waters (Fig. 4) and in TDF (Fig. 5B),
458 probably since DF and TDF practically coincide in high ionic strength waters, with a very low CF in
459 these waters. The qualitative calculation of REE speciation suggests that $[\text{REE}(\text{CO}_3)]^+$ was the most
460 stable complex in the studied river waters; this finding agrees with the observed “ascending” feature
461 characteristic of Type I patterns (Cantrell and Byrne, 1987; Lee and Byrne, 1993; Liu and Byrne,
462 1998). Under higher ionic strength conditions, $[\text{REE}(\text{CO}_3)]^+$ is associated with $[\text{REECl}]^{2+}$ complexes
463 for Ce and Pr and with $[\text{REE}(\text{SO}_4)]^+$ species for La, Nd and Sm.

464 If Zr/Hf values measured in the 2nd sediment fraction are compared with pH, only superchondritic
465 values poorly related with pH are observed (Fig. 15 C). This evidence confirms that this fraction is
466 representative of Mn-bearing phases (Koschinsky and Halbach, 1995), poorly reactive towards Zr

467 and Hf, at least according to coulombic mechanism (Koschinsky and Hein, 2003; Koschinsky and
468 Hein, 2017) and only through impurities of Fe-rich products that preferentially lead to Hf scavenging
469 rather than Zr. The small effect size of the observed relationship between Zr/Hf and pH values in the
470 2nd sediment fraction could be due to the variability of composition of Mn-bearing solids showing
471 points of zero-point-charge changing in a wide pH range (Kosmulski, 2016).

472 Although to a lesser extent, shale-normalised REE patterns in the 2nd sediment fraction show features
473 similar to type II patterns with a fractionation along the REE series showing MREE > LREE ≥ HREE
474 (Fig. 11). These features are similar to those shown by Mn-oxyhydroxides in Mn-Fe crusts and
475 hydrogenetic Mn-Fe nodules (Bau et al., 2014; Xiao et al., 2017 for a comprehensive review). Y/Ho
476 values in this fraction are slightly higher than the chondritic values, suggesting a larger Y affinity
477 relative to Ho towards the 2nd sediment fraction. This is the same evidence recognised by Bau and
478 Koschinsky (2009), who explained it by the occurrence of impurities of Fe-oxyhydroxides in these
479 materials that preferentially retain Ho, leaving Y that is adsorbed onto Mn-rich products. Features of
480 shale-normalised patterns from the 2nd sediment fraction reported in Bau and Koschinsky (2009) are
481 very similar to the patterns obtained from leachates of the 2nd sediment fraction. The main difference
482 observed is the large positive Ce anomaly that is not found in our samples. We suggest that the lack
483 of Ce anomaly can be determined by the organic content of pore waters of sediment where oxidized
484 Ce^{IV} is retained onto surfaces of humic matter (Pourret et al., 2008). According to Liu et al. (2016),
485 this hypothesis is consistent with the observed Ce/Ce* >1 values in some TDF samples (Fig. 5) and
486 confirms that the fine humic-like colloidal fraction of studied waters remained associated to TDF
487 during the collection of 10 KDa fraction (Liu et al., 2016).

488 In the 3rd sediment fraction, pH changes towards more alkaline terms drive the growth of Zr/Hf ratio
489 from subchondritic to chondritic values (Fig. 15D) in the opposite direction from the phenomenon
490 recognised for the 1st sediment fraction (Fig. 15A). This evidence is consistent with the preferential
491 Hf uptake relative to Zr, favoured by the positively charged surface of Fe-oxyhydroxides

492 (Koschinsky and Hein, 2003; 2017; Bau and Koschinsky, 2006; Hein et al., 2013). This hypothesis
493 agrees with the Zr/Hf value, close to the chondritic signature only at pH = 8.6.

494 Features of shale-normalised REE patterns in this sediment fraction show an almost symmetrical
495 MREE enriched distribution (Fig. 11). It is characteristic of Fe-rich sediments that preferentially
496 fractionate these elements relative to LREE and HREE (Bau, 1999). The authigenic/diagenetic origin
497 of Fe-solids from the 3rd sediment fraction agrees with the lack of positive Ce anomaly that is usually
498 found in Fe-oxyhydroxides (Bau et al., 2014), and with the alkaline pH conditions of river waters that
499 determine the precipitation of Fe-oxyhydroxides free from positive Ce anomalies (Bau, 1999).

500 According to the above-mentioned preferential fractionation of Ho relative to Y onto Fe-
501 oxyhydroxides (Bau, 1999; Ohta and Kawabe, 2001; Bau and Koschinsky, 2009), Y/Ho values in the
502 3rd sediment fraction are subchondritic. The abundance of Fe-oxyhydroxides in river sediments is
503 probably the reason for the subchondritic signature of several river sediments (Censi et al., 2007;
504 Viers et al 2008; Garzanti et al., 2010; 2011; Roddaz et al., 2014).

505 The growth of ionic strength up to 0.7 mol kg⁻¹ in studied waters involves the preferential Zr
506 fractionation in CF coupled with the Hf partition in TDF. This phenomenon seems influenced both
507 by pH of waters and mineralogical composition of colloidal nanoaggregates determining whether
508 Zr/Hf values in CF and TDF fall within the range of those measured by Godfrey et al. (2008) in the
509 estuary of the Hudson river. As the highest μ values exceed 0.7 mol kg⁻¹, Zr/Hf values further grow.

510 Considering the larger reactivity of Hf than Zr to Fe-oxyhydroxides and indications provided by Bau
511 and Koschinsky (2006) and Godfrey et al. (2008), the coagulation of colloidal nanoaggregates under
512 ionic strength exceeding that typical of seawater preferentially leads to Hf release rather than Zr,
513 followed by its scavenging onto authigenic Fe-oxyhydroxides in sediments.

514

515 **6. Concluding remarks**

516 The results of this study indicate that the colloidal fraction dispersed in natural waters withstands
517 dissolved salt levels in excess of 200 g l^{-1} , although the amount decreases with increasing ionic
518 strength, as suggested by Al, Fe, REE concentrations in the DF of the studied waters. This evidence
519 can be explained by the inorganic nature of nanoparticles and colloid nanoaggregates formed by Al-
520 oxyhydroxides, carbonate spherules and clay minerals. The humic-like colloidal fraction was not
521 found in CF and seems partitioned in TDF due to its fine size.

522 As ionic strength exceeds 0.7 mol kg^{-1} , Al-oxyhydroxides-based nanoaggregates become
523 progressively less stable, probably as a result of incipient colloidal coagulation. This process results
524 in larger Hf release from CF to TDF than Zr that is followed by preferential Hf scavenging onto
525 authigenic Fe-oxyhydroxides in bottom sediments. Therefore, the occurrence of a coarse inorganic
526 Al-oxyhydroxide colloidal fraction associated with the Fe-oxyhydroxide fraction of river sediment
527 seems to induce a Zr-Hf decoupling during the growth of ionic strength. This could represent the
528 early stage of larger Zr-Hf fractionations occurring along the seawater column. Therefore, Zr/Hf
529 ratios far from the chondritic range of values can be expected in authigenic minerals. The main
530 character that seems to highlight the influence of the Al-rich inorganic colloids relative to the organic
531 colloidal component is their stability under ionic strength conditions overcoming those characterising
532 seawater. Further studies are needed for corroborating this scenario. They should be focused on the
533 recognition of Zr and Hf behaviour in dissolved pools of coastal seawater

534

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542

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795

796 FIGURE CAPTIONS

797 Figure 1 – Geographic sketch map of studied Platani river system illustrating the sampled river
798 portion (in yellow). The enlarged satellite photo shows the Bosco-San Cataldo mine and related
799 landfills.

800 Figure 2 – Zr vs. Hf linear trends and related slopes calculated for water collected along the streams
801 forming the investigated Platani river system. The high ionic strength river waters are those collected
802 downstream the Bosco S. Cataldo mine.

803 Figure 3 –A: Zr/Hf vs. ionic strength in DF samples. B: Y/Ho vs. ionic strength in DF samples. C:
804 overall REE concentration vs. ionic strength in DF samples. D: Zr/Hf vs. ionic strength in CF and
805 TDF samples. E: Y/Ho vs. ionic strength in CF and TDF samples. F: overall REE concentration vs.
806 ionic strength in CF and TDF samples. Chondritic Zr/Hf and Y/Ho ratios are reported by Jochum et
807 al. (1986).

808 Figure 4 – Shale-normalised REE patterns in dissolved fraction of studied river waters relative to
809 PAAS.

810 Figure 5 - Shale-normalised REE patterns in colloidal (A) and truly dissolved fractions (B) of studied
811 river waters relative to PAAS. Shale-normalised REE patterns of corresponding DF fractions are
812 given for comparison (C).

813 Figure 6 – A: Scanning electron microscopic image of dolomite nano-sphere aggregates on the Al-
814 bearing substratum from PL-3 sample. B: Particular of the dolomite nanosphere from the
815 abovementioned sample (see spectrum in Fig. 6E). C: Al-bearing substratum (see spectrum in Fig.
816 6G) and clay mineral microcrysts (see spectrum in Fig. 6F) from sample PL-18. D: Further image of
817 the Al-bearing substratum in sample PL-18 (see spectrum in Fig. 6G). Fe X-ray lines occurring in the
818 reported spectra are probably due to Fe-oxyhydroxide coating of the observed textures. Dashed
819 circles represent the size of x-ray spot for EDS analyses.

820 Figure 7 - Scanning electron microscopic images of colloids from PL-26 water. The distribution of
821 Mg, Al, Si, Ca and Fe is shown in the x-ray maps. In particular, iron is scattered on the whole surface
822 of the colloid, suggesting its occurrence as encrustation of the colloidal surface.

823 Figure 8 - X-ray diffraction patterns (Ni-filtered $\text{CuK}\alpha$ radiation, scan speed 1° min^{-1}) illustrating the
824 minerals occurring in fine ($< 2 \mu\text{m}$) and coarse ($> 2 \mu\text{m}$) sediment fractions collected from the most
825 representative studied sites.

826 Figure 9 – A: X-ray diffraction of suspended particulate matter collected from PL-5 water sample.
827 The diffraction effects of kaolinite, quartz, calcite and dolomite are shown. B: X-ray diffraction of
828 suspended particulate matter collected from PL-37 water sample. C: SEM images of suspended
829 particulate matter ($> 450 \text{ nm}$) from PL-5 water. The coherent distribution of Al and Si reported in
830 related x-ray maps suggests the distribution of clay minerals representing the finest fraction of
831 suspended solids occurring in the background of the SEM image. Areas where Al accumulation
832 occurs relative to Si, probably indicate the occurrence of Al-oxyhydroxides (see the red dashed
833 rectangular area in Al map). Ca, Mg and S maps show that carbonates and gypsum crystals and rock
834 fragments form the coarse fraction of the suspended solids.

835 Figure 10 - Zr vs. Hf values analysed in fractions extracted from studied river sediments. The
836 reported equation represents the linear regression calculated on all the reported analyses.

837 Figure 11 – Shale-normalised REE patterns relative to Post Archean Australian Shale (PAAS)
838 calculated in fractions extracted from river sediments. Features of REE patterns are summarised in
839 terms of HREE/LREE fractionation and extent of MREE enrichment calculated as in Fig. 5. REE
840 analyses of Marls, Evaporitic limestone, Dolostone and Laminar gypsum are average values and are
841 reported in Table S7 of the supplementary on-line material.

842 Figure 12 – Change of Zr/Hf ratio in CF with pH.

843 Figure 13 – (A): Zr/Hf vs. [REE] in dissolved fraction (DF) of studied river waters. The hypothetical
844 end-members of the observed hyperbolic distribution are also indicated as EM-1 and EM-2. The

845 composition of colloids (CF) and truly dissolved fraction (TDF) extracted from selected river waters
846 and high ionic strength waters are also reported. (B): Companion plot illustrating the linear
847 relationship occurring between $1/[REE]$ vs. Zr/Hf ratio in studied DF samples depicted to confirm
848 that the hyperbola in Fig. 9A really represents a mixing path (Langmuir et al., 1978). Chondritic
849 Zr/Hf and Y/Ho ratios are reported by Jochum et al. (1986).

850 Figure 14 – Changes of REE, Al and Fe concentrations in DF with ionic strength.

851 Figure 15 – A: Zr/Hf values in the 1st sediment fraction reported vs. pH. B: Zr/Hf values of the 1st
852 sediment fraction reported vs. saturation index of dolomite assessed in coexisting river waters. C:
853 Zr/Hf values in the 2nd sediment fraction reported vs. pH. D: Zr/Hf values in the 3rd sediment fraction
854 reported vs. pH. Chondritic Zr/Hf ratios are reported by Jochum et al. (1986).

855

856 **TABLE CAPTIONS**

857 Table 1 – Overall REE concentration, ionic strength, Y/Ho, Zr/Hf, Ce/Ce* and Gd/Gd* values
858 measured in studied aqueous samples (DF, CF and TDF) and in extracted sediment fractions. The
859 related error values (Δ_i) values are also given. Features of the shale normalised REE pattern for each
860 sample are also reported in terms of HREE/LREE fractionation and extent of MREE enrichment
861 (MREE/MREE*).

Table

DF	μ mol kg ⁻¹	Σ [REE] nmol kg ⁻¹	Y/Ho	$\Delta_{Y/Ho}$	Zr/Hf molar ratio	$\Delta_{Zr/Hf}$	Ce/Ce*	Δ_{CeCe^*}	Gd/Gd*	Δ_{Gd/Gd^*}	HREE/L MREE/ REE MREE*	
											REE	MREE*
PL-1	0.47	1.02	54.5	0.21	249.8	0.2	1.2	0.5	1.0	0.5	1.6	1.7
PL-2	0.34	1.62	53.4	0.19	105.2	0.6	0.7	0.5	1.0	0.4	0.7	1.1
PL-3	3.83	1.75	90.0	0.15	321.3	0.4	1.1	0.5	1.3	0.5	4.0	0.9
PL-4	0.51	1.57	59.3	0.21	100.2	0.4	0.6	0.5	0.8	0.5	0.7	0.9
PL-5	3.22	1.60	73.2	0.13	350.4	0.5	1.4	0.5	1.2	0.4	5.4	1.0
PL-6	1.77	0.80	81.2	0.23	258.3	1.2	1.2	0.7	1.2	0.6	3.1	1.2
PL-7	5.15	1.74	71.5	0.09	285.0	0.5	1.2	0.3	1.0	0.3	4.7	1.1
PL-8	0.56	0.64	61.2	0.17	112.0	1.5	1.1	0.5	1.7	0.5	5.6	0.9
PL-9	0.80	1.13	60.4	0.12	92.1	0.7	0.9	0.3	3.9	0.3	3.0	2.0
PL-10	0.71	0.48	66.6	0.20	180.1	2.0	1.1	0.8	2.3	0.7	11.9	0.7
PL-11	1.89	1.11	69.0	0.12	104.5	0.9	1.0	0.3	2.9	0.3	3.2	1.8
PL-12	0.51	3.10	54.2	0.06	86.7	0.4	0.9	0.1	1.1	0.1	1.2	1.7
PL-13	0.88	4.95	40.8	0.03	76.7	0.1	0.9	0.1	1.0	0.1	1.8	1.6
PL-15	0.11	0.82	61.2	0.15	120.4	0.8	1.1	0.4	1.4	0.1	4.4	1.3
PL-16	0.31	1.32	57.5	0.11	90.8	0.4	1.1	0.3	1.0	0.4	2.1	1.8
PL-17	0.13	5.37	52.9	0.03	54.7	0.1	1.1	0.1	1.0	0.3	1.5	2.2
PL-18	0.31	0.99	65.0	0.15	135.1	0.4	1.1	0.4	1.7	0.1	5.0	1.2
PL-19	1.07	0.93	53.4	0.18	74.6	0.6	1.0	0.4	6.5	0.4	2.4	3.3
PL-20	0.68	2.72	38.7	0.05	63.5	0.2	1.0	0.1	1.0	0.3	2.0	2.0
PL-21	0.65	1.48	38.1	0.08	79.9	0.4	0.9	0.2	1.0	0.1	2.6	1.7
PL-22	0.19	0.31	42.4	0.21	212.1	5.6	0.9	1.0	3.8	0.2	20.6	0.5
PL-23	0.19	2.22	44.8	0.05	62.1	0.5	1.0	0.1	1.5	0.9	2.8	1.6
PL-24	0.22	0.85	25.3	0.09	54.8	0.6	0.9	0.2	0.9	0.1	5.5	1.7
PL-25	0.36	1.04	60.0	0.16	133.0	1.2	1.0	0.4	1.4	0.2	2.0	1.5
PL-26	0.30	0.76	49.0	0.27	138.7	0.7	1.1	0.8	2.7	0.3	3.3	1.1
PL-27	0.38	3.76	47.0	0.03	58.0	0.3	1.1	0.1	1.1	0.7	1.9	2.0
PL-28	0.57	49.16	47.0	0.00	55.0	0.0	1.1	0.0	0.9	0.1	1.4	2.5
PL-29	0.45	28.18	42.5	0.00	50.3	0.0	1.1	0.0	0.9	0.0	1.4	2.6
PL-30	0.23	16.75	43.0	0.01	51.0	0.1	1.1	0.0	1.0	0.0	1.5	2.4
PL-31	0.27	2.10	42.0	0.05	67.2	0.8	0.9	0.1	0.8	0.0	2.2	2.3
PL-32	0.15	27.39	44.9	0.00	57.3	0.1	1.1	0.0	0.9	0.1	1.4	2.4
PL-33	0.25	3.29	52.8	0.04	60.3	0.4	1.0	0.1	1.2	0.0	1.9	1.9
PL-34	0.32	5.19	55.0	0.03	56.3	0.2	1.0	0.1	1.1	0.1	1.7	2.0
PL-35	0.29	3.29	54.8	0.04	50.3	0.2	1.0	0.1	1.1	0.1	1.9	1.9
PL-36	0.33	6.00	54.5	0.02	53.9	0.1	1.1	0.0	1.1	0.1	1.6	2.1
PL-37	0.28	7.32	55.2	0.02	57.0	0.1	1.1	0.0	1.0	0.0	1.5	2.1
PL-38	0.29	9.65	55.8	0.02	56.6	0.1	0.9	0.0	1.1	0.0	1.3	1.9
CF	μ mol kg ⁻¹	Σ [REE] pmol kg ⁻¹	Y/Ho	$\Delta_{Y/Ho}$	Zr/Hf molar ratio	$\Delta_{Zr/Hf}$	Ce/Ce*	Δ_{CeCe^*}	Gd/Gd*	Δ_{Gd/Gd^*}	HREE/L MREE/ REE MREE*	
PL-1	0.47	0.61	52.0	0.31	234.8	0.8	0.8	0.0	1.0	0.1	1.8	1.5
PL-3	3.83	0.11	39.8	0.04	497.3	0.4	2.5	0.0	1.1	0.0	2.2	0.6
PL-5	3.22	0.25	36.3	0.05	396.7	0.3	2.1	0.0	1.4	0.0	3.6	0.8
PL-8	0.56	0.39	49.7	0.11	164.9	2.5	0.6	0.0	1.6	0.0	4.6	0.9
PL-10	0.11	0.12	24.6	0.07	525.4	4.8	1.5	0.0	3.4	0.0	8.8	0.6
PL-15	0.31	0.58	59.5	0.11	82.3	1.6	0.9	0.1	0.1	0.1	5.0	1.3
PL-18	0.19	0.51	60.7	0.08	146.1	0.4	0.9	0.1	1.7	0.1	5.1	1.0
PL-26	0.30	0.81	63.1	0.24	199.6	1.4	0.6	0.1	3.0	0.1	5.9	1.0
TDF	μ mol kg ⁻¹	Σ [REE] nmol kg ⁻¹	Y/Ho	$\Delta_{Y/Ho}$	Zr/Hf molar ratio	$\Delta_{Zr/Hf}$	Ce/Ce*	Δ_{CeCe^*}	Gd/Gd*	Δ_{Gd/Gd^*}	HREE/L MREE/ REE MREE*	
PL-1	0.47	0.02	37.1	0.31	275.9	1.3	1.1	2.2	1.3	9.4	6.3	0.9
PL-3	3.83	0.59	105.3	0.04	154.6	0.5	1.1	0.1	1.3	0.6	4.1	0.9
PL-5	3.22	0.39	100.4	0.05	172.2	1.5	0.9	0.2	1.1	0.8	7.3	0.8
PL-8	0.56	0.14	90.4	0.11	80.2	1.9	0.7	0.9	2.2	2.3	18.5	0.5
PL-10	0.11	0.23	87.5	0.07	92.0	1.8	0.6	0.5	1.6	1.2	15.8	0.6
PL-15	0.31	0.03	46.7	0.11	142.8	0.8	0.9	1.5	2.7	10.8	3.0	1.1
PL-18	0.19	0.06	55.9	0.08	86.1	1.9	1.0	0.7	1.6	4.6	4.1	1.1
PL-26	0.30	0.08	64.2	0.24	66.5	2.1	1.0	0.6	1.9	3.3	4.6	1.2
1 st sediment fraction	μ nmol kg ⁻¹	Σ [REE] nmol kg ⁻¹	Y/Ho	$\Delta_{Y/Ho}$	Zr/Hf molar ratio	$\Delta_{Zr/Hf}$	Ce/Ce*	Δ_{CeCe^*}	Gd/Gd*	Δ_{Gd/Gd^*}	HREE/L MREE/ REE MREE*	
PL-1	40.7	68.1	0.00	43.8	0.34	0.9	0.9	0.01	1.0	0.0	1.2	2.2
PL-3	28.8	62.7	0.01	117.7	0.90	0.8	0.01	1.0	0.0	0.9	2.4	2.5
PL-5	27.5	67.3	0.01	87.3	0.61	0.8	0.01	1.0	0.0	0.9	2.5	2.4
PL-8	37.0	65.8	0.00	87.0	0.73	0.8	0.01	1.0	0.0	0.9	2.6	2.6
PL-10	37.6	67.8	0.00	96.2	0.86	0.8	0.01	0.9	0.0	0.9	2.2	2.2
PL-18	37.4	66.3	0.00	43.5	0.73	0.8	0.01	0.9	0.0	1.1	2.2	2.2
PL-26	41.8	70.5	0.00	44.8	0.57	0.8	0.01	1.0	0.0	1.0	2.6	2.6
2 nd sediment fraction	μ nmol kg ⁻¹	Σ [REE] nmol kg ⁻¹	Y/Ho	$\Delta_{Y/Ho}$	Zr/Hf molar ratio	$\Delta_{Zr/Hf}$	Ce/Ce*	Δ_{CeCe^*}	Gd/Gd*	Δ_{Gd/Gd^*}	HREE/L MREE/ REE MREE*	
PL-1	1.8	59.3	0.05	92.7	5.88	1.0	0.27	0.9	0.1	2.8	2.2	
PL-3	5.8	72.1	0.02	94.4	2.05	1.1	0.07	0.9	0.1	2.3	2.3	
PL-5	5.8	76.0	0.02	117.5	1.64	0.9	0.06	1.0	0.1	1.5	2.0	
PL-8	4.5	73.9	0.03	170.9	2.04	0.9	0.08	1.0	0.1	1.6	2.4	
PL-10	5.8	82.7	0.02	159.3	4.09	0.9	0.06	1.0	0.1	1.5	2.3	
PL-18	5.8	97.8	0.03	127.6	10.61	0.9	0.05	0.9	0.1	1.5	2.2	
PL-26	4.4	90.9	0.04	114.4	2.70	0.9	0.08	1.1	0.1	1.1	2.2	
3 rd sediment fraction	μ nmol kg ⁻¹	Σ [REE] nmol kg ⁻¹	Y/Ho	$\Delta_{Y/Ho}$	Zr/Hf molar ratio	$\Delta_{Zr/Hf}$	Ce/Ce*	Δ_{CeCe^*}	Gd/Gd*	Δ_{Gd/Gd^*}	HREE/L MREE/ REE MREE*	
PL-1	13.0	48.7	0.01	65.0	0.02	1.1	0.03	1.0	0.0	1.5	2.1	
PL-3	20.1	46.7	0.01	57.1	0.01	1.0	0.02	0.9	0.0	1.3	2.2	
PL-5	22.9	47.1	0.01	58.6	0.01	1.0	0.01	0.9	0.0	1.3	2.2	
PL-8	19.0	47.1	0.01	51.1	0.01	0.9	0.02	0.9	0.0	1.3	2.5	
PL-10	7.1	47.6	0.01	75.4	0.04	1.2	0.05	0.8	0.0	2.0	1.9	
PL-18	21.6	46.6	0.01	58.6	0.02	1.1	0.02	0.9	0.1	1.8	2.2	
PL-26	3.6	51.9	0.03	86.1	0.11	1.0	0.10	0.8	0.0	1.4	2.5	
4 th sediment fraction	μ nmol kg ⁻¹	Σ [REE] nmol kg ⁻¹	Y/Ho	$\Delta_{Y/Ho}$	Zr/Hf molar ratio	$\Delta_{Zr/Hf}$	Ce/Ce*	Δ_{CeCe^*}	Gd/Gd*	Δ_{Gd/Gd^*}	HREE/L MREE/ REE MREE*	
PL-1	26.3	23.4	0.01	79.9	0.00	2.1	0.01	1.7	0.0	1.9	2.9	
PL-3	19.8	58.7	0.01	75.1	0.00	1.5	0.01	0.8	0.0	1.4	1.7	
PL-5	23.7	49.7	0.00	75.0	0.00	1.5	0.02	0.9	0.0	2.1	1.7	
PL-8	27.9	42.4	0.01	76.3	0.00	2.1	0.01	1.5	0.0	1.2	1.6	
PL-10	533.8	34.4	0.00	75.2	0.00	1.1	0.00	1.1	0.0	1.1	1.6	
PL-18	136.0	39.7	0.00	76.2	0.00	1.8	0.00	0.9	0.0	1.4	1.6	
PL-26	43.1	32.8	0.00	71.6	0.00	1.5	0.01	0.8	0.0	1.1	1.4	

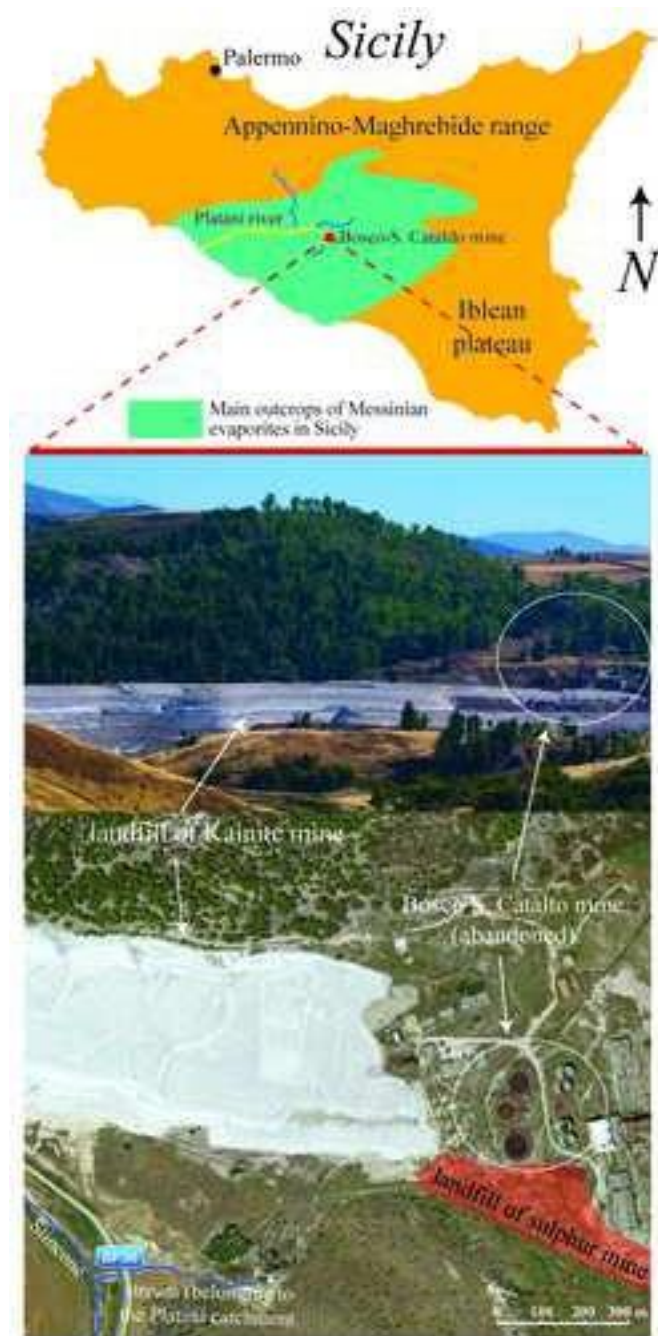


Fig. 1

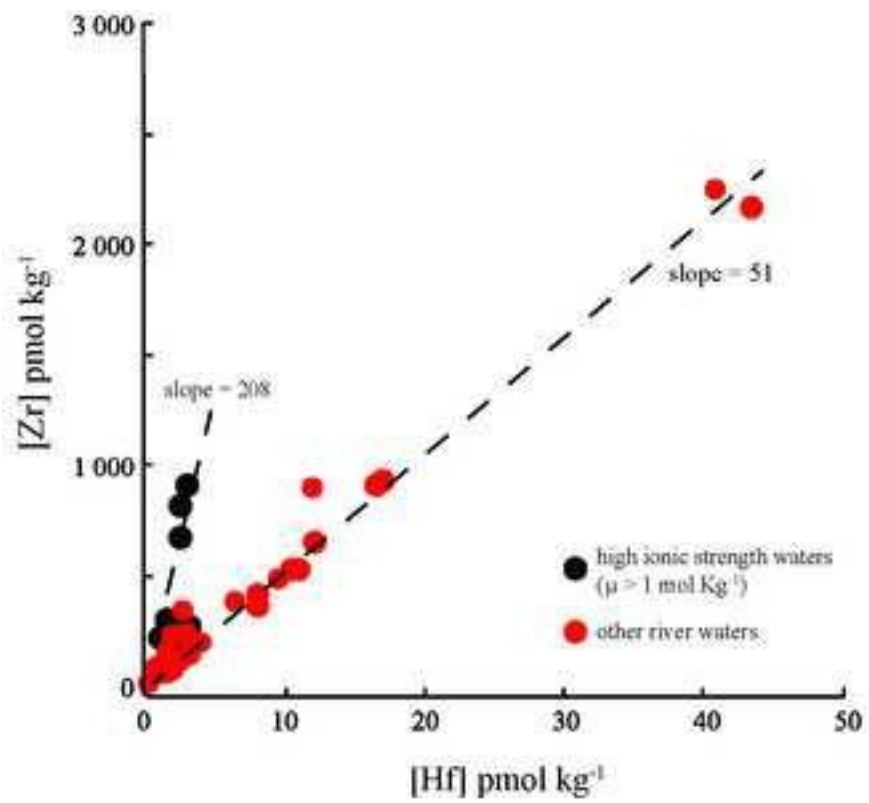


Fig. 2

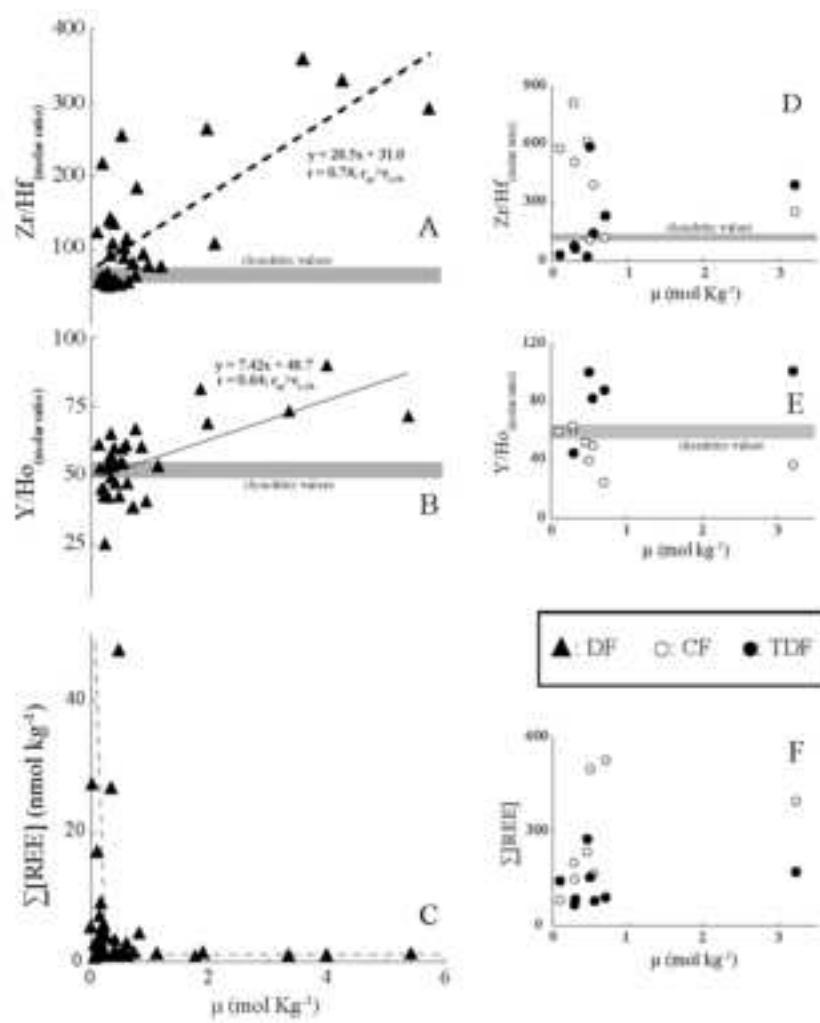


Fig. 3

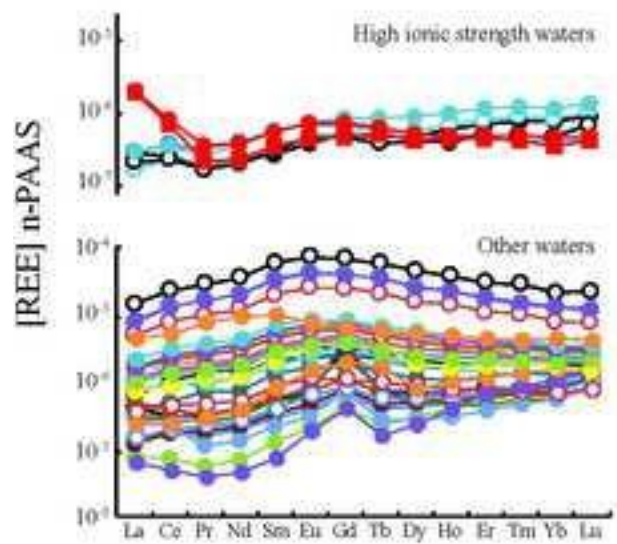


Fig. 4

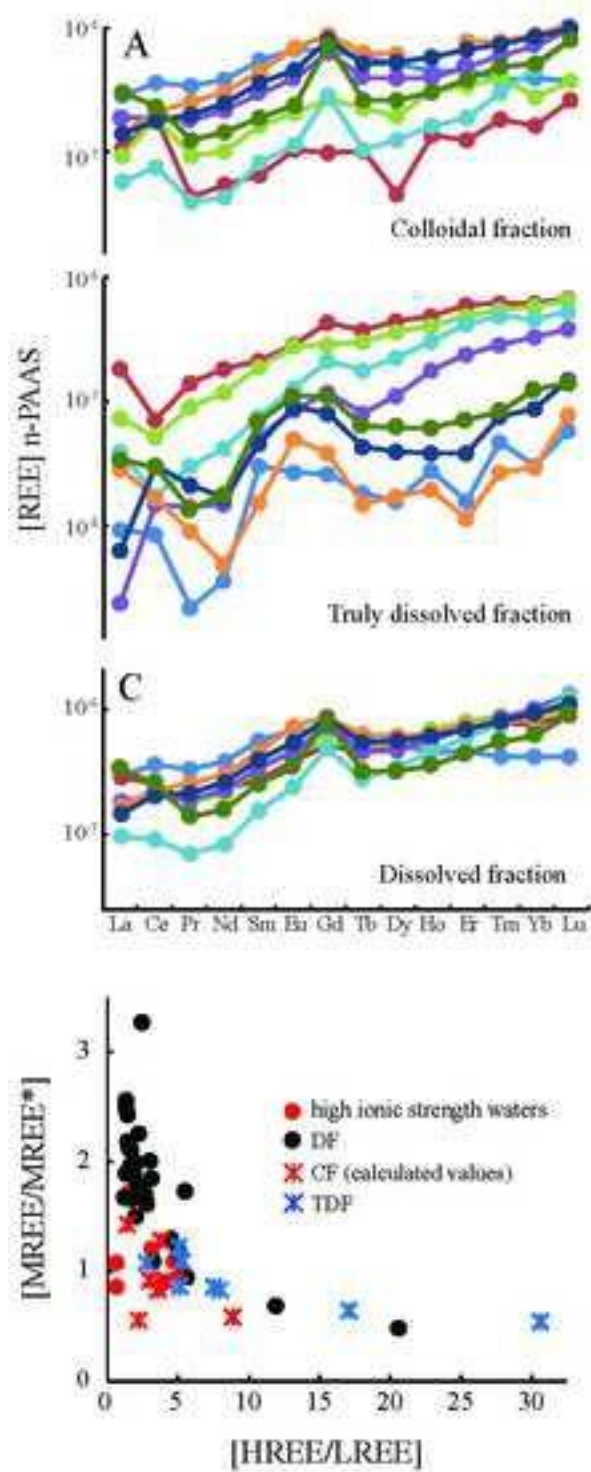


Fig. 5

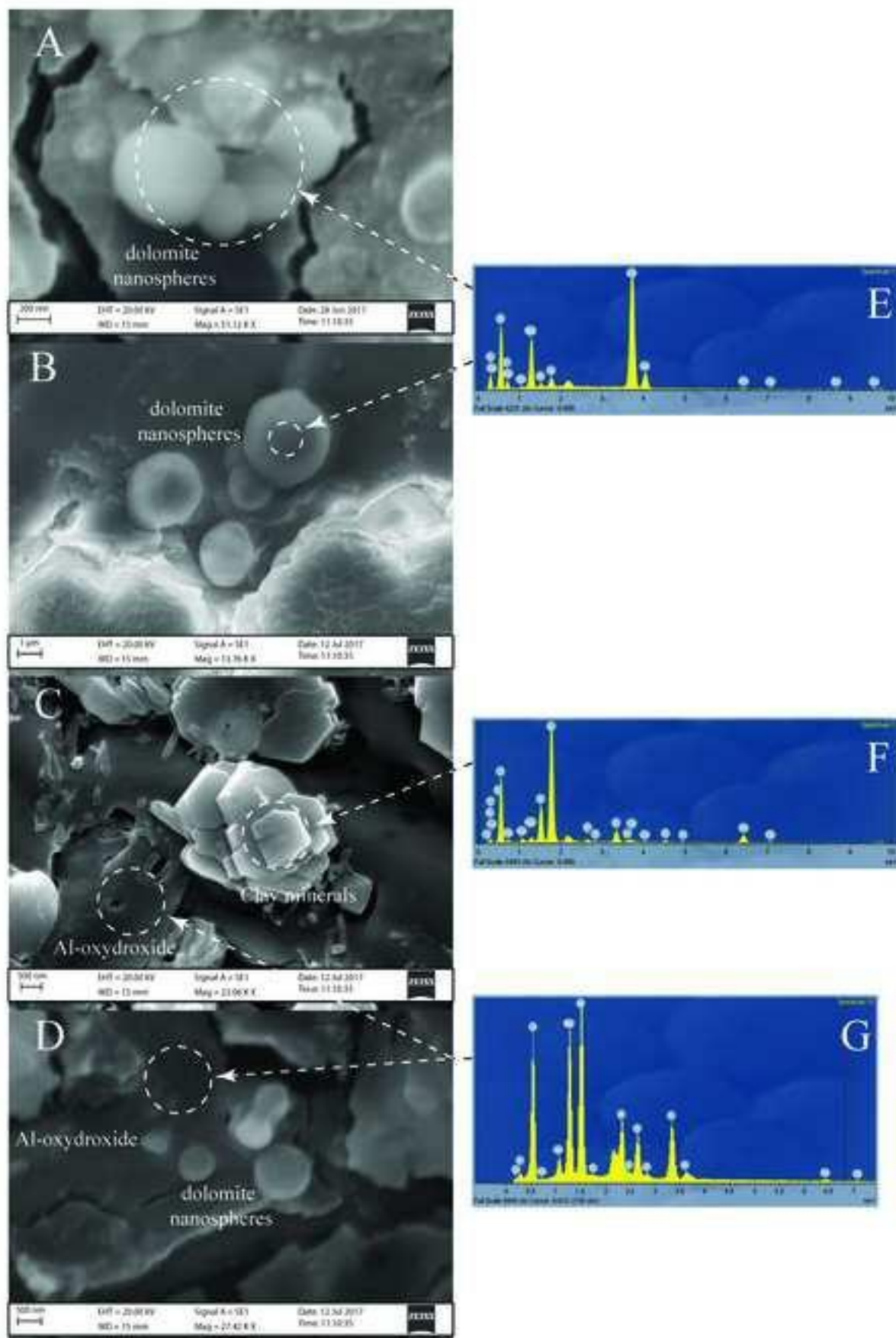


Fig. 6

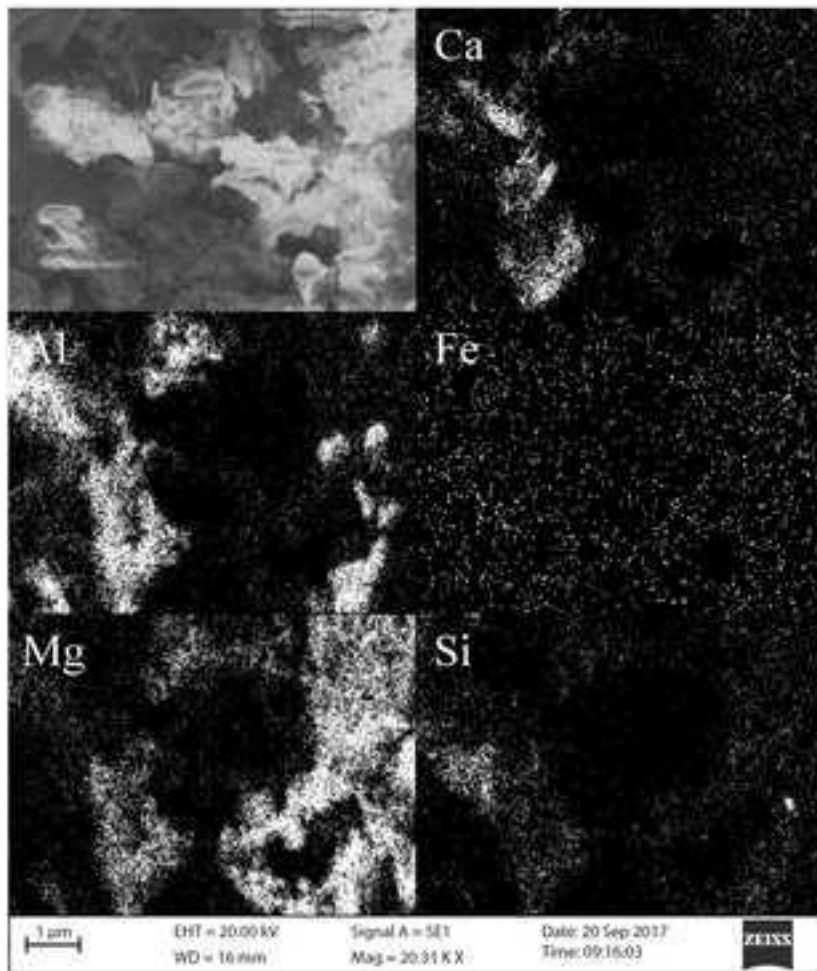


Fig. 7

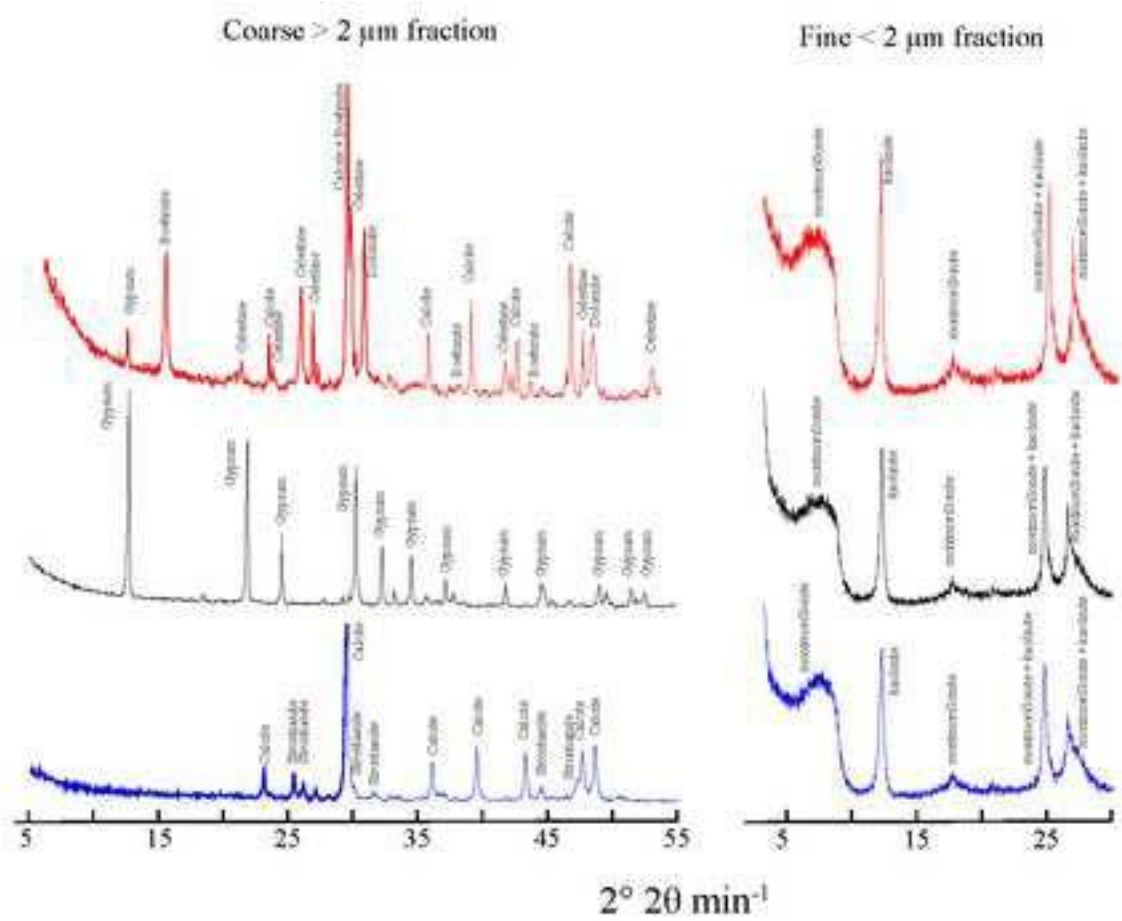


Fig. 8

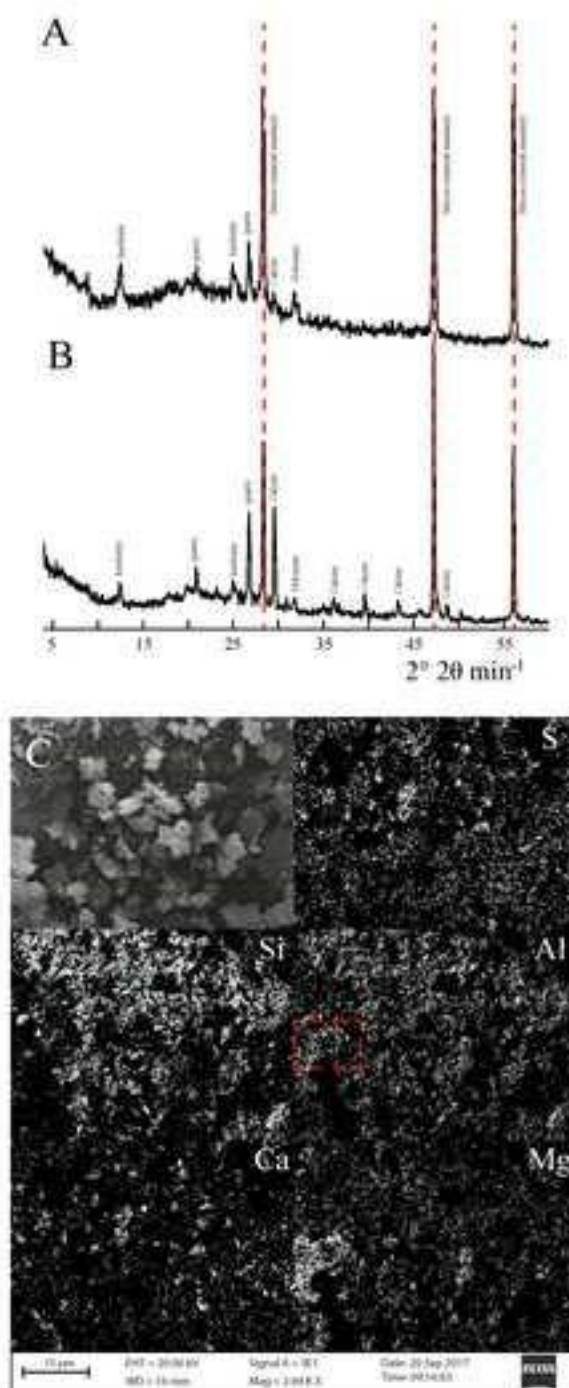


Fig. 9

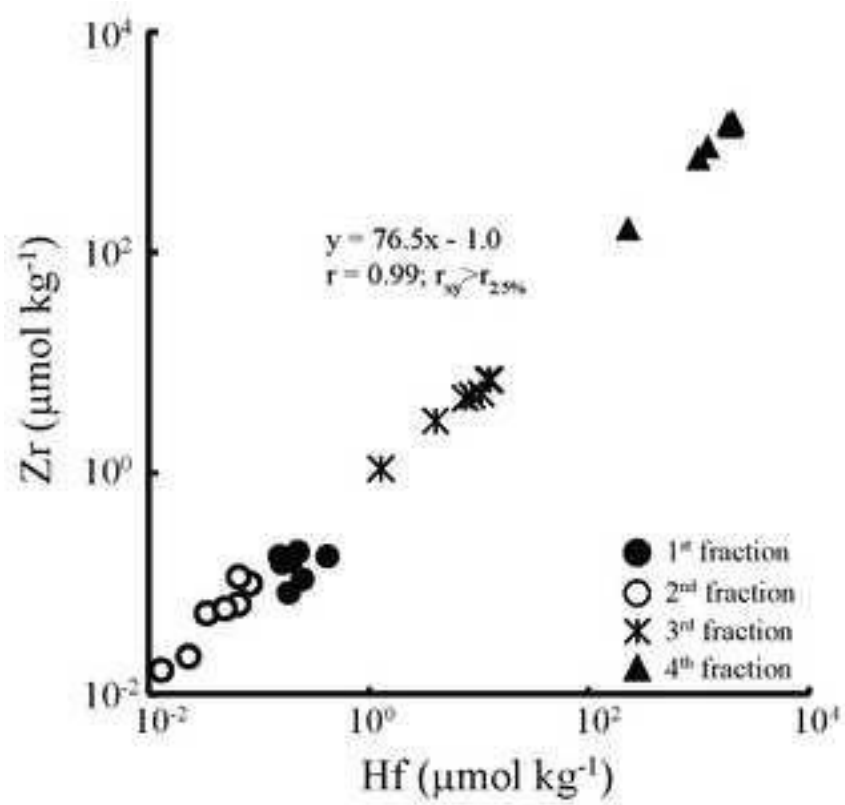


Fig. 10

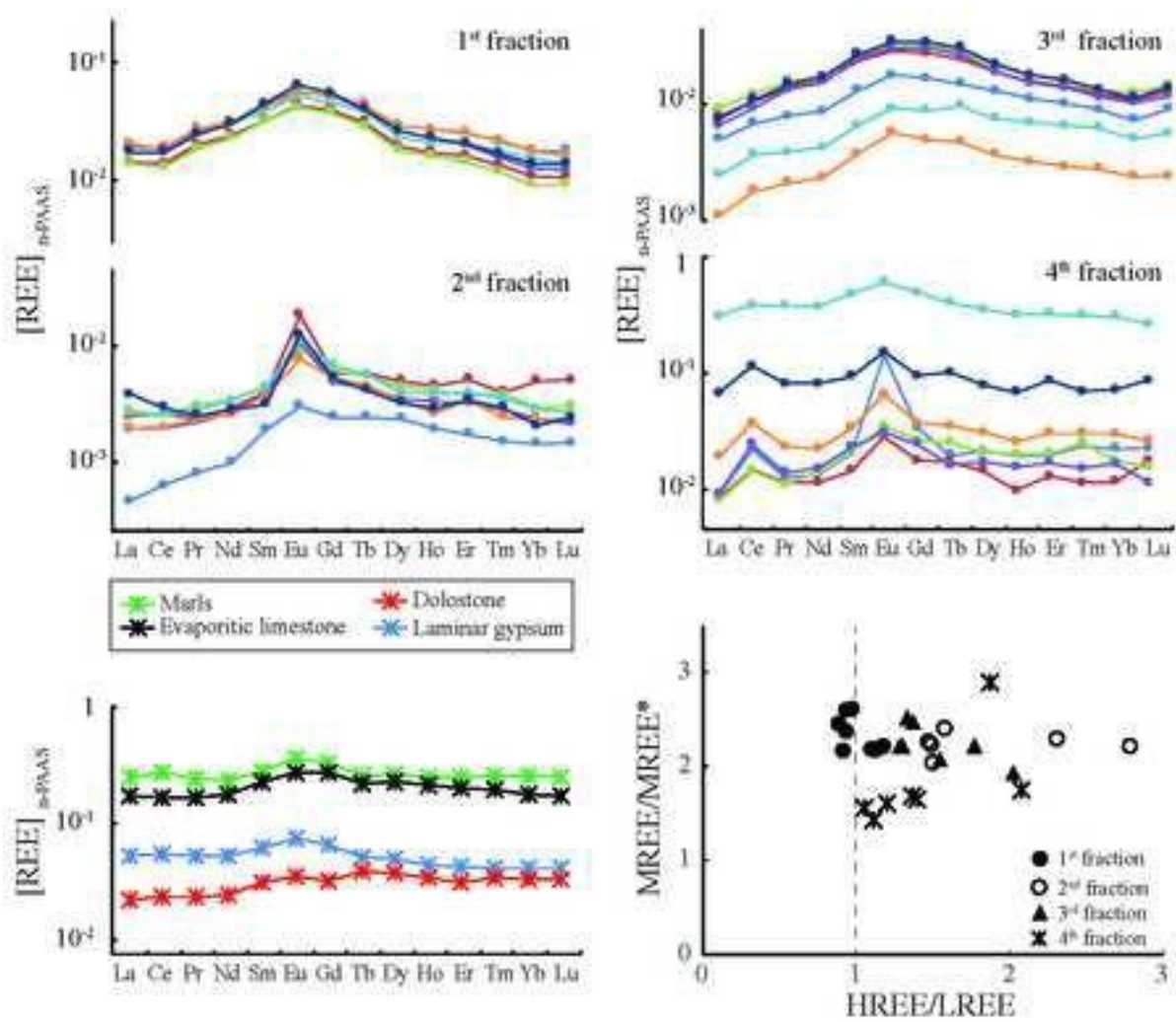


Fig. 11

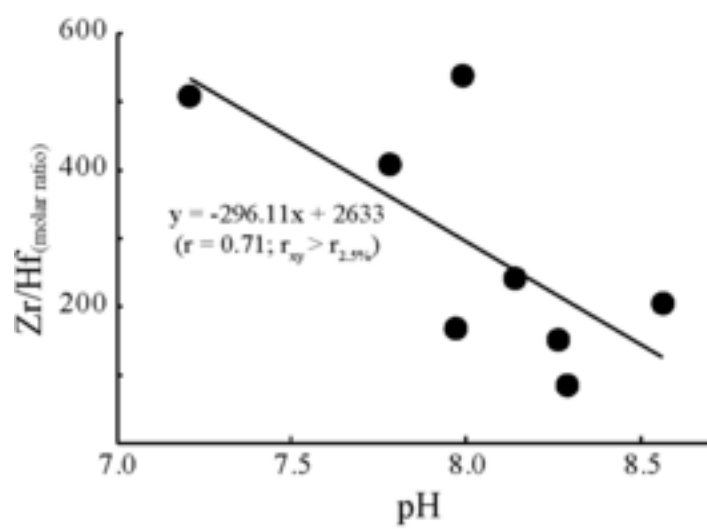


Fig. 12

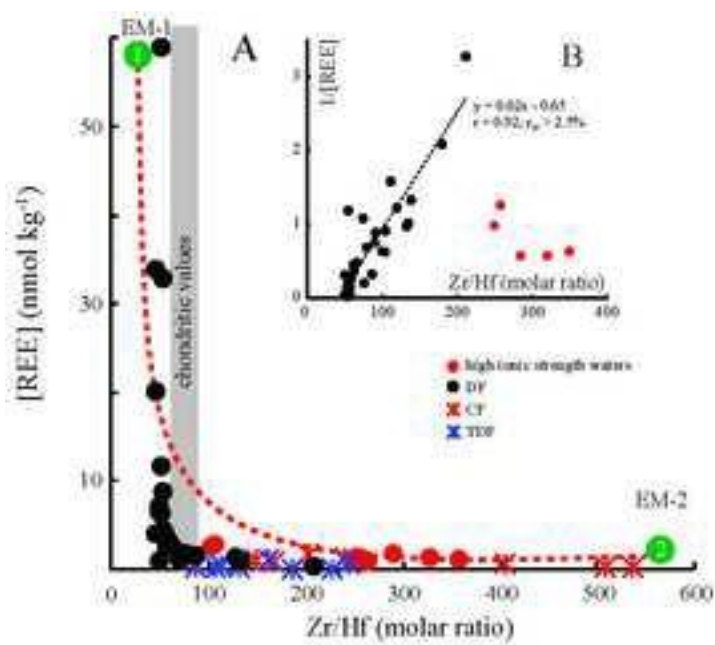


Fig. 13

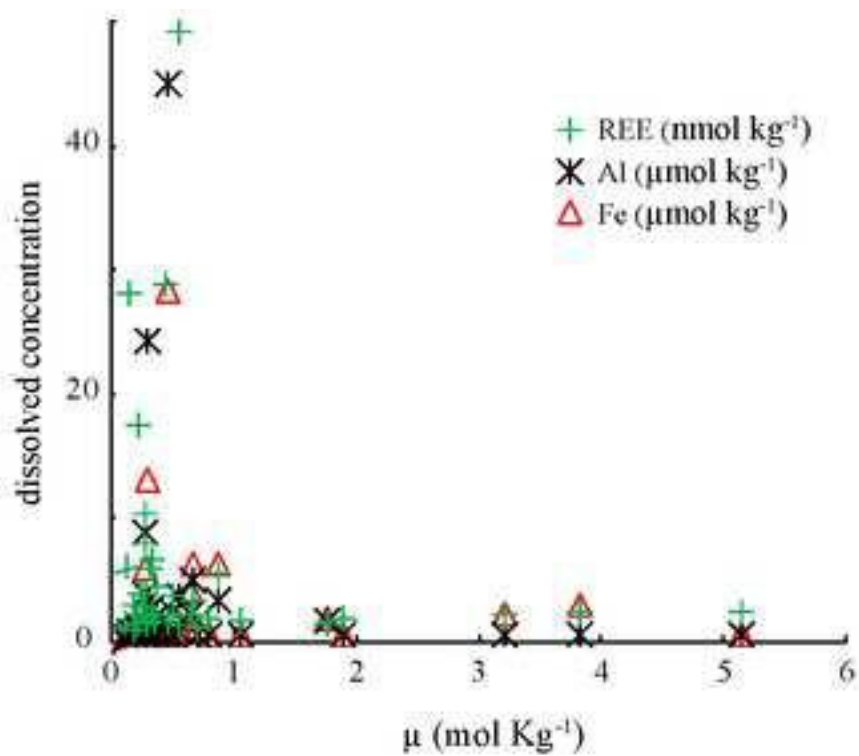


Fig. 14

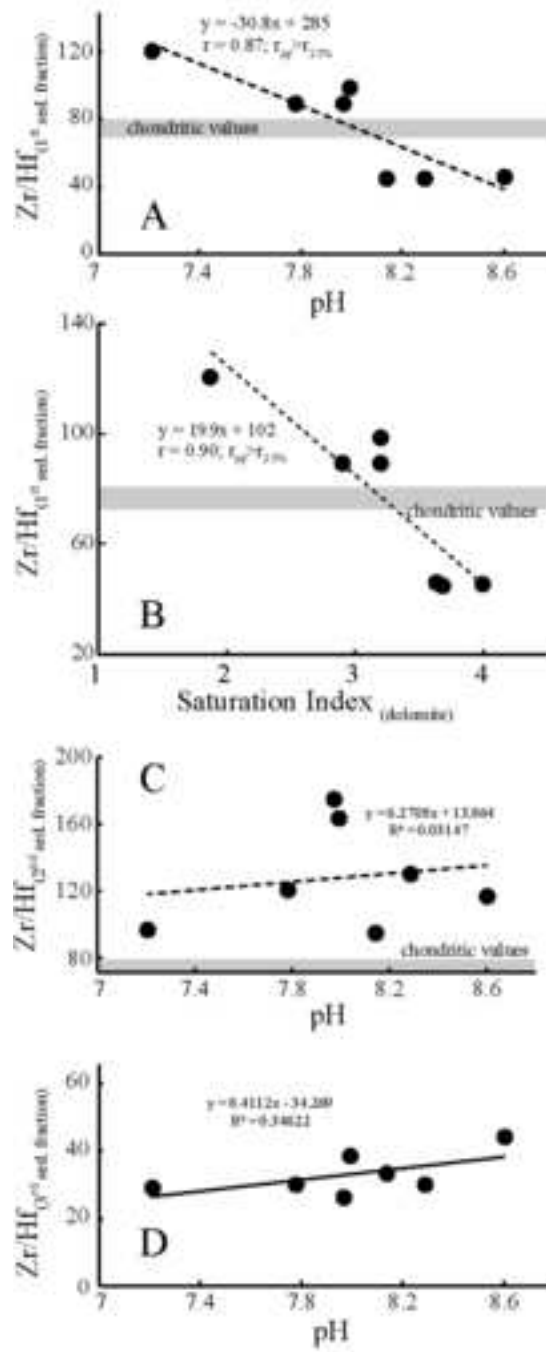


Fig. 15