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## Characterization of the submarine disposal of a Bayer effluent (Gardanne alumina plant, southern France): I. Size distribution, chemical composition and settling rate of particles forming at the outfall

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1 **Characterization of the submarine disposal of a Bayer effluent (Gardanne alumina**  
2 **plant, southern France): I. Size distribution, chemical composition and settling rate of**  
3 **particles forming at the outfall**

4  
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21 ABSTRACT

22           The submarine discharge of the high pH clarified Bayer effluent of the Gardanne  
23 alumina plant (Marseille region, France) leads to the formation of concretions at the outfall  
24 324 meters underwater and to a plume of white particles. Calibration of turbidity using  
25 effluent/seawater mixing experiments and in situ measurements shows that 1 turbidity unit  
26 (NTU) represents about  $4.7 \text{ mg L}^{-1}$  of suspended particles, allowing to trace the effluent  
27 plume in the mixing zone. The bulk chemical composition of the concretions has been  
28 determined by SF-ICP-MS. Mg and Al are the major elements measured in concretions with  
29 concentrations of a few hundred  $\text{mg g}^{-1}$ . Ca and S are also found at concentrations in the range  
30 of  $\text{mg g}^{-1}$ . Among the measured trace elements there is a specific interest in As and V because  
31 of environmental concerns pointed out by regulation authorities. Their concentrations are of  
32 tens to thousands  $\mu\text{g g}^{-1}$ , respectively. The concentrations of the following elements are in the  
33 range of a few hundreds  $\mu\text{g g}^{-1}$ : Si, V, K, Sr, P, As, B, Mo, Fe, Ti, Cu, Zn, Sn. The  
34 concentrations of the other elements are below  $1 \mu\text{g g}^{-1}$  down to a few  $\text{ng g}^{-1}$ : Rb, U, Ba, Cr,  
35 Ni, Co, Sb, Mn, Ag, Cd, Pb, Hg, Th. In order to constrain the dispersion of particles in the  
36 environment and to understand how chemical elements can be scavenged from or released to  
37 seawater, the size distribution of particles composing the concretions has been measured by  
38 settling rate experiments and, for each size class of particles, their chemical composition has  
39 been determined. For example, As and V are mainly associated to particles with mean  
40 diameters between 15.6 and  $63 \mu\text{m}$  and settling rates around  $96 \text{ m d}^{-1}$ . Overall, all the main  
41 elements (Mg, Al, Ca, S) composing concretions are associated to this size class of particles  
42 which represents 53 to 60 % of the total concretion mass.

43

44 **KEYWORDS:** Bayer effluent, trace metals, settling rate, size distribution, Gardanne alumina  
45 plant, Cassidaigne Canyon, Mediterranean Sea.

46       1. Introduction

47       The alumina production plant located in Gardanne (about 30 km North of Marseille in  
48 Southern France) was created more than 120 years ago. It is the place where the Bayer  
49 process was first implemented in 1893 at an industrial scale. It is nowadays operated by the  
50 Alteo Company, which is today one of the first world producers of specialty aluminas.  
51 Specialty (or chemical-grade) alumina is dedicated to technological uses at the difference with  
52 metallurgical (or smelter-grade) alumina mainly used to produce aluminum by electrolysis.  
53 The Bayer process is based on the dissolution of the ore (bauxites) in NaOH solutions at about  
54 250°C and on the precipitation of aluminum hydroxides separated from impurities by  
55 decantation and filtration. Al-hydroxides are precipitated with no addition of chemicals (that  
56 for example would alter the pH), but by changing the temperature to lower their solubilities  
57 and favour nucleation and growth. Oxalate produced during the alkaline degradation of the  
58 organic matter contained in bauxites is removed from solution by addition of lime that leads  
59 to the precipitation of calcium oxalate. Flocculating agents such as starch may be added in the  
60 decanters to increase the settling rate of the particles (Hill and Sehnke, 2006). This industrial  
61 process generates a residue generally called "red mud", a slurry also named Bayer residue or  
62 Bayer precipitate. One also finds the ambiguous denomination Bayer liquor that can be used  
63 to designate either a slurry or a clarified effluent (the liquid part of the red muds). The  
64 production of one ton of alumina generates between 1 and 1.5 tons of red muds (Hill and  
65 Sehnke, 2006).

66       From 1967 to the end of 2015, the Gardanne alumina plant has disposed its residues  
67 (red muds) in the Mediterranean Sea through a 55 km-long pipe, 7 km of which being under  
68 water. The outfall of this pipe is at a depth of 324 m at the top of the Cassidaigne Canyon  
69 which cuts the continental shelf off the coast of the Calanques National Park (Figure 1). New  
70 regulations in force since January 1, 2016 do not allow any longer the disposal at sea of a

71 slurry, but only that of a high pH (12.5) -high metals content clarified liquid effluent obtained  
72 by filtration of the Bayer residue (Bru et al., 2014). The solid part of the waste is now stored  
73 in on-land tailing ponds at the Mangegarri site close to the plant. The authorization for these  
74 new operational conditions has been in place since 2016 and will expire in 2021. During this  
75 5-year authorization period the company is committed to studying the environmental aspects  
76 of the effluent disposal at sea. It is also committed to proposing alternative solutions to the  
77 present Bayer process that would minimize, and ultimately stop the effluent disposal. The  
78 long-term concern of the environmental impacts of this disposal (Dauvin, 2010) had been  
79 enhanced after the Ajka (Hungary) red mud spill in 2010 (Mayes et al., 2016). Furthermore, in  
80 the case of the Gardanne plant regulation authorities have pointed out particular marine  
81 environmental concerns such as the formation of concretions with an important plume of  
82 white suspended particles when the Bayer effluent mixes with seawater (Figure 2). According  
83 to previous studies on red mud neutralization using seawater (Hanahan, 2004; Palmer et al.,  
84 2009), such concretions are made up of hydrotalcite, an Mg-Al Double Layered Hydroxide  
85 (Mills et al., 2012). Because of the high capacity of hydrotalcite to scavenge metals from the  
86 solution (Cavani et al., 1991), concretions and particles that would form at sea in the  
87 Cassidaigne Canyon may play a major role as a sink collection point for metals, or on the  
88 contrary in releasing metals to the coastal zone of the Calanques National Park.

89 In this context, the aims of the present study were (1) to collect concretions and  
90 suspended particles formed at the outfall of the effluent at sea for the first time, (2) to  
91 determine their chemical composition with a specific focus on trace metals, and (3) to  
92 measure their settling rate and determine the distribution of chemical elements as a function  
93 of particle size. The chemical composition of the source effluent and the mineralogical  
94 composition of the concretions are reported in a companion paper (Monnin et al., submitted).  
95 This study was part of a broader survey aiming at determining the impact of the discharge of

96 the Bayer effluent of the Gardanne plant in the Mediterranean Sea, as requested by the French  
97 State. Results from the present work will serve as the basis for further studies on the  
98 behaviour of trace metals in the context of concretions stability field destabilization due to  
99 particle dispersion in seawater or to the effluent discharge suppression or composition  
100 changes as it is planned in 2021. Data presented here are the first of their kind and very  
101 relevant in the need for a detailed characterization and understanding of industrial waste  
102 disposals at sea as well as for an accurate assessment of their consequences (Morello et al.,  
103 2016; Ramirez-Llodra et al., 2015).

## 104 2. Material and methods

105 The Bayer effluent of the Gardanne alumina plant is discharged into the sea at a rate of  
106 around  $270 \text{ m}^3 \text{ h}^{-1}$ . The discharge leads to the formation of concretions at the submarine pipe  
107 outfall and to a plume of white suspended particles (Figure 2). Two sampling cruises took  
108 place on August 24, 2016 and from December 6<sup>th</sup> to 8<sup>th</sup>, 2016 on board the *RV Janus*  
109 (COMEX company) using the ROV Super Achille (also from the COMEX company). These  
110 cruises targeted the zone of the effluent discharge a few kilometres offshore. The effluent  
111 plume was observed up to 100 m above the outfall. These cruises allowed to collect for the  
112 first time concretions and particles created by the residue discharge.

### 113 a) Measurements in samples collected in the effluent plume

114 Water samples were collected from December 6<sup>th</sup> to 8<sup>th</sup> 2016 within the plume and  
115 then processed on board. The ROV was equipped with a clean Teflon seawater sampling  
116 system. Water samples were taken at 5 depths between 310 and 324 m directly above the  
117 outfall of the effluent. An aliquot of about 330 mL of these water samples was filtered on 0.22  
118  $\mu\text{m}$  Durapore® PVDF filters and another one (about 100 ml) on 0.7  $\mu\text{m}$  Whatman® GF/F

119 glass filters. These filters were dried at 65°C and weighted before and after filtering to  
120 determine the mass of particles.

121 The turbidity of the water samples was measured on board using a Seapoint  
122 turbidimeter (Seapoint Sensors Inc., Exeter, USA) installed on a RBR-MAESTRO probe  
123 (RBR Ltd, Ottawa, Canada). Turbidity is expressed in NTU (Nephelometric Turbidity Unit).  
124 The turbidimeter has been calibrated using data collected during the measurements in the lab  
125 of the particle size distribution and their settling rate (see below).

#### 126 b) Effluent/seawater mixing experiments in the laboratory

127 The goal of these experiments was to reproduce in the laboratory the conditions of the  
128 underwater effluent/seawater mixing. The source effluent used for the experiments was  
129 provided by the Gardanne plant. It was collected during the same period as the effluent plume  
130 sampling at sea, i.e. every day at 4 pm between December 4<sup>th</sup> and 9<sup>th</sup>, 2016. The variation in  
131 the effluent composition is negligible during this sampling period (i.e. about a week, see the  
132 companion paper Monnin et al., submitted). For the sake of the laboratory experiments, an  
133 averaged effluent was obtained by mixing the effluent samples collected at these various  
134 dates.

135 The seawater used for the experiments was sampled at a depth of 50 m in the  
136 Mediterranean Sea in the vicinity of the Cassidaigne Canyon but away from the zone of the  
137 effluent discharge. Seawater and effluent aliquots were mixed by volume using five different  
138 effluent/seawater ratios: 1/5, 1/10, 1/20, 1/200 and 1/2000. Turbidity was measured before  
139 filtration using the same Seapoint turbidimeter as described above. The mixture was then  
140 filtered on pre-weighted 0.22 µm Durapore® PVDF filters. Filters were dried at 65°C and  
141 weighted to determine the mass of formed particles.

142 c) Submarine concretions

143 Concretions were collected on August 24 2016 (*RV Janus II*, COMEX) at the direct outfall  
144 of the effluent. Because concretions are very crumbly, a sampling system especially designed  
145 by the COMEX company was installed on the ROV next to the monitoring devices. All  
146 previous attempts to sample concretions by using direct ROV collection (manipulator arm)  
147 were unsuccessful. Briefly, the sampling system designed by COMEX is a cylindrical  
148 structure that can be reversed allowing to smoothly collect the concretions avoiding any  
149 shaking or brutal movement.

150 Concretions were sampled at three locations in the close area of the outfall, respectively  
151 named H1, H2 and H3. H1 was not venting at the time of the cruise (Figure 3A) in contrast to  
152 H2 and H3 as revealed by the presence of a white plume of particles above the concretion  
153 massif (Figures 2 and 3C). Concretions are composed of a soft middle white core crossed by  
154 orange veins, and an external crumbly crust. H1 was subsampled in 2 cm slices from the core  
155 to the external crust (Figure 3B). H2 corresponds to a fragment of the external crust. H3 was  
156 subsampled in the core and in the orange veins of the concretion (Figure 3D). All samples  
157 were then freeze-dried and kept at 4°C until analyses. On average the water content of the  
158 concretions is about 80%. We sorted the samples into three groups (Table 1): samples from  
159 the core (group 1), group 2 represents intermediate samples between the core and the external  
160 crust (group 2) and groups 3 is the samples taken in the external crust. The mineralogical  
161 composition of these concretions is given in a companion paper (Monnin et al., submitted).  
162 Briefly, results of this paper showed that H1, H2 and H3 concretions are mainly dominated by  
163 hydrotalcite, with white core samples containing pure hydrotalcite and samples from other  
164 slices containing assemblage of minerals (hydrotalcite plus calcium carbonate or brucite).



165 d) Measurement of the settling rate and size distribution of particles

166 Due to their high friability particles collected in the effluent plume could not be used for  
167 the settling rate and size distribution measurements. As these particles form in the concretions  
168 before being transferred in seawater through the effluent plume, subsamples taken from the  
169 core of concretions have thus been considered analogous to the white particles in the effluent  
170 plume. Hence subsamples H1 and H3 “soft core” samples (group 1; Table 1) were used in the  
171 experiments.

172 We followed the same experimental procedure as reported in Oursel et al. (2014). Briefly,  
173 the experimental device was composed of a vertical Plexiglas tube (1m long and 10 cm  
174 diameter), open at the top and equipped with a valve on the bottom to collect water samples.  
175 The tube was filled with 7.5 L of seawater sampled at a depth of 50 m in the area of the  
176 Cassidaigne Canyon away from the influence of the discharge. Experiments were performed  
177 with 1.3 g and 2.3 g of the freeze-dried concretion samples H1 and H3, respectively. Particles  
178 were injected at the top of the vertical tube. Water samples have been collected at the bottom  
179 14 times in two weeks. The first sample was taken 2 minutes after the particle injection and  
180 the last one after 15.5 days of experiment, in order to cover a large range of settling rates and  
181 particle diameters. The 14 samples were immediately filtered (150 to 350 mL) after collection  
182 on pre-weighted 0.22  $\mu\text{m}$  Nucleopore PC filters and 0.7  $\mu\text{m}$  Whatman® GF/F glass filters,  
183 dried at 65°C and weighted to determine the mass of particles. Nucleopore PC and GF/F  
184 filters have been used for trace metal and Hg analyses, respectively.

185 Measured settling velocities and particle diameters were then grouped in 4 main size  
186 classes of particles based on the Udden-Wentworth sediment grain size scale, according to  
187 Leeder (1982) and Bainbridge et al. (2012). The recovery of the injected particles was 93%  
188 for H1 and 98% for H3 by weight. This shows that particles did not significantly dissolve  
189 during the time of the experiment.

190 e) Chemical analyses

191 We dissolved H1, H2 and H3 concretion samples and H1 and H3 “soft core” size classes  
192 filters (from settling rate experiments) in a mixture of two acids (HCl/ HNO<sub>3</sub>; all Suprapur  
193 grade). The solutions were then analyzed for major and trace elements using a Sector Field  
194 Inductively Coupled Plasma Mass Spectrometer (SF-ICP-MS; ELEMENT XR,  
195 ThermoElement). The instrument was calibrated using standard solutions, and we used an  
196 external calibration method with In as an internal standard. The efficiency of the dissolution  
197 procedure and the quality of the SF-ICP-MS measurements were controlled by the  
198 determination of element concentrations on Certified Reference Materials (MESS-4, SLRS-5,  
199 SLEW-3 and CASS-5). Particulate Hg was analyzed by cold vapor atomic absorption  
200 spectrometry (CV-AAS, LECO AMA-254).

201 3. Results and discussion

202 As revealed by ROV images of the effluent outfall at sea the pipe is nowadays covered  
203 with historical red muds (i.e. disposed before January 2015) and debris of concretions (Figure  
204 2). After passing through this cover the effluent mixes with seawater and forms concretions  
205 and a plume of white particles. The concretions may form chimneys 3 to 4 m high,  
206 surrounded by debris of these chimneys and covering an area of about 170 m<sup>2</sup>. These  
207 chimneys look like pinnacles observed at the Lost City (mid-Atlantic ocean) or Prony (New  
208 Caledonia) that are natural hyperalkaline hydrothermal vents (Kelley et al., 2001; Monnin et  
209 al., 2014). ROV observations in the Cassidaigne Canyon show that particles from the effluent  
210 plume extend up to 100 m above the outfall (i.e. to a depth of about 200 meters below sea  
211 level).

213 a) Particles concentration, size distribution and settling rate

214 The concentration of particles in the clarified liquid effluent produced by the Gardanne  
215 plant is around  $25 \text{ mg L}^{-1}$ . The suspended particle concentration measured in the water  
216 column within the effluent plume at sea ranges from 20 to  $274 \text{ mg L}^{-1}$  (Figure 4). The relation  
217 between the concentration of suspended particles and turbidity has been established by the  
218 effluent/seawater mixing experiments and is similar to the one obtained from measurements  
219 of the samples collected at sea by the ROV. The two datasets display a unique trend with a  
220 slope of 4.7, which indicates that 1 NTU corresponds to  $4.7 \text{ mg L}^{-1}$  of suspended particles. An  
221 estimate of the mixing ratios of the samples collected at sea can be obtained from the  
222 measured turbidity and from the curve calibrated by the laboratory data. The turbidity of these  
223 samples is between 4.9 and 64.6 NTU. As such, samples collected at sea would correspond to  
224 mixing ratios from 1/8 at the direct outfall to 1/190 10 m above the outfall.

225 The distribution of particles as a function of their settling rate is given in Figure 5. H1  
226 and H3 “soft core” samples present a similar distribution of particle sizes. As reported above,  
227 settling velocities and particle diameters were then grouped in the 4 main size classes of  
228 particles according to the Udden-Wentworth scale (Table 2). Settling rate values range from  
229 less than  $1 \text{ m d}^{-1}$  (fine fraction) to more than  $500 \text{ m d}^{-1}$  (sand). The larger fraction of the  
230 particles lies in the “coarse silt” category, which corresponds to particle diameters between 15  
231 and  $63 \text{ }\mu\text{m}$  and a settling rate of about  $1 \text{ mm s}^{-1}$ , i.e.  $86 \text{ m d}^{-1}$ . The second largest fraction, 22  
232 and 23 % of the sample weight respectively, corresponds to particles whose settling rate is  
233 about  $500 \text{ m d}^{-1}$ , and an estimated diameter larger than  $63 \text{ }\mu\text{m}$  (sand). The remaining fractions  
234 (fine silt and fine fraction) correspond to particles which settling rate is lower than  $10 \text{ m d}^{-1}$ .  
235 Overall, the main particle fractions of concretions have relatively high settling rates.  
236 Compared to natural marine particles, these would correspond to particles generally called  
237 fast-sinking particles. The major part of the particles formed by the mixing of the effluent and

238 seawater will thus rapidly sink and in the vicinity of the outfall, at the difference with the  
239 slurry (red muds) that has been discharged at the top of the Cassidaigne Canyon until 2015  
240 and expanded far away from the outfall by gravity flow.

#### 241 b) Chemical composition of the concretions

242 The major elements of the concretions are Mg, Al, Ca and S (Figure 6A).  
243 Concentrations range from 316 to 626 mg g<sup>-1</sup> for Mg, 84 to 340 mg g<sup>-1</sup> for Al, 7.6 to 52.1 mg g<sup>-1</sup>  
244 for Ca and 2.2 to 12.8 mg g<sup>-1</sup> for S (Table 1). The average concentrations are reported in  
245 Figure 6B-C for the three groups of concretions. Among the minor and trace elements, As and  
246 Co present trends similar to that for Al, with lower concentrations in the core compared to the  
247 crustal layer of the concretion (Figure 7A-A'). Higher V concentrations also appear associated  
248 with the central/intermediate part of the concretion while Fe is mainly concentrated in the  
249 external parts (Figure 7B-B'). Similarly to Fe, Mo and Ti (Figure 7C-C') and Pb and Cd  
250 (Figure 7D-D') are also enriched in the crust, as Mg and Ca. Other elements presenting the  
251 same trend as Al are Cu, Ag, Sn, Hg, Si, P and Rb, while B, Th, Sr, K, U, Ba, Cr, Mn, Ni and  
252 Zn present the same trend as Ca and Mg (not shown). Minimum, maximum and average  
253 values for all the elements analysed are reported in Table 3 next to upper and lower  
254 continental crust values (Wedepohl, 1991) which are generally used to trace material from  
255 continental origin. On average Mg, As and Mo concentrations in the concretions are 23-25  
256 times higher than continental crust values. V and S are 12 times higher and Al is 3 times  
257 higher. Ca (group 3) and Cd concentrations are of the same order as continental crust values.  
258 All the other elements present on average concentrations from 10 to 10<sup>3</sup> times lower than  
259 continental crust values.

260 As reported above, H1 and H3 “soft core” samples (group 1) can be considered  
261 analogous to the white particles found in suspension in the effluent plume at sea. With regards  
262 to concentration levels, these are composed on average by: (1) of Mg, Ca, Al and S at

263 concentrations between a few tens to hundreds of  $\text{mg g}^{-1}$ , (2) few to ten of  $\text{mg g}^{-1}$  of V and Si,  
264 (3) hundreds of  $\mu\text{g g}^{-1}$  of K, Sr, P and As, (4) tens of  $\mu\text{g g}^{-1}$  of B, Mo and Fe, (5) few  $\mu\text{g g}^{-1}$  of  
265 Ti, Cu, Zn and Sn, (6) hundreds of  $\text{ng g}^{-1}$  of Rb, U, Ba, Cr, Ni, Co, Sb, Mn, and (7) tens of  $\text{ng}$   
266  $\text{g}^{-1}$  of Ag, Cd, Pb, Hg and Th (Table 3) .

267 The chemical composition of particles of the different size classes was also  
268 determined. Figure 8 reports the distribution of the chemical elements between the 4 main size  
269 classes of particles, in an order determined by their content in the coarse silt fraction, which is  
270 the larger fraction of particles in H1 and H3 (Table 3). 50 to 70 % in weight of Al, Mg, Ca, S,  
271 V and As are concentrated in this fraction. In contrast, elements found in lower concentrations  
272 are associated to fine silt or sand fractions. Overall, these results outline the importance of for  
273 the size of the particles on the transfer of metals in seawater. A recent study on the levels of  
274 fish contamination in the Cassidaigne Canyon area has shown that fish would especially be  
275 contaminated by Al and to a lesser extent by Ti and V (Bouchoucha et al., 2019). These  
276 elements are indeed among the main elements found in the concretions and particles. The  
277 direct impact of the actual effluent discharge is not easy to assess because element  
278 bioaccumulation in fish is blurred by interaction with biological effects (trophic level and  
279 size). The evolution of the historical red mud deposited on the seafloor can also play a role in  
280 releasing metals to seawater. A better understanding of the different sources of metals  
281 (historical red mud, actual effluent, concretion particles and impacted seawater) and the  
282 trophic structure in the Cassidaigne Canyon will provide greater evaluation of the health risk  
283 for humans consuming fish from the area.

#### 284 4. Conclusion

285 Submarine concretions and white particles plume form when the high pH clarified Bayer  
286 effluent of the Gardanne alumina plant mixes with seawater in the Cassidaigne Canyon (NW-  
287 Mediterranean Sea). We estimated effluent/seawater mixing ratios of around 1/8 at the direct

288 outfall to 1/190 10 m above the outfall. We estimated that 1 NTU (turbidity) would represent  
289 4.7 mg L<sup>-1</sup> of particles, allowing to trace the effluent plume in the mixing zone. Next to the  
290 major elements Mg, Al, Ca and S, As and V are the main trace metals found in the  
291 concretions. Concretions are mainly composed by aggregated particles falling in the category  
292 of coarse silt, according to the Udden-Wentworth scale, thus corresponding to diameters  
293 between 15.6 and 63 µm. When suspended in the water column these particles would settle at  
294 a sinking velocity of around 96 m d<sup>-1</sup>. Particles transferred by the plume will probably rapidly  
295 reach the sediment. However, investigating the fate of the particles formed by the discharge of  
296 the clarified effluent will also require to take into account the dispersion of the particles at the  
297 same time as their dissolution during their transport in the water column. This would allow a  
298 better evaluation of the potential impact of the effluent in the coastal zone.

299

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315 « Transfer of contaminants in the Mediterranean”).

316 Our colleague Cédric Garnier, who had played key roles in the elaboration and  
317 advancement of this project has passed away during this work. May he rest in peace.

318 [Figure captions](#)

319 Figure 1: Location of the effluent outfall at 324 m depth at the top of the Cassidaigne Canyon  
320 (south of France; north-western Mediterranean Sea).

321  
322 Figure 2: View of the outfall of the effluent at sea (ROV images). The mixing between the  
323 effluent and seawater leads to the formation of massive concretions, with an important plume  
324 of white particles.

325  
326 Figure 3: Concretions sampled in the Cassidaigne Canyon: (A) column H1 at sea (ROV  
327 image), (B) column H1 subsampled in 2 cm slices from the core to the external crust of the  
328 concretion, (C) column H2 and particles plume at sea (ROV image) and (D) fragment of  
329 column H3 presenting orange veins.

330

331 Figure 4: Relationship between the concentration in suspended particles ( $\text{mg L}^{-1}$ ) and turbidity  
332 (NTU) using in situ measurements with the ROV and laboratory mixing experiments.

333

334 Figure 5: Variation of the percentage of particles for each class as a function of their settling  
335 rate and calculated diameter for H1- and H3- “soft core” samples.

336

337 Figure 6: Concentrations (log scale) of the major elements (Mg, Al, Ca and S) of concretions  
338 in  $\mu\text{g g}^{-1}$  (A). Average concentrations ( $\text{mg g}^{-1}$ ) of same elements for the three groups of  
339 concretions: (B) Mg and Al and (C) Ca and S. Group 1: core samples, Group 2: intermediate  
340 samples and Group 3: crustal samples.

341

342 Figure 7: (A-D) Concentrations in Co ( $\text{ng g}^{-1}$ ) and As ( $\mu\text{g g}^{-1}$ ), Fe and V ( $\mu\text{g g}^{-1}$ ), Ti and Mo  
343 ( $\mu\text{g g}^{-1}$ ) and Pb and Cd ( $\text{ng g}^{-1}$ ) for all the samples. (A'D') Concentrations of the same  
344 elements for the three groups of concretions. Groups: same as reported in Figure 7.



345

346 Figure 8: Element distributions between each of the 4 main size classes of particles, ordered  
347 by increasing content of coarse silt (15-63  $\mu\text{m}$ ; settling rate between  $2.0 \times 10^{-2}$  and  $3.3 \times 10^{-1}$   
348  $\text{cm s}^{-1}$ ), the major fraction of particles composing H1 and H3 soft core concretions.

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350

351 **Tables**

352 **Table 1:** Concentrations of the major elements in the concretions: Mg, Al, Ca and S ( $\text{mg g}^{-1}$ ).

353 On average water content of the concretions is about 80%. Group 1: core samples, Group 2:

354 intermediate samples and Group 3: crustal samples.

355

356 **Table 2:** Characteristics and chemical composition of the 4 main size classes of particles

357 composing H1 and H3 “soft core” concretion samples. Measured settling velocities and

358 particle diameters are grouped in 4 main size classes of particles based on the Udden-

359 Wentworth sediment grain size scale, according to Leeder (1982) and Bainbridge et al.

360 (2012): sand ( $> 63 \mu\text{m}$ ; settling rate  $> 3.3 \times 10^{-1} \text{ cm s}^{-1}$ ), coarse silt ( $15\text{-}63 \mu\text{m}$ ; settling rate

361 between  $2.0 \times 10^{-2}$  and  $3.3 \times 10^{-1} \text{ cm s}^{-1}$ ), fine silt ( $3.9\text{-}15 \mu\text{m}$ ; settling rate between  $1.3 \times 10^{-3}$

362 and  $2.0 \times 10^{-2} \text{ cm s}^{-1}$ ), and fine fraction ( $< 3.9 \mu\text{m}$ ; settling rate low  $< 1.3 \times 10^{-3} \text{ cm s}^{-1}$ ).

363

364 **Table 3:** Minimum, maximum and average concentrations of all the elements analysed in the

365 concretions, next to UCC and LC reference values (Wedepohl, 1991). UCC: continental crust,

366 LC: lower crust. Elements are ordered by decreasing mean concentrations for group 1 (from

367  $\text{mg g}^{-1}$  to  $\text{ng g}^{-1}$ ).

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