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Reply to Comment by Terence McCarthy and Marc Humphries on “ Highly contrasted geochemical pattern in sediments of the Okavango Delta, Botswana driven by dust supply, hydrological heritage and biogeochemical reactions”

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1 **Reply to Comment by Terence McCarthy and Marc Humphries on « Highly contrasted**
2 **geochemical pattern in sediments of the Okavango Delta, Botswana driven by dust supply,**
3 **hydrological heritage and biogeochemical reactions».**

4
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16
17 **Abstract**

18 In southern Africa, the Okavango Delta is a large alluvial fan sustaining a unique wetlands
19 ecosystem in the heart of the Kalahari desert. The Delta is fed by an annual flood that brings water
20 from the Angolan plateaus to the north, down to the Okavango region. The fan is characterized by
21 vegetated, permanent or seasonal floodplains, dotted with thousands of sandy islands of various
22 origin (inverted paleo-channels, paleo-dunes, meander bars, etc). On at least some of these islands,
23 shallow groundwater is characterized by a high pH (>8) and a high concentration of metals and
24 metalloids, making it naturally toxic. In the 1990s, McCarthy and co-workers explain the chemistry
25 of that water through an evapotranspiration model, the flood-water being pumped by the vegetation
26 towards the center of the islands and progressively enriched in elements by evapotranspiration. This
27 model has been widely applied to all islands in the Okavango, not considering their individual
28 specificities nor that of the surrounding floodplain. Our work, based on a multidisciplinary
29 approach including sedimentology, mineralogy and geochemistry, and discussed by McCarthy and
30 Humphries, questions the established model suggesting that the alkaline water cannot derive from
31 simple concentration of the floodwater.

32
33 **1. Introduction**

34

35 Developing in a semi-arid climate and sustaining unique aquatic and terrestrial ecosystems, the
36 Okavango Delta is one of the last pristine sub-tropical wetlands in the world (Figure 1). It has been
37 widely studied, especially since the 1970s, in terms of ecological, geological, hydrological and
38 geochemical processes. Among these investigations, we would like to acknowledge the significant
39 contribution made by the group from the University of the Witwatersrand and associated
40 researchers. This group developed a hydro-geochemical model to explain the fate of the estimated
41 380 000 tonnes of solutes that enter the Delta each year (McCarthy, 2006) and the occurrence of
42 alkaline water below the central part of the islands (McCarthy et al., 1991a; 1993). The model
43 proposes that proto-islands in the alluvial fan grow by aggradation from precipitation of mainly
44 calcium and magnesium carbonates and amorphous silica (McCarthy et al., 2012). Plants colonizing
45 the islands are suggested to play a major role in this process by pumping water from the floodplain,
46 enhancing groundwater circulation from the floodplain toward the islands and concentrating
47 minerals in the rim of the islands, leading to their growth. The highly soluble salts, especially
48 sodium bicarbonate, would accumulate below the central part of the islands, forming brines that
49 ultimately sink due to their density contrast with the surrounding water in the aquifer (Bauer et al.,
50 2006; Bauer-Gottwein et al., 2007). The occurrence of such alkaline water below the center of the
51 islands would explain the peculiar vegetation pattern of some of those islands, made of a ring of
52 large trees planted on a ridge ringing the islands, an area covered with small shrubs and finally a
53 barren central zone, sometimes covered with grass. The model is based on sediment coring, major-
54 element and stable-isotope (C and O) analysis of sediment and water, measurement of hydrological
55 parameters (piezometry, water discharge) and geophysical imaging. The results of Jolivet et al.
56 (2023), and previously of Dauteuil et al. (2021), challenge this model with new sedimentological
57 and geochemical data. We suggest that the alkaline water is hosted in a confined aquifer, possibly
58 inherited from a previous phase of construction of the alluvial fan, and capped by a layer of
59 authigenic clay.

60

61 **2. Nature of the islands and floodplain dynamics.**

62

63 The exact onset of deposition of the Okavango alluvial fan is still poorly known although some
64 Optically Stimulated Luminescence data suggest that it started around 40 ka. The initiation of the
65 fan followed an episode of flooding, especially marked by over-washing of aeolian dune sand some
66 100 ka ago (Ringrose et al., 2008). The dune pattern is still preserved in the toe of the fan
67 immediately north of Maun town (Figure 1). In that region, the islands are generally elongated
68 west-east, parallel to the direction of the major dune fields of the northern Kalahari (Thomas, 1988;

69 Thomas et al., 2000). During the last 40 ka, the hydrodynamics of the fan varied several times,
70 following regional climate changes. Tooth et al. (2021) highlighted a period of high discharge in the
71 7 to 4 ka interval, leading to the formation of >100 m wide meandering channels. Remnants of
72 some of these channels are still preserved in the topography. The present-day channels are a few
73 meters to <20 m wide and generally incise the floodplain topography (McCarthy et al., 1991b,
74 1997). Those channels are avulsing, changing their course. This avulsion mechanism is suspected to
75 be largely controlled by vegetation developing on both banks and leading to the formation of levees
76 that ultimately fail, creating a new water course (McCarthy et al., 1992; Stanistreet et al., 1993).

77 The origin of the thousands of islands that form the Okavango alluvial fan is thus very variable.
78 Some, especially north of Maun town derive from paleo-dunes that have been dissected by the
79 invading channels, others are remnants of meander bars accumulated by large paleo-channels
80 (possibly those described by Tooth et al. (2021) at 7 to 4 ka), some are large portions of land
81 emerging today from the floodplain but supporting evidence of paleo-channels, some may be either
82 paleo sand-bars or inverted channels, and finally a large proportion of them have no clear origin,
83 formed through multiple dissection episodes of surface morphologies. Given their highly variable
84 origin, each island must have a specific sedimentary structure with varying grain size and sediment
85 facies. Although the previous studies performed by the authors of the comment and their co-workers
86 have investigated several islands (they claim the description of 18 islands through up to 200 auger
87 holes), no detailed description of the sediment has been provided. An exception is formed by
88 indications on the type of material from few islands such as in McCarthy and Ellery (1995). The
89 authors of the comment refer to deep boreholes in Thata Island (Figure 1) but the provided
90 reference is an unpublished PhD thesis from ETH Zurich, for which only a short abstract can be
91 found. This variability in sediment structure of the islands remains to be assessed in detail by
92 precise descriptions of sediment logs. We initiated such a study in the work discussed here (Jolivet
93 et al., 2023), which presents – to our knowledge for the first time – a log description of the
94 boreholes, including grain-size variations, mineralogy and observable sediment structures. The
95 detailed sediment parameters (porosity, mineral composition, amount of organic matter, etc) of the
96 islands certainly plays a major role in the hydro-bio-geochemical processes that control the local
97 composition of the groundwater (for example, the role of micro-organisms would be very
98 interesting to explore). In that respect, the comment that “*None of these studies have revealed a
99 stratigraphic break between an upper sand layer and a lower clay-rich layer*” is contradicted by our
100 description of the sediment, the grain size analysis and the Al₂O₃ content, three independent
101 markers that corroborate a stratigraphic change, also marked by the Sr stable isotopes. The authors
102 of the comment suggest that the Al₂O₃ content may be controlled by termite activity. This is indeed

103 a possibility, but aiming at a geochemical analysis we have been very careful to avoid termite
104 mounds, and as stated above, Al is not the only marker we used. We agree with the authors that clay
105 is largely airborne from the Makgadikgadi pan to the SE of the Delta (this we conclude from the Sr
106 isotopes (Jolivet et al., 2023)), but once again, the use of this clay by termites would not lead to the
107 layered stratigraphic pattern we observed, nor to the conjunction of this layer with the water table
108 and the incipient carbonate layer. Finally, the aggradation process (i.e. the growth of the islands
109 through mineral precipitation) proposed by the “brine drop” model (McCarthy et al., 2012), which
110 indeed nicely explains the fate of the solutes entering the Delta will vary from one type of structure
111 to the other, depending on sediment porosity, permeability and mineralogy. Altogether, the
112 topography of the Delta, can be explained by the variable origin of the islands combined with the
113 dynamics of the rivers, and does not necessarily require aggradation.

114 The dynamics of the floodplain is also variable in the Delta: the Panhandle region (Figure 1) and the
115 upper reaches of the alluvial fan are flooded most of the time. The floodplains along the Boro river
116 (western side of the central Chiefs Island) are only flooded during a few months (generally May to
117 October) and dry the rest of the year, some water pools being filled during the rain season or
118 preserved from complete drying. The vegetation composed of grass and reeds dies during the dry
119 season. The Maunachira and Mboroga rivers, east of Chiefs Island, are permanent and a large
120 portion of the floodplain remains flooded, supporting a permanent, thick vegetation of reeds and
121 papyrus (Figure 1). In that respect, Nxaraga island is not situated “*at the lower fringe of the*
122 *permanent swamp*” as indicated in the comment but indeed in the region of semi-permanent
123 flooding, west of Chiefs Island. This difference in hydrological dynamics has an impact on the
124 concentration of salt, both on the ground and in groundwater (McCarthy and Metcalfe, 1990).

125

126 **3. Salt and alkaline waters.**

127

128 Dauteuil et al. (2021) published a first series of stable and trace element geochemical data from
129 water samples from both surface and groundwater in Nxaraga Island, in the SW seasonal swamps of
130 the Delta (Figure 1). They demonstrated, based on the Rare Earth Element (REE) pattern that the
131 alkaline groundwater could not be obtained from concentration through evaporation or
132 evapotranspiration of the surface freshwater. Dauteuil et al. (2021) also showed, based on water-
133 table measurements from October 2017 to January 2019 using a line of 13 piezometers over a
134 horizontal distance of 300 m, that the two aquifers (surface and groundwater) had independent
135 hydrological cycles. In comparison, McCarthy and Ellery (1994) performed water-table
136 measurements over a similar period using 4 non-equipped drilling sites over a distance of 250 m,

137 that they regularly re-opened for measurement. We thus suggested the occurrence of two different,
138 non- or poorly-connected aquifers. This conclusion has been re-enforced in our publication (Jolivet
139 et al., 2023) based on a complete analysis of the sediments (stratigraphy, sediment structure,
140 mineralogy, grain size, major and trace elements geochemistry, C, Sr, Nd stable isotopes analysis)
141 hosting the aquifer.

142 McCarthy and Metcalfe (1990), indicated that “*trona-encrusted islands tend to be more common in*
143 *the permanent swamps than in the seasonal swamps*” and McCarthy et al. (1986) reported that
144 “[salt] *generally occurs on the fringes of islands as well as on the margins of pans, but occasionally*
145 *may be found in the interior of smaller islands*”. During two field-expedition in July 2022 and July
146 2023, we indeed observed frequent salt efflorescence on islands of variable size (from a few 100 m²
147 to several km²) in the permanent swamps along the Maunachira and Mboroga rivers (Figure 1). This
148 salt is generally found along the shore of shallow swamps, connected to the main rivers by a small
149 (< 1 m wide, <50 cm deep) channel. The swamps, and the shores are vegetated, mostly with grass
150 and reeds but also with bushes and sometimes trees. Several authors suggested that these salts, as
151 well as solutes concentrated in the swamps, are washed out of the Delta during the rainy season
152 (November to March) and annual flooding (June to September) when hydraulic connectivity is
153 established between the rivers and the swamps (Ramatlaping et al., 2021; 2023; Letshele et al.,
154 2023). This may partly explain the fate of the solutes entering the Delta, although we agree that the
155 model should be further developed, especially by establishing the final sink of those solutes. Each
156 year from 2018 to 2023 we visited many islands along the Boro river (i.e., in the seasonal
157 floodplains of the western Delta), at two different periods of the year (June – July and October –
158 December) and could not observe any occurrence of salt on the surface, neither in the central part of
159 the islands nor on the shores like in the east. As reported in Dauteuil et al. (2021) and Jolivet et al.,
160 (2023), geochemical analyses of surface samples (down to about 2 m) show low (<0.5 % weight)
161 concentrations in Na₂O or K₂O that could trace the occurrence of trona, thermonatrite or sylvinite,
162 the main mineral species observed in the efflorescences (McCarthy et al., 1986). Assuming the
163 occurrence of such salt on the surface, the geochemical pattern reported in our studies would require
164 a perfectly complete leaching of those elements by rain water to a depth of at least 2 m. Our
165 sampling was done in November 2018, before the onset of the rain season, and in July 2019 during
166 the dry season, minimizing the chances of such leaching.

167 Finally, we do not fully understand the comment about partitioning of REEs into calcite, as this is
168 exactly what we propose: “*The REE patterns in the sediments are controlled by carbonate nodules*
169 *(Figure 7 and 10)*” (see section 5.1.2 of Jolivet et al. 2023). We also indicate that, at high pH and
170 high carbonate concentration, organic matter most probably plays a role in shaping the REE pattern,

171 especially by favoring the partitioning of Ce towards the water (through adsorption on colloids),
172 leading to the negative Ce anomaly in our soil samples. The calculation of partition coefficients
173 (D^{REE}) proposed in Zhong and Mucci (1995) and Voigt et al. (2017) are of great interest but the
174 experiments were conducted at neutral pH instead of the high pH values (>8) observed in Nxaraga
175 with incipient calcrete developing. The pH plays a role in modifying the solid-liquid D^{REE}
176 (Sholkovitz, 1995; Dia et al., 2000), especially in the carbonate system, in which a competition
177 between REE incorporation/adsorption into the solid phase and REE complexation by dissolved
178 carbonates occurs. Sawada et al. (2005) investigated the effect of pH and observed an increase of
179 $D^{\text{Gd}}/D^{\text{Yb}}$ with increasing pH, which should be related to the solution speciation of REE. With
180 increasing pH, REEHCO_3^{2+} that weakly fractionate REE because complexation constants for all
181 REE are similar, will give way to $\text{REE}(\text{CO}_3)_2^-$ whose stability constant drastically increases with
182 atomic number (Luo and Byrne, 2004), hence favoring the occurrence of HREE in the aqueous
183 phase (Pourret et al., 2007). It has also been shown that dissolved organic matter induces similar
184 effects as carbonates (more pronounced HREE complexation at high than at low pH), which can be
185 explained by the joint effects of site heterogeneity and cation competition (Marsac et al., 2010, 2011,
186 2012, 2013). As indicated in Jolivet et al. (2023), in the water table compartment, “[...] *water and*
187 *sediment are at equilibrium: the groundwater REE pattern exhibits both a strong HREE enrichment*
188 *and a positive Ce anomaly.*”. Figure 2 shows the REE patterns of water samples from the Boro river,
189 from the groundwater in the center of Nxaraga Island and of two representative soil and carbonate
190 nodule samples from the water table compartment (see Table 1, Dauteuil et al., 2021 and Jolivet et
191 al., 2023 for data). The Boro river water, the sediment and carbonate nodules are HREE depleted
192 with $2.18 < \text{Gd}/\text{Yb} < 3.31$ and $2.47 < \text{Gd}/\text{Yb} < 2.80$ values respectively. Comparatively, the groundwater
193 is enriched in HREE with $0.06 < \text{Gd}/\text{Yb} < 0.16$ values. These data show that the REE pattern of the
194 groundwater is largely controlled by solute carbonates and most probably organic matter, that
195 specifically complex HREE.

196

197 **4. Conclusion**

198

199 Our definition of two different hydrological compartments is not solely based on REE patterns, but
200 on the combination of all the independent data acquired (clay content, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (indicating
201 massive dust input from the Makgadikgadi pan), major and trace element concentrations, $\delta^{13}\text{C}$ ratio
202 on water and soil organic matter, hydrology). We do appreciate the significance of the work already
203 done on the Delta but we are of the opinion that our new data should be the base to question at least
204 the unicity of the “brine drop” model. As explained above, the sedimentology and hydrology of the

205 Delta is complex and variable from one location to the other. The nature of the islands, their
206 sedimentological structure and composition, as well as the hydrology and ecology of the
207 surrounding alluvial plains, should generate differences in hydro-geochemical functioning. Finally
208 we agree with the authors of the comment that “[...] *further understanding will only be obtained by*
209 *large-scale interdisciplinary research.*”; an approach we are now taking.

210

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213

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322 **Open Research**

323 Data Availability Statement: the geochemistry used in this reply are all available in Table 1 or in
324 published works (Dauteuil et al., 2021; Jolivet et al., 2023).

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332 **Figure caption**

333 Figure 1: Map of the Okavango Delta and its surrounding region (modified from Jolivet et al., 2023)

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335 Figure 2: Rare earth element spectrum (normalized to UCC standard) for water and sediment from

336 Nxaraga Island and the Boro river. CF13-2018 (Dauteuil et al., 2021) and CF13-2019 (this study,

337 Table 1) are groundwater samples from the center of the island collected in November 2018 and

338 July 2019; Boro-2018#1, #2 and #3 are water samples from the Boro river or related channels taken

339 in November 2018 (see samples OkaRiv, ChaNx and ChaAv in Dauteuil et al., 2021); Boro-2019 is

340 a water sample from the Boro river taken in July 2019 (this study, Table 1); Log1-310cm is a

341 sediment sampled at 310 cm depth in the center of Nxaraga Island (in the water table compartment)

342 and Log1-310cm-(nodule) is a carbonate nodule sampled at the same location (see data in Jolivet et

343 al., 2023).

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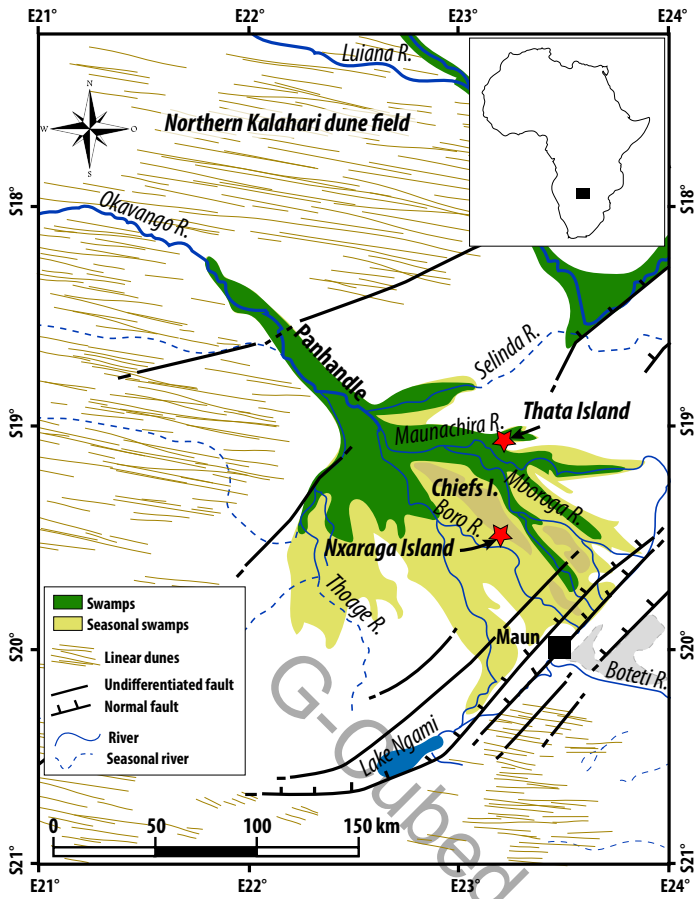
345 Table 1: Rare earth elements concentrations in ppm for the groundwater collected in the central part

346 of Nxaraga Island in July 2019 and the Boro river water collected in July 2019.

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Figure 1.

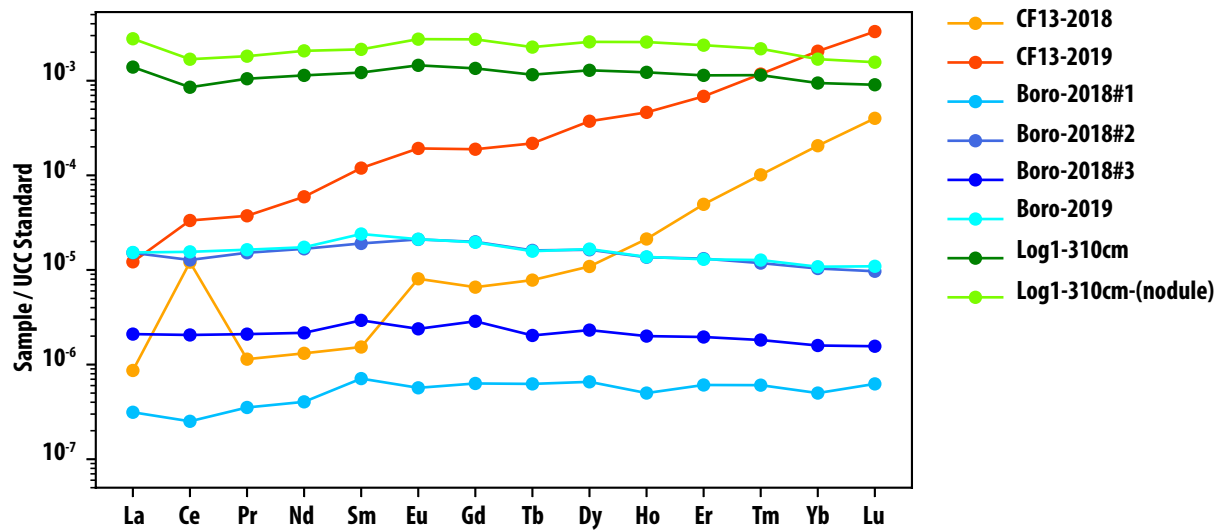
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Figure 2.

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Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
CF13-2019	0.366	2.133	0.265	1.543	0.537	0.169	0.171	0.139	1.306	0.370	1.572	0.388	4.512	1.059
Boro-2019	0.459	0.995	0.116	0.452	0.108	0.019	0.075	0.010	0.058	0.011	0.030	0.004	0.024	0.004

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