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Lukas Aschwanden, Paul Wersin, Mathieu Debure, Daniel Traber

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1 **Experimental study of water-extractable sulphate in Opalinus Clay and implications for**
2 **deriving porewater concentrations**

3 Lukas Aschwanden^{1*}, Paul Wersin¹, Mathieu Debure² and Daniel Traber³

4 *¹Rock-Water Interaction, Institute of Geological Sciences, University of Bern, Baltzerstrasse*
5 *1–3, 3012 Bern, Switzerland*

6 *²BRGM, French Geological Survey, 3 av. Claude-Guillemin, 45060 Orléans, France*

7 *³NAGRA, National Cooperative for the Disposal of Radioactive Waste, Hardstrasse 73, 5430*
8 *Wettingen, Switzerland*

9

10 *Corresponding author: lukas.aschwanden@geo.unibe.ch

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13

14 **Abstract**

15 In northern Switzerland, the Opalinus Clay, a Jurassic claystone formation, is foreseen as host
16 rock for a deep geological repository for radioactive waste. Characterizing its porewater is of
17 particular importance for assessing the mobility of radionuclides and the stability of the
18 engineered barriers. Although the porewater composition of the Opalinus Clay is fairly well
19 known, there is still controversy on the sources of sulphate obtained by different porewater
20 characterization methods. A striking observation is that sulphate concentrations from aqueous
21 extraction and recalculated to in-situ conditions are consistently much higher than sulphate
22 concentrations measured in borehole waters, squeezed waters and advectively displaced
23 waters ("excess sulphate"). Accordingly, the main objective of this study is to better
24 investigate the processes affecting dissolved sulphate concentrations during aqueous
25 extraction and, thus, to reduce uncertainties in predicting the concentrations of this compound
26 in the Opalinus Clay porewater. To this end, a series of extraction experiments were
27 conducted using variable solid/liquid ratios, extraction times and extract solutions. In order to
28 suppress sulphide-mineral oxidation, all the experiments were performed in a glovebox under
29 oxygen-free conditions (atmosphere and solutions). Measurements of the sulphur and oxygen
30 isotope composition of the dissolved sulphate in aqueous extracts are aimed to further
31 constrain the source of the "excess sulphate". Finally, the plausibility of the SO₄ data from
32 extraction experiments in terms of their representativeness for in-situ conditions was
33 evaluated by simple geochemical modelling. The modelling shows that SO₄ concentrations

34 from aqueous extracts recalculated to in-situ conditions imply dissolved and exchangeable
35 cation concentrations which are not consistent with measured data, thus, attesting non-
36 conservative behaviour for sulphate during aqueous extraction. However, the various
37 extraction experiments showed that pyrite oxidation was successfully suppressed during the
38 experiments and neither contributions from e.g. organic material, congruent calcite
39 dissolution and/or sulphate mineral dissolution provide enough SO_4 to explain the "excess
40 sulphate". Ultimately, the various extraction experiments failed to definitely identify the
41 source of the "excess sulphate" in aqueous extracts. However, the good agreement found
42 between the $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of dissolved SO_4 in aqueous extracts and those of borehole
43 waters suggest that the "excess sulphate" might be weakly bound to mineral surfaces.

44

45 **1 Introduction**

46 In northern Switzerland, the Opalinus Clay (OPA), a Jurassic (early Aalenian) claystone
47 formation, is foreseen as host rock for a deep geological repository for radioactive waste.
48 Since the last 30 years Nagra – the Swiss National Cooperative for the Disposal of
49 Radioactive Waste – and several partner organizations have been carrying out an extensive
50 site and host rock investigation program that aims at selecting a suitable site for a deep
51 geological repository. An important aspect of this program refers to characterizing the
52 porewater of the Opalinus Clay, which is of particular importance for assessing the mobility
53 of radionuclides and the efficiency of the technical barriers - i.e. the bentonite tunnel backfill
54 or carbon steel canisters in which the radioactive waste is stored (Nagra, 2002). For example,
55 it is conceivable that, following repository closure, once anaerobic conditions re-established,
56 microbial reduction of dissolved sulphate and associated production of sulphide could occur
57 in some locations (e.g. in the excavation disturbed zone surrounding the emplacement
58 tunnels). This could increase sulphide diffusion to the canisters, and possibly affect corrosion
59 (e.g. Pekala et al., 2020). Accordingly, knowledge on the inventory of the dissolved sulphate
60 and the processes that control its concentration in the porewater of the Opalinus Clay is of
61 particular importance for the design of the technical barriers.

62 Although the porewater composition of the OPA is fairly well known (Pearson et al., 2003;
63 Wersin et al., 2013; Waber & Rufer 2017; Wersin et al., 2020; Wersin et al., 2022), there is
64 still controversy on the sources of sulphate in different porewater characterisation methods. A
65 striking observation is that sulphate concentrations obtained by aqueous extraction and
66 recalculated to in-situ conditions are consistently much higher than sulphate concentrations

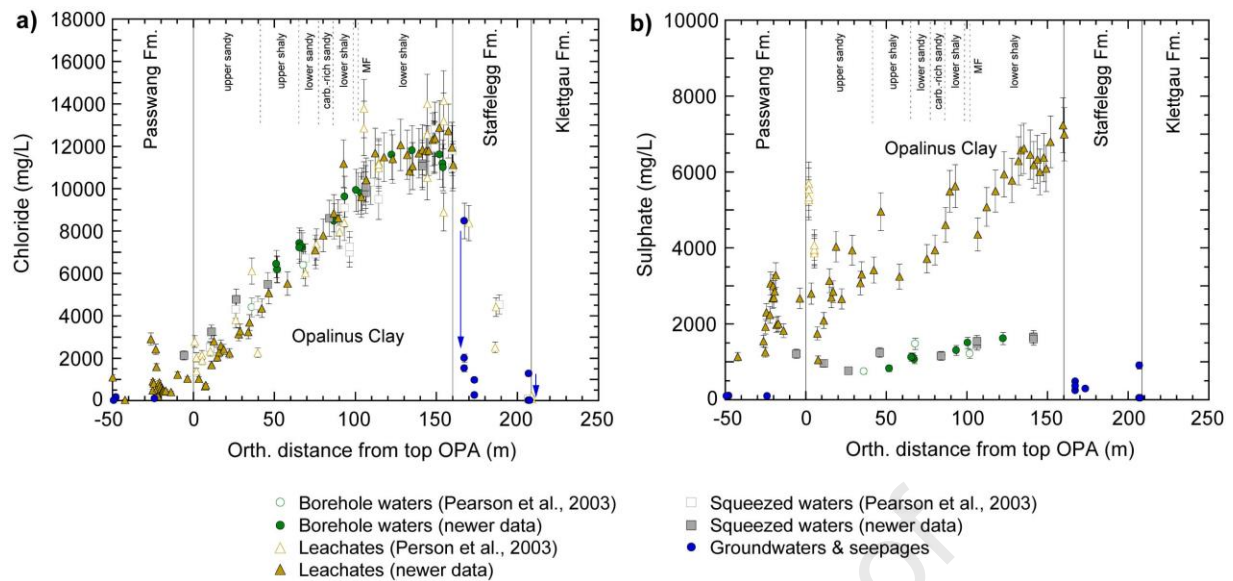
67 measured in borehole waters or in squeezed waters and advectively displaced waters (i.e.
68 "excess sulphate"; Wersin et al., 2013; Waber & Rufer 2017; Wersin et al., 2020). This is
69 illustrated in Fig. 1, which shows the profiles of chloride and sulphate concentrations in the
70 Opalinus Clay porewater across the Mont Terri Rock Laboratory obtained by the different
71 sampling methods. For chloride – a conservative anion (see below) – there is good agreement
72 between the different methods. Mazurek et al. (2011) modelled the profile of chloride (and
73 other tracers) by 1D diffusive exchange with the bounding aquifers and showed that the
74 asymmetric curved shape of the profile can be explained by diffusion only. Regarding
75 sulphate, squeezed and borehole waters also show consistent concentrations, however, in-situ
76 sulphate concentrations of the porewater recalculated from aqueous extraction are distinctly
77 higher. Methodological differences regarding porewater sulphate concentrations are not only
78 observed for the Opalinus Clay but also for other claystones currently being investigated in
79 the context of radioactive waste disposal, such as the Callovo-Oxfordian claystones at Bure in
80 France (Gaucher et al. 2009) or for Boom Clay at Mol in Belgium (De Craen et al. 2004).
81 In contrast to high-pressure squeezing (Mazurek et al., 2015 and references therein) and
82 advective displacement (Mäder, 2018) where the porewater is directly extracted from the
83 rock, aqueous extraction constitutes a technique for indirect porewater characterisation. The
84 basic principle of the method is to immerse a known mass of water-saturated rock into a
85 known volume of ultra-pure water for a specific amount of time during which the system re-
86 equilibrates. Thus, the solutes in aqueous extracts originate from different potential sources:
87 1) constituents originally dissolved in the porewater, 2) induced mineral dissolution and
88 precipitation, cation exchange and sorption reactions during the extraction test, and 3)
89 possibly minor contributions from fluid inclusions in minerals (i.e. small quantities of
90 diagenetic fluid trapped within a mineral during its growth). Accordingly, conversion of
91 solute concentrations measured in aqueous extracts to porewater solute concentrations can
92 only be applied for ions that are not involved in any reactions - i.e., that behave
93 conservatively - and for which the only source is the porewater. For the Opalinus Clay these
94 conditions are met for the anions Cl and Br (Waber et al., 2003; Wersin et al. 2013, Waber &
95 Rufer 2017, Wersin et al., 2020), whereas all other anions and cations are, to variable degrees,
96 involved in mineral reactions. For sulphate, for example, oxidation of pyrite before and/or
97 during the aqueous leaching experiments would obviously explain the observed difference.
98 However, the drillcore samples used for extraction experiments were vacuum-sealed
99 immediately after core recovery and the experiments were conducted in a glovebox – i.e.
100 under oxygen-free conditions. Thus, pyrite oxidation is not considered plausible.

101 Alternatively, dissolution of a sulphate phase, such as diagenetic anhydrite or gypsum in
102 addition to the porewater sulphate could control sulphate concentrations in the aqueous
103 extracts. However, despite of the extensive mineralogical characterization of the Opalinus
104 Clay (Pearson et al. 2003, Lerouge et al. 2014, Pekala et al. 2018, Jenni et al. 2019, Mazurek
105 et al. 2023) no occurrences of diagenetic anhydrite or gypsum have been reported. Moreover,
106 porewaters, as sampled in boreholes and squeezed waters, generally indicate undersaturation
107 with respect to these minerals (Wersin et al. 2020; some exceptions reported in Kizcka et al.
108 2023). Alternatively, Wersin et al. (2013) suggest that dissolution of celestite (SrSO_4) or
109 barite (BaSO_4), which have been identified as trace phases in the Opalinus Clay (e.g. Lerouge
110 et al. 2014), could control sulphate concentrations in the aqueous extracts. Considering that
111 borehole waters, squeezed waters and waters extracted by advective displacement are close to
112 equilibrium with respect to celestite, this seemingly is a viable hypothesis. Gaucher et al.
113 (2009) uses a similar hypothesis for explaining the observed sulphate levels in aqueous
114 extracts of the Callovo-Oxfordian claystones at Bure.

115 On the other hand, a spectroscopic study by Jenni et al. (2019) found that – apart from pyrite
116 – the sulphur inventory in the Opalinus Clay is dominated by calcite and apatite, whereas the
117 contribution of celestite is of lesser quantitative importance. Both calcite and apatite can
118 incorporate sulphur (or sulphate) as trace constituent, however, neither the mode of
119 incorporation nor its structural position is exactly known (Fichtner et al., 2017).

120 As a third option, sulphur associated with organic matter could also play a role (Wersin et al.
121 2013). However, all these hypotheses have never been specifically tested in extraction
122 experiments. Accordingly, the main objective of this study is to better investigate the
123 processes affecting dissolved sulphate concentrations during aqueous extraction and, thus, to
124 reduce uncertainties in predicting the concentrations of this compound in OPA porewater. For
125 the extraction experiments, a set of seven drillcore samples from the Opalinus Clay was tested
126 using different solid/liquid (S/L) ratios, sample masses, extraction times, preparation methods
127 (i.e. crushed vs. milled material) and extract solutions. Moreover, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved
128 sulphate in extract solutions and borehole water were measured. Finally, geochemical
129 modelling based on cation exchange data, which constitutes an independent dataset, was
130 performed in order to assess the plausibility of the two variants for SO_4 concentrations in the
131 porewater of the Opalinus Clay obtained from the different characterization methods (i.e.
132 high- SO_4 variant by aqueous extraction versus low- SO_4 variant by advective displacement,
133 high-pressure squeezing and borehole waters).

134



135

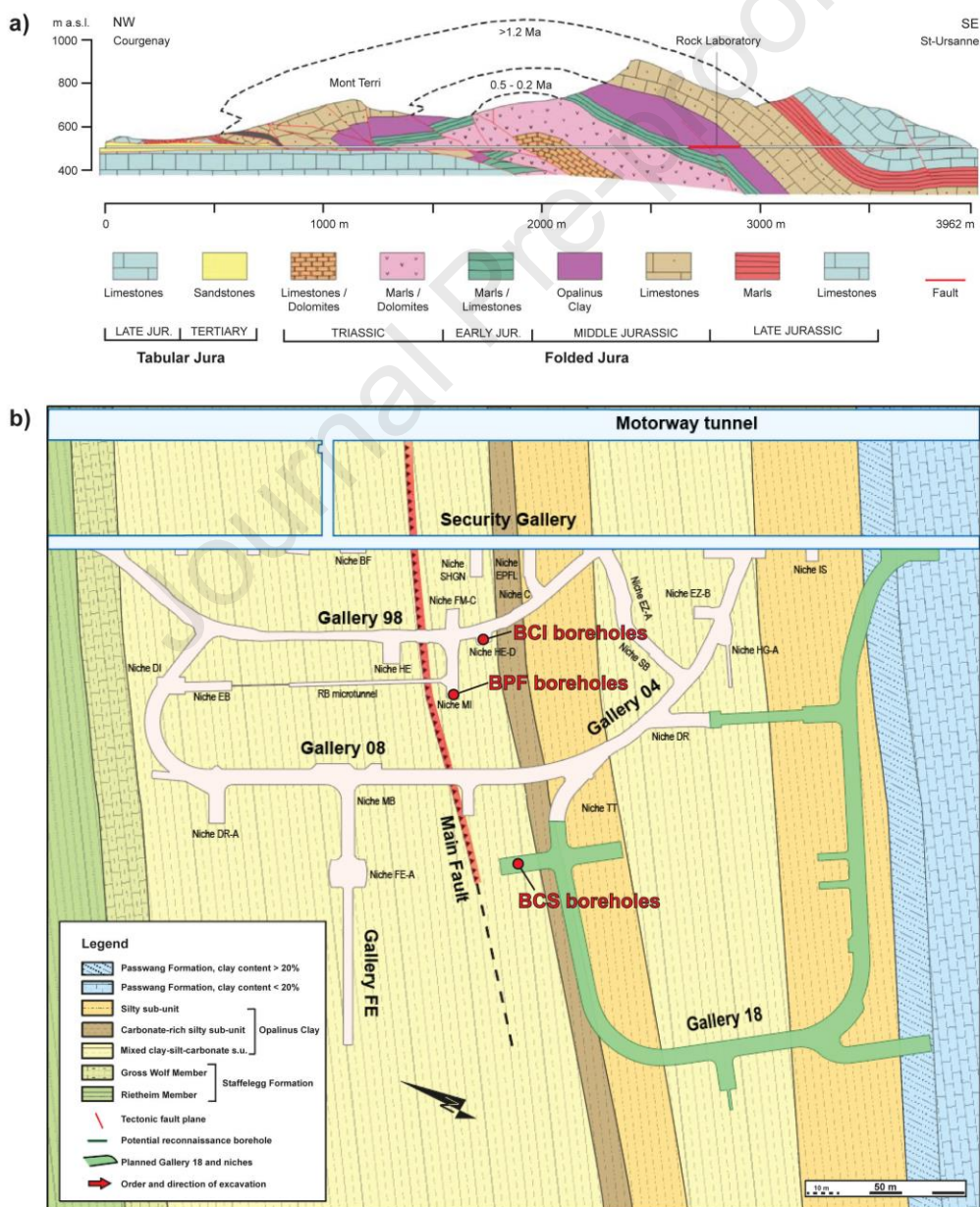
136 Fig. 1: a) Chloride and b) sulphate profile from the Mont Terri Underground Rock Laboratory for squeezed,
 137 borehole and seepage waters in comparison with data from aqueous extracts (modified after Wersin et al., 2020).
 138 Anion concentrations from aqueous extraction are recalculated to in-situ conditions using an anion-accessible
 139 porosity fraction of 0.54 (Person et al., 2003).

140

141 2 Sample description

142 A total of seven drillcore samples from the Opalinus Clay were investigated in this study. The
 143 mineralogical composition of the Opalinus Clay is well known. According to the rock
 144 parameter database compiled by Mazurek (2017) the main mineral fractions of the Opalinus
 145 Clay are (in wt.% $\pm 1\sigma$): clay minerals (52.9 ± 14.9), quartz (21.4 ± 9.6) calcite (18.2 ± 11.7)
 146 and feldspars (3.3 ± 2.2). The clay minerals in the fraction $<2 \mu\text{m}$ include mainly illite,
 147 illite/smectite mixed layers and kaolinite, whereas chlorite contents are subordinate. Pyrite
 148 and organic matter are ubiquitous ($<0.1 - 2.0 \text{ wt.}\%$ and $0.5 - 1.5 \text{ wt.}\%$, respectively).
 149 Moreover, accessory minerals are present, which are commonly not identified by X-ray
 150 diffraction. For example, diagenetic celestite and Ba-Sr sulphate have been detected at
 151 instances by microscopic techniques, usually as large grains ($> 100 \mu\text{m}$; Wersin et al. 2013;
 152 Lerouge et al., 2014; Lerouge et al., 2015; Pekala et al. 2018). Based on electron microscopy
 153 and X-ray spectroscopy Jenni et al. (2019) also found indications for small amounts (<0.047
 154 g/kg dry rock) of sub- μm -sized celestite grains finely disseminated in the rock matrix. In
 155 addition, sulphate associated with calcite is also present and constitutes a larger sulphate pool
 156 ($<0.84 \text{ g/kg dry rock}$). No other diagenetic sulphate minerals have been identified in the rock
 157 matrix of the Opalinus Clay, despite extensive mineralogical investigations (Pearson et al.
 158 2003, Lerouge et al. 2014, Pekala et al. 2018, Jenni et al. 2019, Mazurek et al., 2023).

159 Five of the investigated drillcore samples are from the Mont Terri Rock Laboratory – an
 160 important international underground research facility for deep geological disposal of
 161 radioactive waste (Pearson et al., 2003). It is situated to the north of St-Ursanne in the canton
 162 of Jura, Switzerland (Fig. 2a) approximately 300 m underground and comprises around 1200
 163 m of tunnels and niches for experiments. The samples were retrieved from three different
 164 boreholes: 1) from the BCI-21 borehole at depths of 3.05 m and 5.75 m from the tunnel floor
 165 (samples BCI-21A-290-319 and BCI-21-550-600, respectively), 2) from the BCS-7 borehole
 166 at 10.5 m depth (sample BCS-7) and 3) from the BPF1 borehole at depths of 3.90 m and 4.30
 167 m (samples BPF1-3.90 and BPF1-4.30, respectively).
 168



169

170 Fig. 2: a) Geological Profile across the Mont Terri anticline and location of the underground rock laboratory.
171 Schematic representation of the erosion history (modified after Freivogel and Huggenberger, 2003). b) Map view
172 of the Mont Terri Underground Rock Laboratory with location of boreholes (borehole mouth) from which
173 drillcore samples were extracted for the present study (modified from map provided by D. Jäggi, Swiss Federal
174 Office of Topography swisstopo).

175 The other two samples investigated in this study are from the Bülach-1-1 borehole (BUL1-1-
176 858.60-RP and BUL1-1-909.24-RP) - an exploratory borehole drilled by Nagra in 2019 -
177 situated between the villages of Glattfelden and Bülach (18 km to the north of the city of
178 Zürich; for details see Mazurek et al., 2021).

179

180 **3 Methods**

181 The extraction experiments performed in this study involved 1) aqueous extraction at different
182 solid/liquid (S/L) ratios, sample masses, extraction times and preparation methods (i.e.
183 crushed vs. milled material) for identifying potential experimental artefacts, 2) sequential
184 aqueous extracts in order to provide quantitative information on the inventory and the
185 potential release of SO_4 during the experiments, 3) measurements of organic carbon in
186 aqueous extracts to identify potentially associated SO_4 contributions, 4) nickel-
187 ethylenediamine extracts for determining the exchangeable cation population and the total
188 inventories of Sr and Ba and 5) acid extractions for specifically addressing the question of
189 SO_4 released from the carbonate fraction. Moreover, analyses of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved
190 sulphate in aqueous extracts and borehole water are aimed to better constrain the processes
191 controlling sulphate concentrations in aqueous extracts.

192 The extraction experiments were performed at two different laboratories, at the Institute of
193 Geological Sciences, University of Bern, Switzerland and at the French Geological Survey
194 (BRGM), Orléans, France. Methodological details are described in the following subsections.
195 Apart from the various extraction experiments and isotope measurements the analytical
196 program also involves determination of the rock properties such as the gravimetric water
197 content and the bulk-rock mineralogy by X-ray diffraction (XRD) and CNS analyser
198 (elemental contents of inorganic and organic carbon and total sulphur). These standard
199 techniques follow the general principles described by Waber and Rufer (2017) and Wersin et
200 al. (2020) and are not further detailed here.

201

202 3.1 Sample preparation for extraction experiments and experimental conditions

203 The fundamental principle of porewater investigations relies on preserving the initial state of
204 the drillcore samples upon recovery by minimizing their desiccation, oxidation and outgassing
205 by sealing into evacuated and gas-tight bags (PET-Aluminium-Polyethylene compound foil)
206 on-site, immediately after core recovery. For experiments performed at the University of Bern
207 the samples were rapidly unpacked in the lab (under atmospheric conditions) where the rim as
208 well as the bottom and top part of the drillcore samples were trimmed off (1.5 cm; potentially
209 contaminated by the drilling fluid and pre-exposed to the atmosphere). The central rock
210 material was disintegrated to 0.5–1 cm sized fragments, of which a subsample was milled
211 with a tungsten carbide disc mill (120 s at 720 rpm; <63 μm grain size). Crushed and milled
212 material were then transferred into a glovebox where the extraction experiments were
213 performed under anaerobic conditions ($\text{pO}_2 < 1$ ppm). The preparation time under atmospheric
214 conditions – i.e. from unpacking the samples until transfer into the glovebox – was minimized
215 to <8 minutes to suppress sulphide mineral oxidation and porewater evaporation as much as
216 possible. For experiments performed at BRGM the entire process of sample preparation was
217 performed in a glovebox at fixed N_2 and CO_2 levels. The sample rims were also removed and
218 the central rock material was freeze-dried. The freeze-dried sample was then split into two
219 batches: one was grinded and sieved (<63 μm grain size), the other was crushed to 0.5–1 cm
220 sized fragments.

221

222 3.2 Aqueous extracts

223 The aqueous extraction experiments performed at the University of Bern followed the general
224 procedures described by Waber and Rufer (2017). Experiments performed by BRGM
225 followed the methodology described by Debure et al. (2018). Generally, degassed oxygen-
226 and CO_2 -free ultra-pure water was used for the extractions. The experiments involved
227 numerous tests at variable S/L ratios (0.05–1 g/mL), extraction times (0.2–168 h) and using
228 crushed and milled material. Note that milling reduces the grain size and opens fluid
229 inclusions that contribute solutes. Moreover, milling increases the reactive surface of the
230 sample, which may enhance mineral reactions (such as dissolution or precipitation) and also
231 ion-exchange.

232

233 3.3 Sequential aqueous extracts

234 Sequential aqueous extractions involved 3–4 repeated aqueous extractions on the same
235 sample material at a constant S/L ratio of 0.2 g/mL and extraction times of 24 h. The first
236 sequence followed the procedure described in the previous section. At the end of the first
237 sequence, the rock slurry that remained after filtration of the supernatant solution was again
238 mixed with degassed, oxygen- and CO₂-free ultra-pure water, maintaining an S/L ratio of 0.2
239 g/mL. This procedure was repeated for another 2–3 extraction sequences.

240

241 3.4 Cation-Exchange-Capacity (CEC)

242 Extraction experiments for determining the CEC, i.e. the exchangeable cations adsorbed on
243 the clay mineral surfaces, were performed on the original sample material, as well as on
244 sequentially H₂O extracted material (section 3.3) using a constant S/L ratio of 0.2 g/mL and
245 extraction times of 24 h. The experiments followed the same procedures as described for
246 aqueous extracts, however, using a different extract solution. CEC measurements rely on the
247 use of a strongly sorbing index cation that replaces all other, originally adsorbed cations. The
248 experiments were performed at the University of Bern by using the nickel ethylenediamine
249 (Ni-en) method elaborated by Baeyens & Bradbury (1994) and Bradbury & Baeyens (1998).
250 The CEC is then determined from the difference between the concentrations of the index
251 cation in the initial stock solution and in the final extract solution. Alternatively, it can be
252 determined from the sum of the exchanged cations by measuring their concentrations in the
253 final extract solution. For the latter method the extracted cation data need to be corrected for
254 cations dissolved in the porewater and the cations released from (potential) mineral
255 dissolution. Such corrections were applied based on the assumption that the main cations Na,
256 K, Ca and Mg are attributed to the main anions Cl and SO₄ (Bradbury & Baeyens 1998, Hadi
257 et al. 2019). The CEC is then calculated from the sum of the cations minus the concentrations
258 of Cl and SO₄ (normalised to meq/kg_{dry rock}).

259

260 3.5 Acid extractions

261 Acid extractions (in combination with aqueous extractions) were performed for one sample
262 from the BUL1-1 borehole (BUL1-1-909.24-RP; containing 4.5 wt.% calcite) using two
263 different S/L ratios: 1) 0.05 g/mL and 2) 0.2 kg/L. Extraction time was 24 h. Degassed
264 oxygen- and CO₂-free acetic acid (20%; 3.5 mol/L) was used for the experiments as it
265 constitutes a weak acid that is known to dissolve carbonate but not pyrite. The acidic solution

266 was further diluted with ultra-pure water according to the amount of carbonate present in the
267 sample material, thus, preventing unnecessary high acid dosing that potentially triggers
268 unwanted mineral reactions. Final acid concentrations were 0.09 mol/L for the experiment
269 with an S/L ratio of 0.05 g/mL and 0.35 mol/L for the experiment with an S/L ratio of 0.2
270 g/mL.

271

272 3.6 Chemical analyses of extract solutions

273 3.6.1 *Measurements at the University of Bern*

274 The chemical analyses of the extract solutions involved determination of pH, alkalinity,
275 concentrations of the major anions and cations and for the BUL1-1 samples also dissolved
276 organic and inorganic carbon. The alkalinity and pH were determined by using a Metrohm
277 Titrator system (HCl titration) and Merck 4, 7 and 9 buffers. Concentrations of major cations
278 and anions were determined at the University of Bern by ion chromatography using a
279 Metrohm 850 ProfIC AnCat MCS IC system with automated 4–50 µl injection loops. Cation
280 concentrations of Al, Sr, Ba, Fe and Si that either cannot be analysed by the ion
281 chromatographic method or that were usually close to or below the detection limit, were re-
282 analysed using a Varian 720-ES ICP-OES system. Dissolved organic and inorganic carbon
283 was measured by infrared spectrometric techniques using an Analytic Jena Multi N/C 2100S
284 equipped with an infrared NDIR-detector.

285

286 3.6.2 *Measurements at BRGM*

287 The measurement of pH in batch solutions was carried out with a Mettler Toledo, SevenMulti
288 pH meter using NIST 4, 7, and 10 buffers. Alkalinity was measured using a Titrando 905 and
289 a Dosino 800 equipped with a 5 mL syringe (Metrohm) for HCl (10^{-3} mol/L) injection.
290 Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jobin Yvon) or mass
291 spectroscopy (ICP-MS, Thermo Fisher Scientific) were used to measure cations
292 concentrations. Anions were analysed by ionic chromatography (HPLC, Dionex). The
293 elemental concentrations in solution were determined with a relative uncertainty of 3%.

294

295 3.7 Recalculating ion concentrations in extract solutions to in-situ conditions

296 As outlined in the introduction, conversion of solute concentrations measured in aqueous
297 extracts to porewater solute concentrations is applicable for ions that are not involved in any

298 reactions during extraction experiments - i.e., that behave conservatively - and for which the
 299 only source is the porewater. However, for clay-rich rocks, such a conversion requires that the
 300 anion accessible porosity fraction is known, which is anion-specific. Anion-accessibility or
 301 anion-exclusion is due to the repulsion of anions by the negatively charged surface of clay-
 302 minerals, resulting in the exclusion of anions from a certain fraction of the pore space. For the
 303 conservative chloride the anion-accessible porosity fraction is fairly well known (Zwahlen et
 304 al., 2023; and references therein), however, not for sulphate. From double layer theory, the
 305 exclusion of SO₄ in clayrocks is predicted to be higher because of its higher charge (Gimmi &
 306 Alt-Epping 2018). On the other hand, SO₄ has a larger tendency to form weak complexes,
 307 such as with alkaline earths, thus partly compensating the charge effect. Also, data for
 308 selenate (which displays similar chemical properties as sulphate) in Opalinus Clay from Mont
 309 Terri suggest a similar diffusion regime as for Cl (Gimmi et al., 2014). Thus, for the
 310 experiments performed in this study a similar anion-accessible porosity fraction is used for
 311 SO₄ as for Cl, which is 0.54 for Mont Terri samples (Pearson et al., 2003) and 0.52 for
 312 Bülach1-1 samples (Mazurek et al., 2021). Scaling extract concentrations to in situ porewater
 313 concentrations can be done via equation 1 below:

$$314 \quad C_{free\ pw} = \frac{C_{aqex}}{(S/L) \cdot w_w \cdot f_a} \quad (1)$$

315 where $C_{free\ pw}$ is the in-situ solute concentration in the free porewater (mg/L_{free pw}), C_{aqex} is the
 316 solute concentration in the aqueous extract (mg/L), S/L is the solid/liquid ratio (S = mass of
 317 dry rock in grams; L = mass of ultra-pure water plus mass of porewater in millilitres), w_w is
 318 the gravimetric water content (wt.%) relative to dry mass of the sample material and f_a is the
 319 anion-accessible porosity fraction. Cation concentrations are reported as mg/L_{bulk pw}, i.e. full
 320 accessibility of the pore space is assumed.

321

322 3.8 Sulphur and oxygen isotopes of dissolved sulphate in aqueous extracts

323 Analyses of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved sulphate in aqueous extracts were performed by
 324 Hydroisotop GmbH, Schweitenkirchen, Germany. The dissolved SO₄ in the aqueous extracts
 325 was precipitated as BaSO₄, filtered, dried and measured by Element Analyser Isotope Ratio
 326 Mass Spectrometry (EA-IRMS) with an uncertainty of 0.5‰ (1 σ) for both $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$. The
 327 measurements were normalized to the international VSMOW-scale for oxygen isotopes and to
 328 the VCDT-scale for sulphur isotopes.

329

330 3.9 Geochemical modelling

331 The scope of this modelling exercise was to evaluate SO₄ data obtained from aqueous
332 extraction in terms of their compatibility with exchangeable cation data and, in more general
333 terms, with regard to their representativeness for in-situ conditions based on the well-
334 established database of the Mont Terri Rock Laboratory (Wersin et al., 2022). For this
335 purpose, a hypothetical exchanger composition was calculated from aqueous extraction data
336 (S/L ratios of 1 g/mL) based on simple geochemical modelling and then compared with the
337 exchanger composition obtained from Ni-en extracts on the same samples. The calculations
338 were performed for the Opalinus Clay samples from the Mont Terri Rock Laboratory. The
339 modelling approach relies on some simplifying assumptions, including:

- 340 • The ionic charge is assumed to be carried by the main compounds Na, Ca, Mg, Cl and
341 SO₄. Other compounds, such as TIC, K and Sr were neglected.
- 342 • The Ca concentrations of in-situ porewater were derived from assuming gypsum
343 equilibrium. Note that this reflects the maximum possible Ca concentration. Mg
344 concentrations were set to the same concentrations as Ca (based on the similarity of
345 their concentrations in OPA porewater at the Mont Terri Rock Laboratory; Wersin et
346 al., 2022).
- 347 • Na concentrations of in-situ porewater are derived via charge balance.

348 The calculations were performed using PHREEQC (Parkhurst & Appelo, 2013) and the
349 PSI/Nagra 2012 thermodynamic database (Thoenen et al., 2014) assuming a temperature of
350 25°C. In a first step, Cl and SO₄ concentrations from the aqueous extracts were recalculated to
351 in-situ conditions (section 3.7), then Na-Ca-Mg-Cl-SO₄ solutions were speciated, assuming
352 gypsum equilibrium and charge balance as mentioned above. In a next step, the corresponding
353 exchanger compositions were derived considering cation exchange selectivity coefficients for
354 Opalinus Clay from Pearson et al. (2011) and the cation exchange capacities obtained from Ni
355 consumption of the corresponding Ni-en extracts. The calculated exchanger compositions
356 were then compared with those obtained from Ni-en extracts.

357

358 **4 Results and discussion**

359 4.1 Bulk-rock mineralogy, carbon, total sulphur and gravimetric water content

360 Table 1 shows the mineralogy of the investigated samples based on XRD and CNS analyses,
361 as well as water contents based on gravimetry. All samples show clay-mineral, carbonate and

362 quartz contents in the range of 28 – 72 wt.%, 7 – 26 wt.% and 12 – 35 wt.%, respectively.
 363 Based on the classification of Füchtbauer (1988) and Naef et al. (2019) they are all classified
 364 as very sandy/silty claystones. Pyrite contents range from <1 to 2 wt.% but sulphate minerals
 365 were detected by XRD (sensitivity of approx. 1 wt.%). Organic carbon ranges from 0.4 wt.%
 366 to 1.1 wt.%.

367 Tab. 1: Results of bulk-rock mineralogical analyses by XRD and CNS, as well as gravimetric water
 368 contents of the investigated samples.

[wt.%]	BCI-21- 550-600	BCI-21A- 296-319	BCS-7	BUL1-1- 858.60-RP	BUL1-1- 909.24-RP	BPF1- 4.30m	BPF1- 3.90m	
Calcite	5.6		11.4	25.9	4.5	17.23	19.4	
Dolomite / Ankerite	<1		<1					
Albite	1.7	No XRD and CNS data available	1.2	3.6	3.4	1.8	2.7	
K feldspar	2.9		2.3	5.6	5.7	2.6	2.7	
Pyrite	2.0		1.1	1.3	<1	<1	1.8	
Siderite	1.2		2.5		2.5		2.1	
Quartz	15.0		13.4	34.6	21.8	12.3	11.8	
Anhydrite								
Celestite								
Clay minerals	71.5		67.4	28.6	61.4	66.0	60.1	
S	1.09		0.58	0.68	0.39	0.63	0.94	
C(inorg)	0.83		1.74	3.11	0.81	2.07	2.57	
C(org)	1.07	0.84	0.43	1.01	0.75	0.80		
Water content relative to wet weight	7.37	7.11	7.31	3.77	4.81	6.93	6.51	
Water content relative to dry weight	7.96	7.65	7.89	3.92	5.01	7.45	6.96	

369

370

371 4.2 Aqueous extracts at different S/L ratios, extraction times, sample masses and sample
 372 preparation

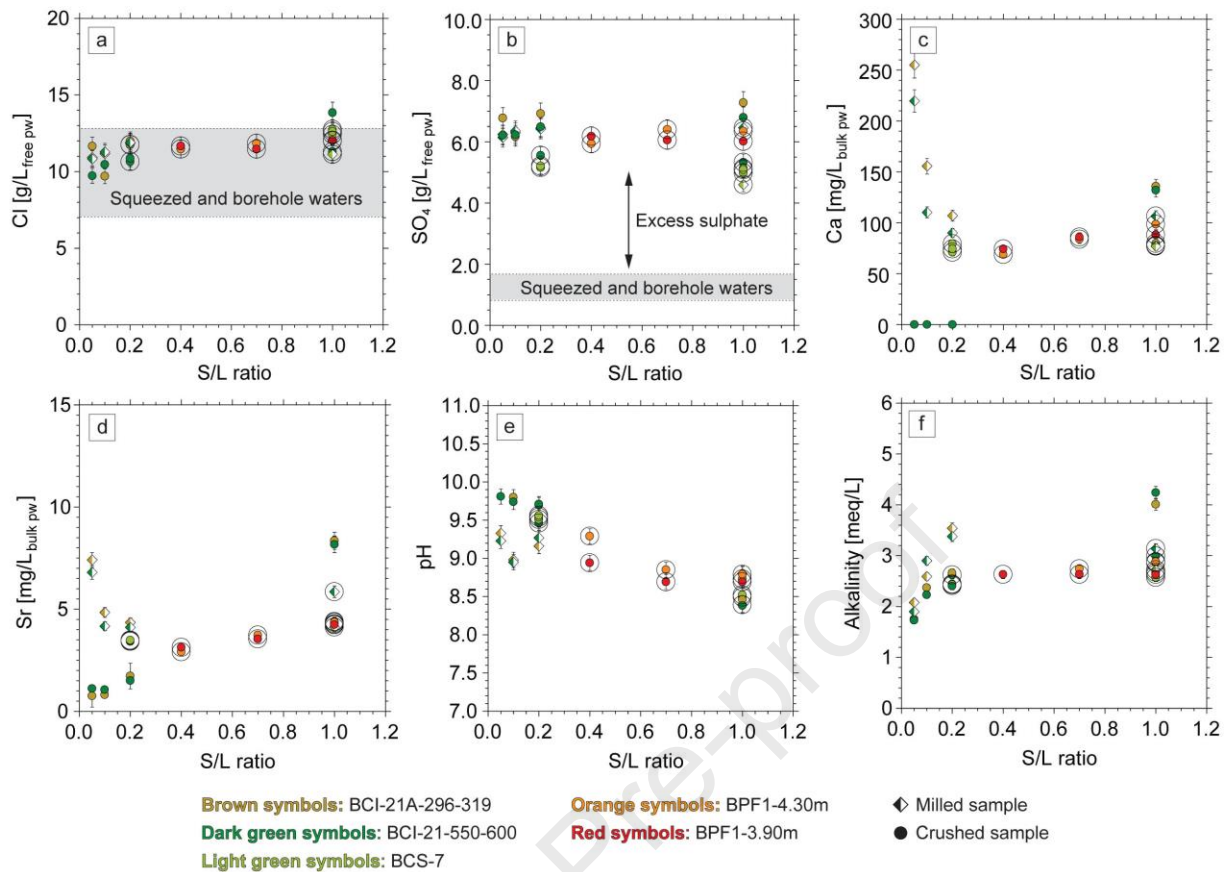
373 Figure 3 shows the results of aqueous extracts performed on Mont Terri samples at different
 374 S/L ratios and at constant extraction time of 24 h using crushed and milled sample material.
 375 At S/L ratios ≤ 0.2 g/mL chloride concentrations in the aqueous extracts slightly increase with
 376 increasing S/L ratio to values of around 10.8 – 11.9 g/L_{free pw} and remain at constant levels
 377 towards higher S/L ratios suggesting conservative behaviour (similarly, conservative
 378 behaviour is suggested for bromide; not shown in Fig. 3). There is a good agreement with the
 379 chloride concentrations from squeezed waters and borehole waters (Fig. 3a; Mazurek et al.,

380 2017; Waber & Rufer 2017; Wersin et al., 2020). Sulphate concentrations vary between 5.2
381 and 7.3 g/L_{free pw} but individual samples show constant concentrations as a function of S/L
382 ratio. However, these concentrations are by a factor of around 3–4 higher than those obtained
383 from squeezed and borehole waters (Fig. 3b). Note that this difference cannot simply be
384 attributed to anion-accessibility, which is somewhat uncertain for sulphate (section 3.7), it is
385 also observed – to a lesser degree (by a factor of around 1.5–2) – when scaling SO₄
386 concentrations to water-loss porosity (i.e. bulk porewater concentrations when assuming f_{SO_4}
387 = 1).

388 Strontium and calcium concentrations show very similar and distinct trends as a function of
389 S/L ratio, clearly indicating non-conservative behaviour, likely attributed to calcite dissolution
390 (see below). Moreover, at S/L ratios ≤ 0.2 g/mL there are large differences in ion
391 concentrations depending on whether crushed or milled sample material was used for the
392 experiments. Extracts of the latter systematically show higher ion concentrations. These
393 differences decrease with increasing S/L ratio. The exact reason(s) for this behaviour is not
394 known, however, it is conceivable that milling potentially induces unwanted effects such as
395 an increase of the reactive surface of the sample material which enhances mineral reactions,
396 evaporation of porewater and milling induced opening of fluid inclusions potentially present
397 in mineral phases (mainly in quartz and carbonates). In any case, the inventory of dissolved
398 strontium (0.8–8.4 mg/L_{bulk pw}) in aqueous extracts is far too low to explain the "excess
399 sulphate" (4–6 g/L_{free pw}) by celestite dissolution alone. The only possibility how celestite
400 dissolution could explain the "excess sulphate" would be adsorption of the released strontium
401 by the clay minerals owing to a shift in the cation exchange equilibrium. This is further
402 discussed in section 4.4. Barium concentrations (not shown in Fig. 3) show a similar trend as
403 observed for Sr, however, at distinctly lower concentrations (< 1 mg/L_{bulk pw}).

404 The pH (Fig. 3e) continuously decreases as a function of S/L ratio (from around 9.3–9.8 down
405 to 8.3–8.8). This trend mainly reflects the higher buffer capacity of extracts performed at high
406 S/L ratios, which results from the comparatively higher content of clay minerals (i.e., the
407 larger surface area available for complexation reactions; see Wersin & Pękala 2017, Wersin et
408 al., 2020).

409



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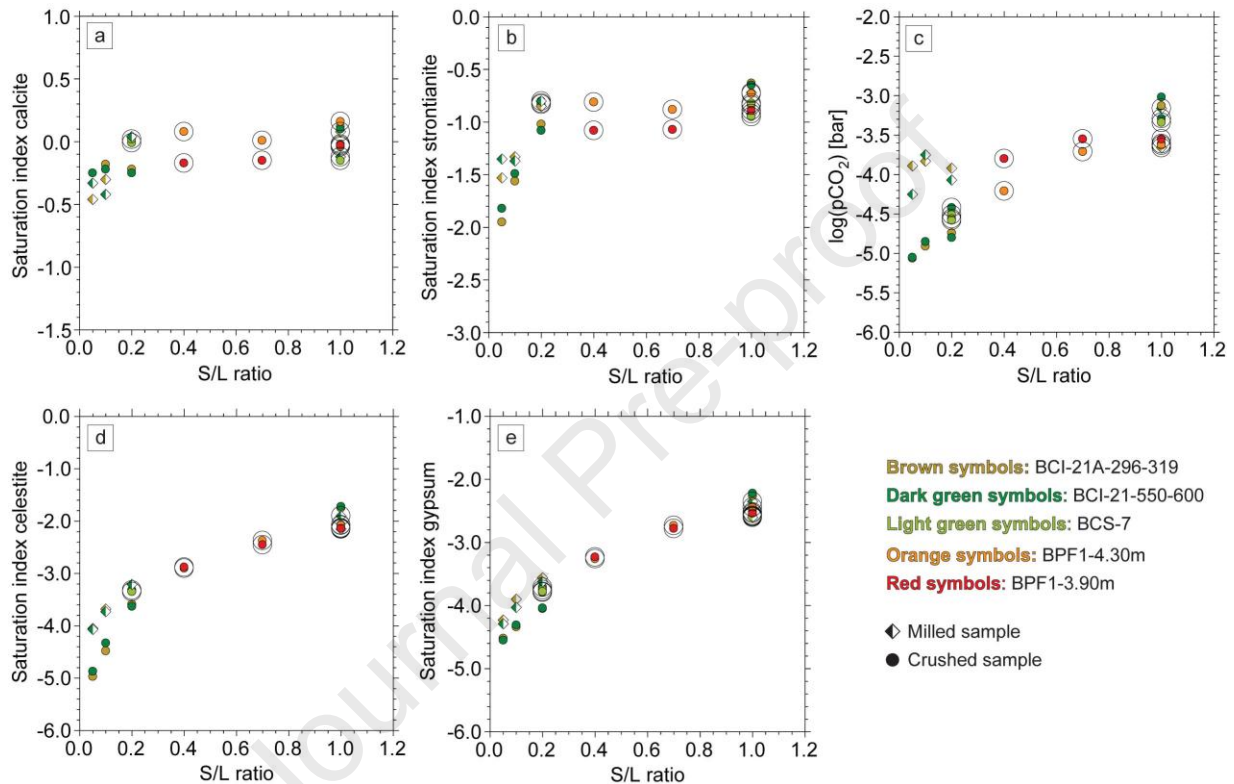
411 Fig. 3: Results of aqueous extracts performed on Mont Terri samples at variable S/L ratios. Extraction
 412 time was 24 h. Experiments with black circles were performed at the University of Bern. Calcium
 413 concentrations plotting at zero are below the detection limit of 0.5 mg/L_{extract}. Data for squeezed and
 414 borehole waters are from Mazurek et al. (2017) and Pearson et al. (2003). Concentrations of Cl and
 415 SO₄ are recalculated to in-situ conditions using an anion-accessible porosity fraction of 0.54 (Person et
 416 al., 2003).

417

418 Alkalinity shows an increase at low S/L ratios (≤ 0.2 g/mL) and virtually constant values at
 419 higher S/L ratios (Fig. 3f). A similar trend is observed for the calculated calcite saturation
 420 indices of the aqueous extracts at variable S/L ratios (i.e. for original extract concentrations;
 421 Fig. 4a). For the calculation of saturation indices the software PHREEQC by Parkhurst &
 422 Appelo (2013) and the PSI/Nagra 2012 thermodynamic data base (Thoenen et al., 2014) were
 423 used. For S/L ratios > 0.2 g/mL calcite dissolution during aqueous extraction imposed
 424 equilibrium or near-equilibrium conditions, whereas undersaturation with respect to calcite is
 425 observed for aqueous extracts with S/L ratios ≤ 0.2 g/mL, probably owing to a limitation in the
 426 availability of calcite at these low S/L ratios.

427 Saturation indices for strontianite show a similar trend as for calcite, however, the extracts
 428 being slightly undersaturated even at S/L ratios > 0.2 g/mL (Fig. 4b). The calculated partial
 429 pressure of CO₂ generally increases with increasing S/L ratio from around 10^{-5} – 10^{-4} bar to 10^{-}

430 ^{3.5} bar (Fig. 4c) and with distinct differences between extracts of crushed and milled material
 431 for low S/L ratios. Note that the sub-atmospheric pCO₂ levels result from using degassed
 432 water as extract solution and the CO₂-free atmosphere of the glovebox in which the
 433 experiments were performed (section 3.2). The saturation indices of celestite and gypsum
 434 continuously increase with increasing S/L ratio but remaining distinctly undersaturated (Fig.
 435 4d,e).
 436



437
 438 Fig. 4: Calculated mineral saturation indices of aqueous extracts (i.e. for original extract
 439 concentrations) performed on Mont Terri samples at variable S/L ratios. For the modelling the
 440 software PhreeqC and the PSI/Nagra 2012 data base (Thoenen et al., 2014) were used. Experiments
 441 with black circles were performed at the University of Bern.

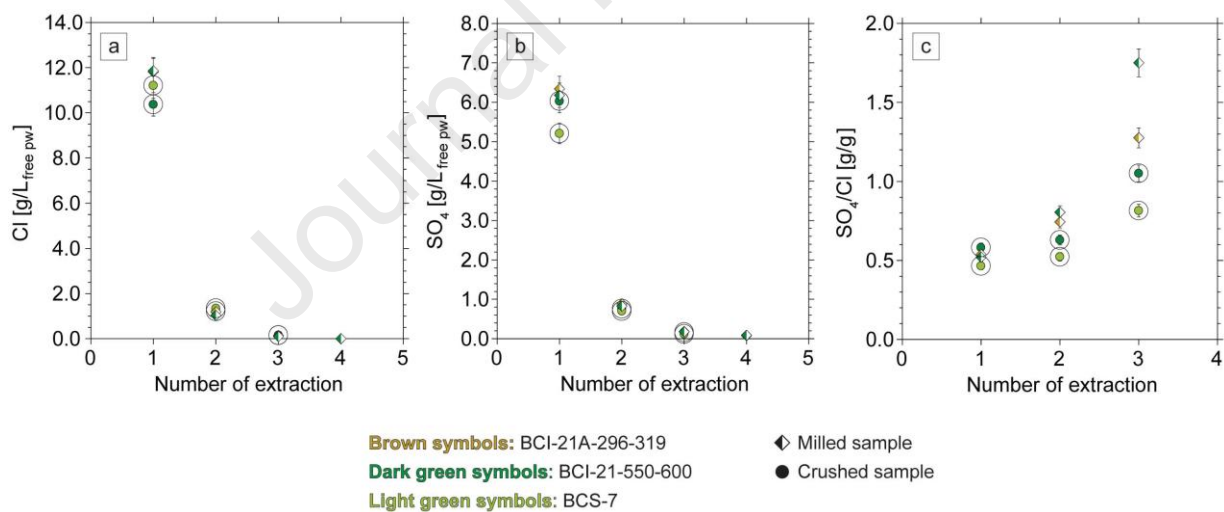
442
 443 In addition to extraction experiments at variable S/L ratios and constant extraction time and
 444 sample mass, kinetic tests were performed at constant S/L ratios but variable extraction times
 445 (10 min up to 7 days) and sample masses (4–20 g). Sulphate and chloride concentrations
 446 (mg/L_{bulk pw}), as well as pH and alkalinity are virtually constant as a function of these
 447 experimental parameters. Note that the constant SO₄ concentrations as a function of extraction
 448 time and S/L ratio, as well as the lack of correlation between "excess sulphate" and pyrite
 449 content of the samples (see Tab. 1) indicate that oxidation reactions are deemed to have been
 450 successfully suppressed during aqueous extraction.

451

452 4.3 Sequential aqueous extracts

453 Figure 5 shows the concentrations of chloride and sulphate, as well as their ratios for
 454 sequential aqueous extracts of Mont Terri samples. All of the investigated samples show the
 455 same general trends with strongly decreasing concentrations upon progressively diluting the
 456 porewater until complete removal after the third extraction sequence (Figs. 5a,b).
 457 Contrastingly, the SO_4/Cl ratio exponentially increases (Fig. 5c) suggesting release from a
 458 sulphate-bearing phase. Accordingly, no fully conservative behaviour can be attested for
 459 sulphate. However, from a quantitative perspective, the SO_4 released during the second, third
 460 and fourth extraction sequence is only of minor importance. If the same behaviour is assumed
 461 for sulphate as for chloride – a conservative species – then the absolute increase of sulphate in
 462 the subsequent extractions is in the range of 44–292 mg/L_{free pw}, thus only a small amount
 463 compared to the amount leached during the first extraction step (Fig. 3b). Consequently, the
 464 source of the "excess sulphate" constitutes a limited reservoir that is almost completely
 465 exhausted during the first extraction.

466



467

468 Fig. 5: Concentrations of Cl and SO_4 (recalculated to in-situ conditions using an anion-accessible
 469 porosity fraction of 0.54; Person et al., 2003) and their ratios during sequential aqueous extraction of
 470 Mont Terri samples. Experiments with black circles were performed at the University of Bern.

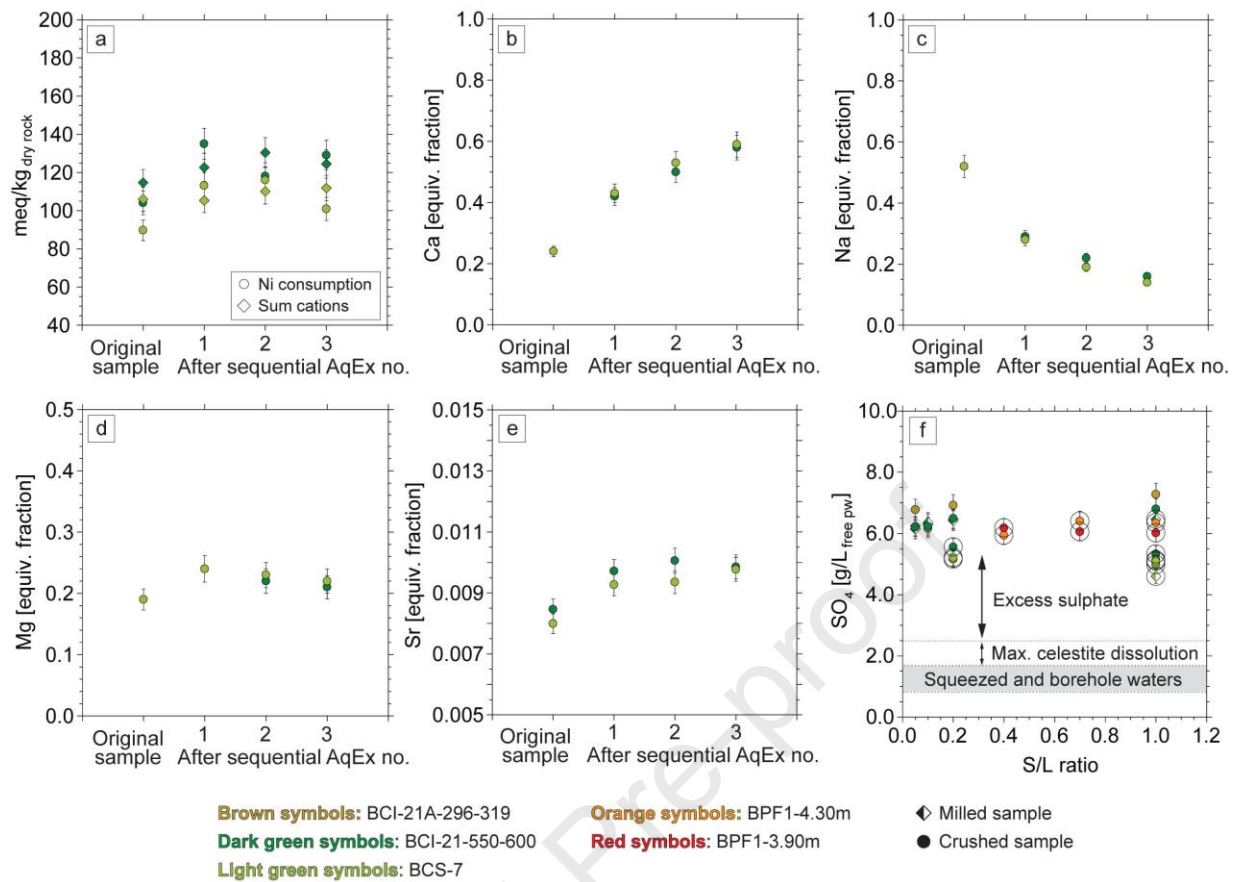
471

472 4.4 Ni-en extracts

473 Figure 6 illustrates the results of the Ni-en extractions of Mont Terri samples. The CEC
 474 derived from Ni consumption ranges from 89.8 to 116.0 meq/kg_{rock} for sample BCS-7 and
 475 104.0–134.7 meq/kg_{rock} for sample BCI-21-550-600 (Fig. 6a). The values for the CEC derived

476 from the corrected sum of cations agree reasonably well. The small differences in Ni
477 consumption and sum of cations between the two investigated samples reflect the
478 comparatively higher clay mineral content of sample BCI-21-550-600 sample (Tab. 1). Both
479 of the investigated samples show the same general trends with slightly lower CEC derived
480 from Ni-en extracts of original sample material compared to the CEC derived from Ni-en
481 extracts of previously H₂O extracted material. For extracts of the original sample material the
482 main extracted cation is Na, followed by Ca and Mg (Fig. 6b–d). During progressive dilution
483 of the porewater (i.e. with increasing number of sequential H₂O extractions), Ca and Na
484 concentrations show opposed trends in the Ni-en extracts with increasing Ca concentrations
485 and equally decreasing Na concentrations. This is because the total solute concentration
486 affects the selectivity of the exchanger for Ca in that the higher charged ion is preferred more
487 strongly on the exchange sites when the total solute concentration in the solution decreases
488 (Gaines & Thomas 1953). Accordingly, the trends observed for Ca in aqueous extracts as a
489 function of S/L ratio (i.e. different degrees of dilution of the porewater; Fig. 3c) do not only
490 reflect calcite dissolution (section 4.2) but also variable magnitudes of cation exchange.
491 Magnesium on the other hand appears much less sensitive to such an effect (Fig. 6d),
492 potentially reflecting differences in the dissolution kinetics between calcite and dolomite.
493 Strontium concentrations in Ni-en extracts are low, ranging from 0.85 to 1.31 meq/kg_{rock}
494 corresponding to 0.008–0.010 equivalent fractions on the clay exchanger (Fig. 6e). Modelling
495 of seepage waters at Mont Terri indicates SrX₂ equivalent fractions that are a factor 2–3 lower
496 than those obtained from Ni-en extracts. This difference has been explained by the dissolution
497 of celestite during Ni-en extraction (Wersin et al. 2020). Since the exchangeable strontium in
498 the Ni-en extracts of the sequentially H₂O extracted material does not markedly vary (Fig.
499 6e), dissolution of the Sr bearing mineral phase must have occurred mainly during the first
500 sequence of aqueous extraction, which is in line with the results from sequential aqueous
501 extracts (section 4.3). However, the strontium inventory (dissolved plus exchanged) is not
502 sufficiently large to explain the "excess sulphate" by celestite dissolution alone (~0.8 g/L_{free}
503 pw; Fig. 6f). Thus, celestite constitutes a limited SO₄ reservoir that is completely exhausted in
504 each extraction. Barium concentrations are below the detection limit of 0.05 mg/L_{extract}
505 (corresponding to 0.004 meq/kg_{rock} or 3.4 mg/L_{bulk pw}) in all analysed extracts.

506



507

508 Fig. 6: a–e) Results of Ni-en extractions of Mont Terri samples. The extraction tests were performed
 509 on the original sample material, as well as on sequentially H_2O extracted material. f) Inventory of
 510 strontium (dissolved plus exchanged) is not sufficiently large to explain the "excess sulphate" in
 511 aqueous extracts by celestite dissolution alone. Data for squeezed and borehole waters are from
 512 Mazurek et al. (2017) and Pearson et al. (2003). Concentrations of Cl and SO_4 are recalculated to in-
 513 situ conditions using an anion-accessible porosity fraction of 0.54 (Person et al., 2003).

514

515 4.5 Acid extracts

516 Acid and aqueous extracts were performed on a drillcore sample from the Bülach1-1 borehole
 517 and the results are illustrated in Fig. 7. Chloride concentrations in aqueous extracts (11.9–13.1
 518 g/L_{free pw}) agree well with those in squeezed and advectively displaced waters. At low S/L
 519 ratios (0.05 g/mL) acid extracts show slightly higher Cl concentrations compared to aqueous
 520 extracts. This difference becomes distinctly larger at higher S/L ratios (0.2 g/mL). Moreover,
 521 at higher S/L ratios the acid extract of milled material shows much larger Cl concentrations
 522 compared to the acid extract of crushed material. For chloride, which has shown to be a
 523 conservative anion (section 4.2; Wersin et al., 2020 and references therein), these differences
 524 are likely to reflect contributions from fluid inclusions. As fluid inclusions are not
 525 homogeneously distributed within the rock – in OPA they are potentially associated with
 526 diagenetic calcite and detrital quartz – the intensity of this effect can vary among extracts of

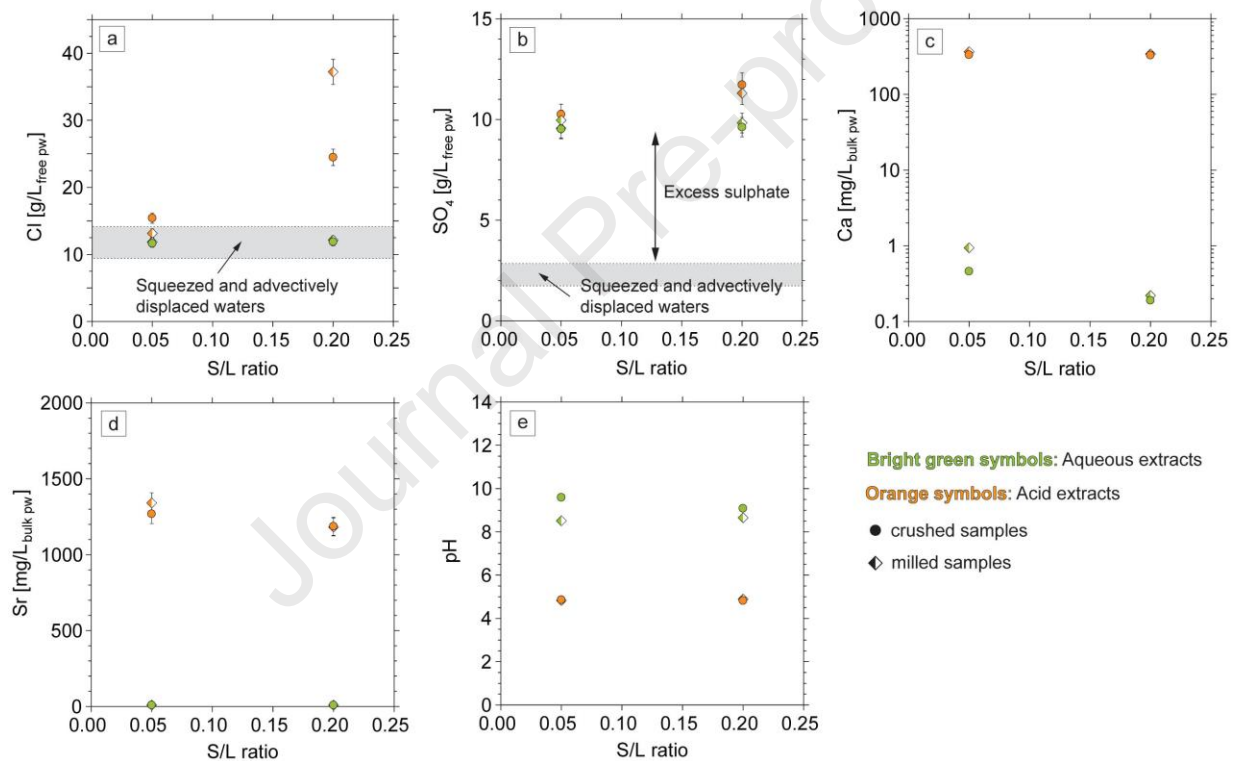
527 the same sample. However, in general it can be assumed that the contribution of fluid
528 inclusions increases with 1) increasing S/L ratio, 2) with increasing calcite and/or quartz
529 contents and 3) with increasing mineral dissolution (e.g. favoured by increasing the reactive
530 surface of a sample by milling).

531 Similar differences between aqueous and acid extractions are also observed for sulphate,
532 however, somewhat less well pronounced. Moreover, sulphate concentrations derived from
533 extracts of crushed and milled material show good agreement. The same applies to the Mont
534 Terri samples, SO_4 concentrations in aqueous extracts are a factor of 3–4 higher compared to
535 those obtained from direct porewater sampling techniques. For obvious reasons Ca
536 concentrations are much higher in acid extracts than in aqueous extracts (Fig. 7c). By taking
537 this difference as a rough measure for how much calcite is dissolved during acid extraction, a
538 value of around 90% is obtained. Acid extracts at an S/L ratio of 0.2 g/mL show SO_4
539 concentrations that are about 1.6 mg/L_{free pw} higher than in aqueous extracts (Fig. 7b). If we
540 assume that the difference is exclusively due to dissolution of calcite containing SO_4
541 impurities, and that calcite dissolution that potentially occurs during aqueous extraction is
542 insignificant compared to that occurring during acid extraction, then the calcite must contain
543 around 700 – 800 ppm sulphate. At first sight this value appears rather high, however, Wynn
544 et al. (2018) have shown that calcite that precipitates under lab conditions from low-ionic
545 strength solutions of pH 7–8 and containing 2 mg/L SO_4 , incorporates around 100 ppm
546 sulphate. Moreover, they show that keeping the pH constant but increasing the sulphate
547 concentration of the parent solution to 20 mg/l increases the amount of the incorporated
548 sulphate to 400 – 450 ppm. Considering that a substantial part of the carbonate in the
549 Opalinus Clay is biogenic and, thus, precipitated from seawater with around 2.7 g/L sulphate,
550 then 700 – 800 ppm sulphate incorporated in calcite is not unrealistic. This is corroborated by
551 Lerouge et al. (2014) who found sulphur contents of <500 ppm and <2000 ppm in diagenetic
552 calcite and bioclastic material, respectively, in the Opalinus Clay of the Benken borehole in
553 northern Switzerland. Nevertheless, the acid extractions show that the sulphate concentrations
554 in calcite – although they appear to be rather high at first sight – are far too low to explain the
555 "excess sulphate" in the aqueous extracts by congruent calcite dissolution. For example,
556 taking the calcium inventory (dissolved plus exchanged) as a rough measure of the maximum
557 amount of calcite that was dissolved during aqueous extraction, then a value of around 4% is
558 obtained. Dissolution of 4% of the available calcite contributes roughly 60 mg/L_{free pw}
559 sulphate, thus a very small amount compared to the "excess sulphate" (Fig. 7b). Moreover, it
560 must be recalled that the concentration of 700 – 800 ppm sulphate in calcite was determined

561 based on the assumption that all of the sulphate in the acid extracts originates from calcite
 562 dissolution and thus, the 700 – 800 ppm represent a maximum value.

563 Strontium and barium show detectable concentrations only in the acid extracts. Also iron is
 564 present in the acid extracts at rather high concentrations (0.3 – 1.0 g/L_{extract} depending on S/L
 565 ratio; not shown in Fig. 7). Potentially this iron could originate from pyrite dissolution.
 566 However, taking into account that acid extracts performed at S/L ratios of 0.05 g/mL show
 567 similar sulphate concentrations as the aqueous extracts, pyrite dissolution is not considered to
 568 play a major role. Most likely the iron stems from the dissolution of Fe-bearing carbonates:
 569 based on the XRD data (Tab. 1) the investigated Bülach1-1 sample contains 2.5 wt.-% siderite
 570 and thus, providing sufficient iron to explain the observed concentrations.

571



572

573 Fig. 7: Results of acid and aqueous extracts of the Bülach1-1 sample. All experiments performed at
 574 University of Bern. Data for squeezed and advectively displaced waters are from Mazurek et al.
 575 (2021) Concentrations of Cl and SO₄ are recalculated to in-situ conditions using an anion-accessible
 576 porosity fraction of 0.52 (Mazurek et al., 2021).

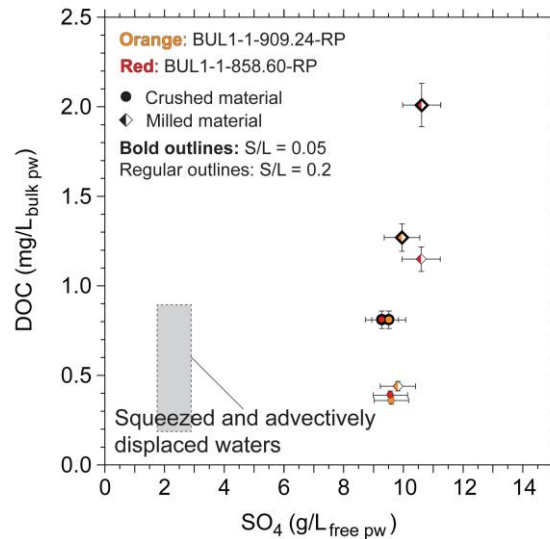
577

578 4.6 Dissolved organic carbon in aqueous extracts

579 Figure 8 shows DOC concentrations in aqueous extracts of the Bülach1-1 samples as a
 580 function of S/L ratio, sample preparation and sulphate concentration. For comparison data
 581 from squeezed and advectively displaced waters are illustrated too (Mazurek et al., 2021).

582 Note that DOC concentrations in aqueous extracts are reported as $\text{mg/L}_{\text{bulk pw}}$. However, a
583 significant part of the dissolved organic material (DOM) contains anionic functional groups
584 (Huclier-Markai et al., 2010; 2018) and, thus, the DOM likely behaves similar as inorganic
585 anionic compounds, i.e., it is affected by anion exclusion and no or only weak sorption
586 (Charlet et al. 2017, Chen et al. 2018). Consequently, DOC concentrations in the free
587 porewater are somewhat higher compared to the concentrations in the bulk porewater
588 illustrated in Fig. 8. For the investigated samples the DOC concentrations in aqueous extracts
589 vary as a function of sample preparation – i.e. extracts of milled material consistently show
590 higher concentrations than extracts of crushed material – and also as a function of S/L ratio –
591 i.e. extracts performed at low S/L ratios show higher concentrations than extracts performed
592 at high S/L ratios. In contrast, sulphate concentrations do not markedly vary neither as a
593 function of sample preparation nor as a function of S/L ratio (Fig. 8). Overall, this lack of
594 correlation between DOC and sulphate concentration indicates that sulphur associated with
595 organic matter is not likely to be the source of the "excess sulphate" in aqueous extracts. This
596 is supported by mass balance considerations: For example, the aqueous extract of milled
597 sample material at an S/L ratio of 0.05 g/mL, shows DOC concentrations that are $\sim 1.5 \text{ g/L}_{\text{bulk}}$
598 pw higher than those of squeezed waters. If the difference in sulphate concentration between
599 squeezed waters and the aqueous extract is due to sulphur released from dissolved organic
600 matter, then the DOM must show C/S mass ratios of around 0.75 (or slightly higher
601 considering anion exclusion for DOM; see above). This value then decreases with decreasing
602 difference in DOC between aqueous extracts and squeezed waters. Such low C/S mass ratios
603 are not considered realistic. Thus, a major release of sulphur from dissolved organic material
604 during aqueous extraction experiments, which could explain the "excess sulphate", is
605 unlikely.

606



607

608 Fig. 8: Concentrations of sulphate and dissolved organic carbon (DOC) in aqueous extracts of
 609 Bülach1-1 samples. For comparison data from squeezed and advectively displaced waters are
 610 illustrated too (Mazurek et al., 2021). Sulphate concentrations are recalculated to in-situ conditions
 611 using an anion-accessible porosity fraction of 0.52 (Mazurek et al., 2021).

612

613 4.7 Sulphur and oxygen isotopes in aqueous extracts and borehole water at Mont Terri

614 Re-equilibration during aqueous extraction does not only affect chemical constituents but also
 615 isotopes. Thus, the oxygen and sulphur isotope composition of dissolved sulphate in aqueous
 616 extracts reflects contributions from 1) the original porewater 2) mineral reactions and 3)
 617 oxygen isotope exchange between dissolved SO₄ and H₂O. However, the latter is very slow
 618 and not relevant on timescales of the extraction experiments (Krouse & Mayer, 2000).

619 Figure 9a shows the $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of dissolved sulphate in aqueous extracts of the
 620 Mont Terri samples. For comparison it also includes isotope data for vein celestite in the
 621 Opalinus Clay at Mont Terri (Pearson et al., 2003), whole-rock gypsum and/or anhydrite from
 622 the underlying Triassic evaporites (Gipskeuper, Muschelkalk; Mazurek & de Haller, 2017),
 623 marine sulphate during different geological periods (Claypool et al., 1980 and Balderer et al.,
 624 1991) and sulphate in present-day porewater (borehole waters) of the Opalinus Clay at Mont
 625 Terri (Pearson et al., 2003; Müller and Leupin, 2012). Figure 9b shows a histogram for the
 626 $\delta^{34}\text{S}$ values of diagenetic pyrite and sphalerite from the Dogger–Liassic rock sequence at
 627 Mont Terri (De Haller et al., 2014). They show a Gaussian distribution, ranging widely from -
 628 48.2‰ VCDT to 57.8‰ VCDT, centred at 0‰ VCDT. Pyrite from the Benken borehole
 629 analysed by Lerouge et al. (2014), falls within the same range.

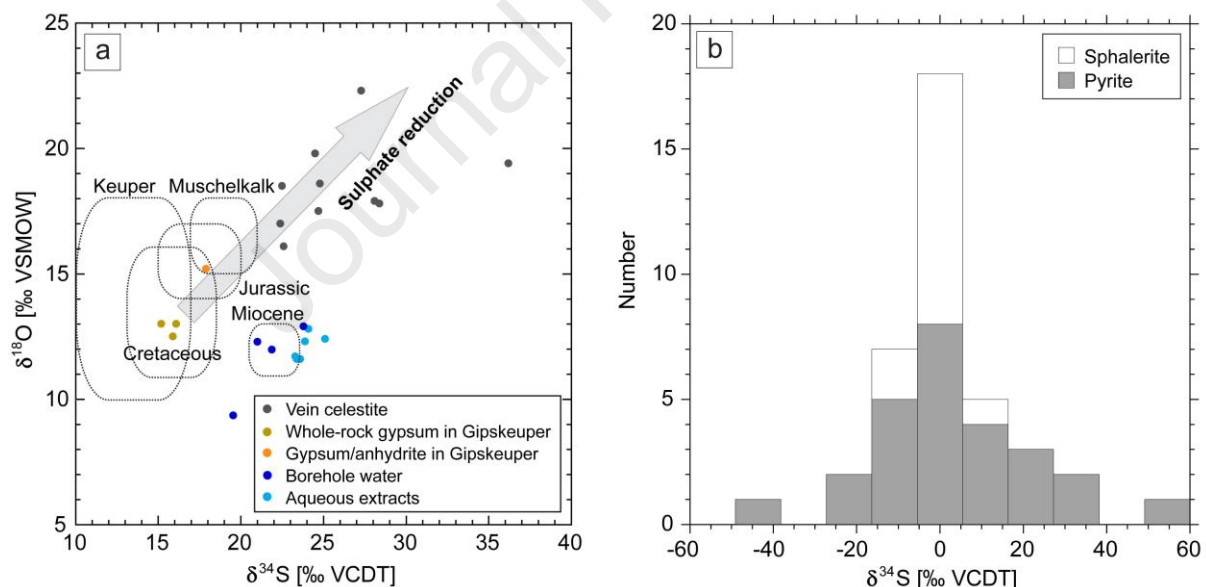
630 $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of dissolved sulphate in aqueous extracts range between 11.6–12.8‰
 631 VSMOW and 23.3–25.1‰ VCDT, respectively. These values are in good agreement with the

632 present-day porewater in the Opalinus Clay at Mont Terri, which is enriched in ^{34}S relative to
633 Mesozoic marine sulphate and depleted in ^{18}O relative to vein celestite (Fig. 9a). Although
634 partly overlapping, $\delta^{34}\text{S}$ values of sulphide minerals in the OPA are generally lower than
635 those of dissolved sulphate in aqueous extracts. Thus, the isotope composition of dissolved
636 sulphate in aqueous extracts seemingly represents the original porewater in the Opalinus Clay
637 without any major contributions from e.g. sulphide mineral oxidation or celestite dissolution.
638 As a hypothesis, the "excess sulphate" could be weakly bound to mineral surfaces, so that
639 isotopes can readily exchange with the porewater. In fact, laboratory and field experiments
640 have shown that sulphur and oxygen isotope fractionation during adsorption and desorption of
641 sulphate is negligible (Mayer et al., 1995; Van Stempvoort et al., 1990). In contrast, sulphate
642 that is strongly bound in crystal lattices of e.g. celestite is fractionated relative to porewater
643 sulphate (Fig. 9) and a shift away from the porewater isotope signature would be observed if
644 congruent mineral dissolution is the main contributor for the "excess sulphate" in aqueous
645 extracts. However, this is not the case.

646 Sorption of sulphate is well known for soils, where pH (Guadalix & Pardo 1991, Bhatti et al.
647 1997) and the presence of hydrous oxides of iron and aluminium (Chao et al. 1964a, Fuller et
648 al. 1985) are the main controlling factors but also total sulphate concentrations, ionic strength,
649 competing anions and clay content can have an influence (Chao et al. 1964b, Charlet et al.
650 1993, Comfort et al. 1992, Inskeep 1989). For indurated claystones, such as the Opalinus
651 Clay, anionic sorption has been much less studied and very little is known regarding the
652 uptake mechanisms. Also, there are some reservations concerning its relevance at high pH
653 conditions. Anionic sorption mainly operates at low pH (i.e., below the point of zero charge
654 of clay-minerals), whereas at high pH it is considered small to negligible (e.g. Guadalix &
655 Pardo 1991). However, in batch, column and through-diffusion experiments using Callovo-
656 Oxfordian claystone samples, Bazer-Bachi et al. (2007) and Descostes et al. (2008) observed
657 a weak retention of sulphate that depends on the mineralogical composition of the solid phase
658 and the sulphate concentration in the porewater with K_d values of 0.15–0.37 L/kg for sulphate
659 concentrations in the range of 5×10^{-7} to 4.4×10^{-3} mol/L at a pH of 7.3. Similarly, Van
660 Loon et al. (2018) also observed a weak retention of sulphate in through-diffusion
661 experiments performed on Opalinus Clay samples. The derived K_d values of 0.06–0.09 L/kg
662 for sulphate concentrations of 10^{-2} mol/L (pH = 7.9) are in good agreement with the findings
663 of Bazer-Bachi et al. (2007), i.e., extrapolating their Langmuir fit. These K_d values imply
664 concentrations of weakly bound SO_4 of 0.6–0.9 mmol/kg_{rock}. This corresponds to a
665 contribution of roughly 1.7–2.6 g/L_{free pw} from aqueous extracts, i.e., not large enough to

666 explain the "excess sulphate" (~ 35–52%). Note that although sulphate retention has been
 667 demonstrated for indurated claystones, the exact mechanism could not be identified in the
 668 aforementioned studies. One hypothesis is that kaolinite significantly contributes to the
 669 retention of sulphate in claystones as indicated by previous experimental studies (Rao &
 670 Sridharan 1984, Matusik 2014, Sadeghalvad et al. 2021). However, at the current stage it is
 671 not entirely clear why weakly bound sulphate would be released during aqueous extraction:
 672 concerning sorption processes the mixing of the water-saturated rock sample with ultra-pure
 673 water imposes a strong dilution of the porewater, i.e. the ionic strength of the system
 674 decreases and the electrostatic effect results in an anionic sorption than compared to in-situ
 675 conditions (Charlet et al. 1993). In contrast, anionic sorption is stronger at a pH of 7 (i.e., in-
 676 situ conditions) compared to a pH of around 9 (i.e., aqueous extracts; Guadalix & Pardo
 677 1991). However, it is not considered likely that this difference in pH would make a major
 678 difference in the amount of sulphate released. Thus, currently this remains on a hypothetical
 679 level and further efforts must be taken in order to better constrain potential contributions from
 680 weakly bound sulphate.

681



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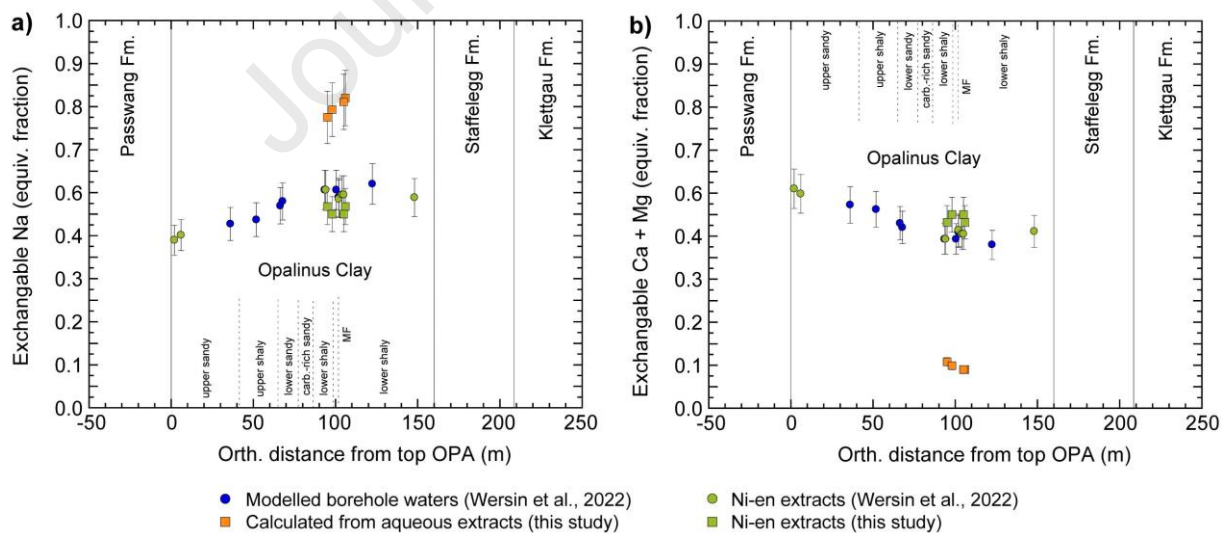
683 Fig. 9: $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values for dissolved sulphate in aqueous extracts of Mont Terri samples
 684 compared to the isotopic composition of sulphate of vein celestite (Pearson et al., 2003), whole-rock
 685 gypsum and/or anhydrite from the underlying Triassic evaporites (Gipskeuper, Muschelkalk; Mazurek
 686 & de Haller, 2017), marine sulphate during different geological periods (Claypool et al., 1980 and
 687 Balderer et al., 1991) and sulphate in present-day porewater (borehole waters) of the Opalinus Clay at
 688 Mont Terri (Pearson et al., 2003; Müller and Leupin, 2012). Analytical uncertainties are 0.5‰ (1 σ) for
 689 both $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$. b) Histogram for the $\delta^{34}\text{S}$ values of diagenetic pyrite and sphalerite from the
 690 Dogger–Liassic rock sequence at Mont Terri (de Haller et al., 2014).

691

692 4.8 Plausibility checks by geochemical modelling

693 The plausibility of the SO_4 data from aqueous extracts in terms of their representativeness for
 694 in-situ conditions was tested by simple geochemical modelling as described in section 3.9. On
 695 the basis of the Cl and SO_4 concentrations recalculated to in-situ conditions, a simplified
 696 exchanger composition including the main cations Na, Ca and Mg was derived for four of the
 697 Mont Terri samples. The calculations yield high exchangeable Na occupancies of ~ 0.8
 698 (equivalent fraction; Fig. 10a) and low exchangeable Ca + Mg occupancies of ~ 0.2
 699 (equivalent fraction; Fig. 10b). These results are at odds with the exchanger composition
 700 obtained from Ni-en extracts of the same samples, which yield distinctly lower Na but higher
 701 Ca + Mg occupancies. The latter data are, however, in good agreement with Ni-en extraction
 702 data reported by Wersin et al. (2022) as well as with data calculated from borehole waters.
 703 This comparison indicates that SO_4 recalculated from aqueous extracts implies dissolved and
 704 exchangeable cation concentrations which are not compatible with the measured
 705 exchangeable cation data and, in more general terms, not compatible with the well-established
 706 porewater chemistry database for Mont Terri (see compilation by Wersin et al., 2022). This
 707 simple geochemical modelling exercise thus underlines that SO_4 from aqueous extraction
 708 experiments is affected by mineral-water reactions, i.e., reflecting non-conservative
 709 behaviour.

710



711

712 Fig. 10: a) Exchangeable Na and b) sum of exchangeable Ca+Mg (equivalent fractions) vs. distance
 713 (m) from top Opalinus Clay at the Mont Terri Rock Laboratory. Orange squares: calculated from SO_4
 714 and Cl concentrations in aqueous extracts (see text). Green symbols: measured cation data from Ni-en
 715 extracts (corrected for dissolved cations in the porewater). Blue circles: modelled cation data based on
 716 borehole waters documented in Wersin et al. (2022).

717

718 5 Conclusions

719 Oxidation reactions are deemed to have been successfully suppressed during aqueous
720 extraction. This is indicated by 1) the lack of correlation between "excess sulphate" and pyrite
721 contents in the samples, 2) constant SO₄ concentrations as a function of extraction time and
722 S/L ratio and 3) $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of dissolved sulphate in aqueous extraction being in
723 good agreement with those measured for borehole waters.

724 The extraction experiments yielded conservative behaviour for Cl, which is in line with earlier
725 findings (e.g. Waber et al. 2003, Wersin et al. 2013, Waber & Rufer 2017, Wersin et al.
726 2020). All other cations and anions (except bromide) behave clearly non-conservatively, i.e.
727 their concentrations in the extract solutions vary as a function of S/L ratio and extraction time.
728 Although SO₄ concentrations in aqueous extracts are constant as a function of S/L ratio and
729 extraction time, the SO₄/Cl ratio increases during sequential extraction indicating release from
730 a sulphate-bearing phase, thus, suggesting non-conservative behaviour. However, from a
731 quantitative perspective the major release occurs during the first extraction, whereas release
732 during subsequent sequential extractions is minimal. Thus, celestite constitutes a limited SO₄
733 reservoir that is nearly completely exhausted in each extraction. However, Ni-en extracts
734 show that the strontium inventory (dissolved plus exchanged) is not sufficiently large to
735 explain the "excess sulphate" by celestite dissolution alone (roughly 15% of the "excess
736 sulphate" can be explained by celestite dissolution). Acid extracts indicate that calcite in the
737 Opalinus Clay contains a maximum of around 700 – 800 ppm sulphate, which is in line with a
738 study by Wynn et al. (2018). Considering the small amount of calcite which is dissolved
739 during aqueous extraction (~4%), these concentrations are far too low to explain the "excess
740 sulphate" by congruent calcite dissolution. However, uncertainties exist on how the sulphur
741 associated with calcite occurs (i.e. incorporated in the crystal lattice or as solid inclusions of
742 an S-bearing phase) and that incongruent rather than congruent calcite dissolution could be a
743 key process to explain the "excess sulphate" in aqueous extracts. These uncertainties could be
744 addressed by transmission electron microscopy (TEM) and Scanning-TEM (STEM) studies,
745 which provide high-resolution data on the quantity and spatial distribution of S in calcite.
746 Measurements of the dissolved organic carbon in aqueous extracts yield no correlation with
747 sulphate concentrations. Moreover, mass balance considerations show that in order to explain
748 the "excess sulphate", the dissolved organic material must show unrealistic low C/S mass
749 ratios. Thus, a major release of sulphur from organic material during aqueous extraction
750 experiments, which could explain the "excess sulphate", is unlikely.

751 Ultimately, the various types of extraction experiments failed to definitely identify the source
752 of the "excess sulphate" in aqueous extracts. However, based on the good agreement between
753 the $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of dissolved SO_4 in aqueous extracts and those of borehole waters
754 the "excess sulphate" could be weakly bound to mineral surfaces (e.g. clay-minerals), so that
755 isotopes can readily exchange with the porewater. This hypothesis is in line with diffusion
756 studies by Bazer-Bachi et al. (2007), Descostes et al. (2009) and Van Loon et al. (2018) who
757 observed a weak retention of sulphate in their experiments performed on Callovo-Oxfordian
758 claystones and also Opalinus Clay samples. The retention mechanisms are not exactly known
759 but derived K_d values imply potential sulphate contributions in the range of 1.7–2.6 $\text{g/L}_{\text{free pw}}$
760 in aqueous extracts. Together with the contributions from celestite dissolution this would
761 explain roughly 60% of the "excess sulphate". However, there are some reservations
762 regarding the process by which sulphate would be released during aqueous extraction. Thus,
763 at the current state this remains on a hypothetical level and further efforts must be taken in
764 order to better constrain potential contributions from weakly bound sulphate, e.g., by anion-
765 exchange experiments.

766 Although, the reasons for the differences in SO_4 concentrations for OPA porewater derived
767 from aqueous extraction and direct sampling techniques – i.e. borehole waters, squeezing and
768 advective displacement experiments – are still not fully understood, the good consistency
769 between the latter methods suggests that the derived sulphate concentrations represent the
770 conditions in the in-situ porewater reasonably well. This is further supported by simple
771 plausibility tests by geochemical modelling showing that SO_4 concentrations from aqueous
772 extracts recalculated to in-situ conditions imply dissolved and exchangeable cation
773 concentrations which are not consistent with the measured exchangeable cation data from Ni-
774 en extracts or those calculated from borehole waters. Again, this underlines the non-
775 conservative behaviour of sulphate during aqueous extraction.

776

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785

786

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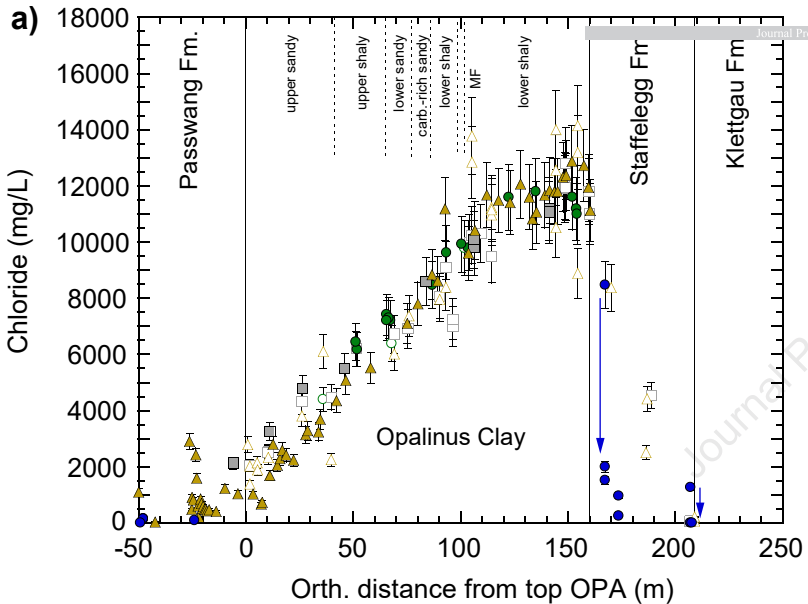
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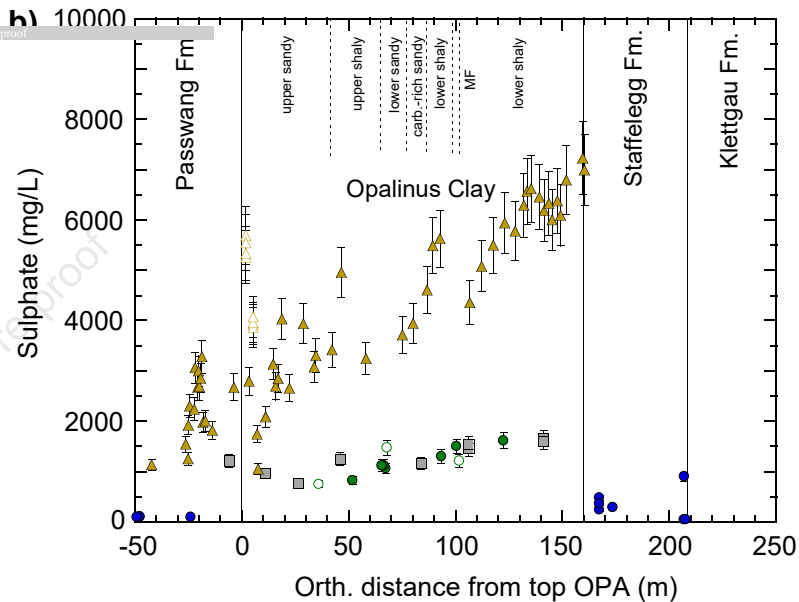
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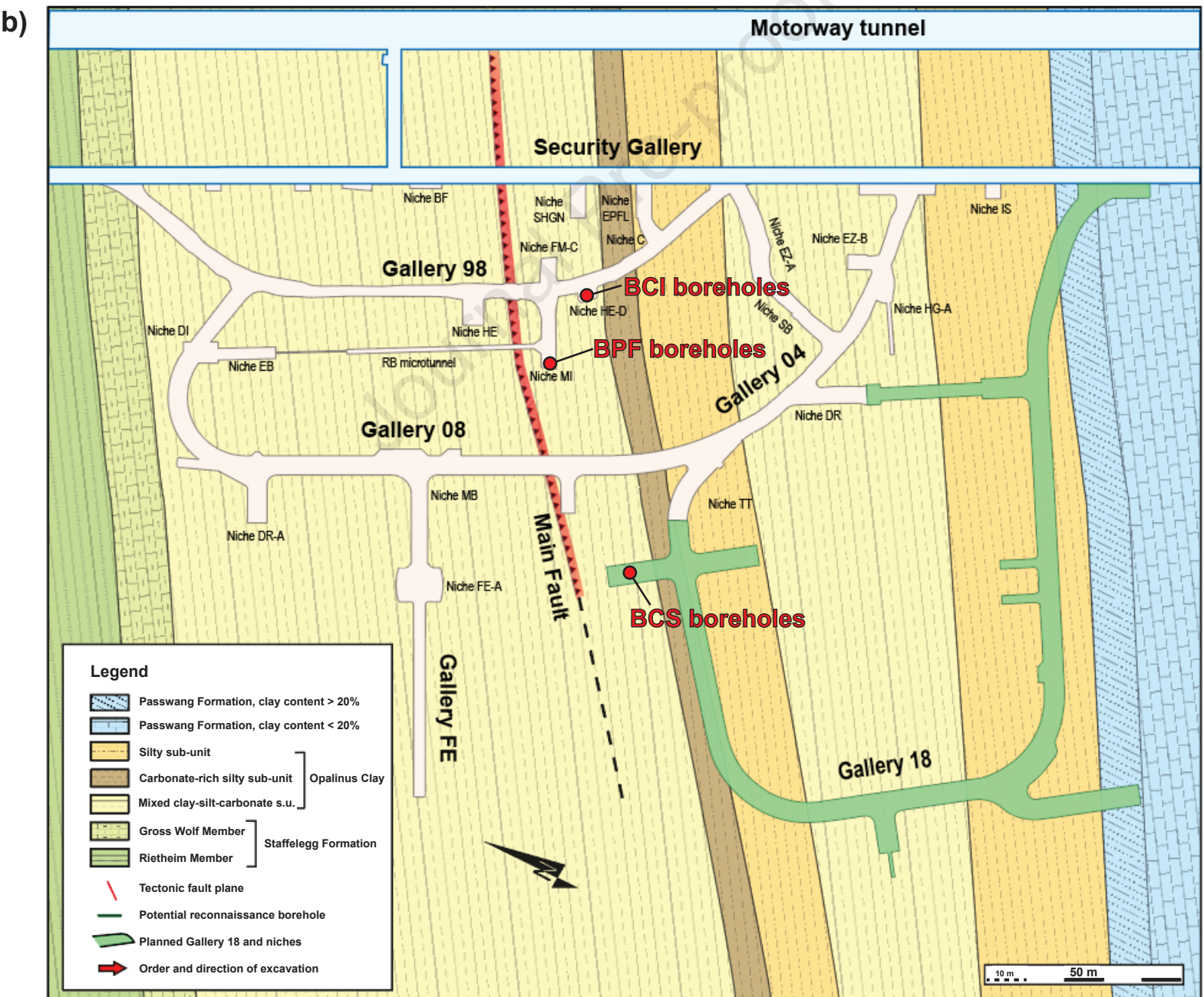
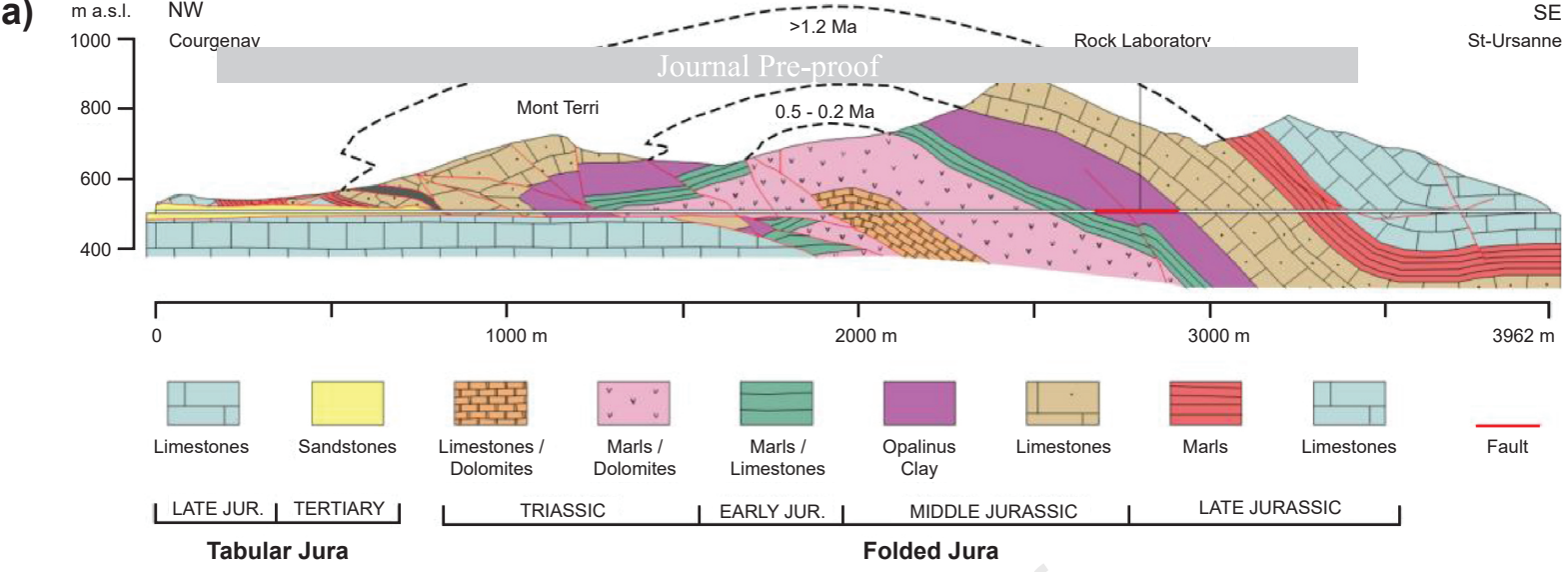
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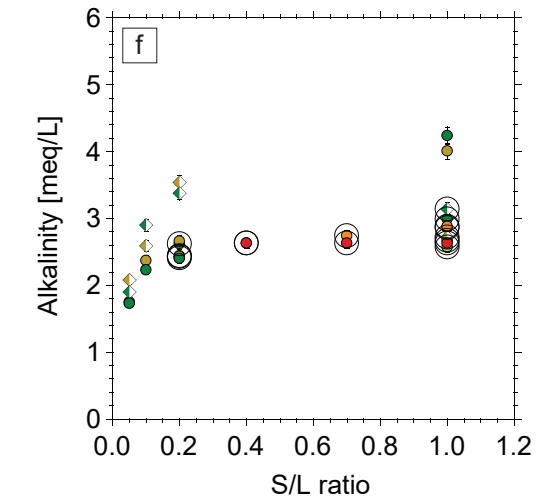
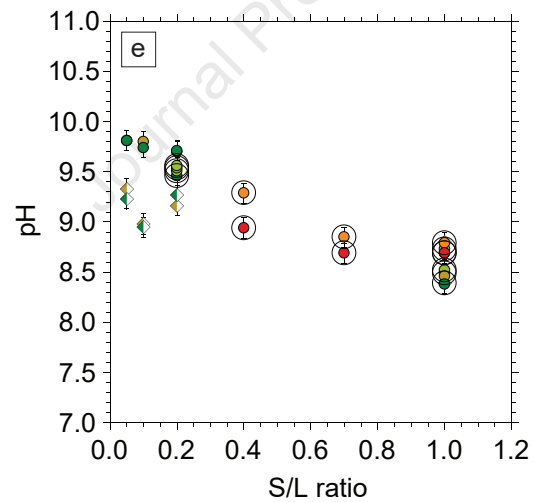
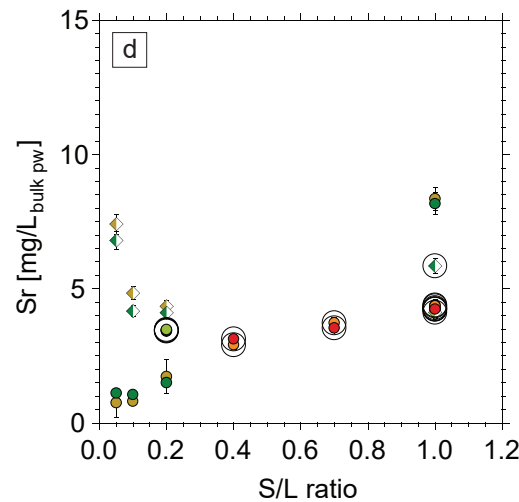
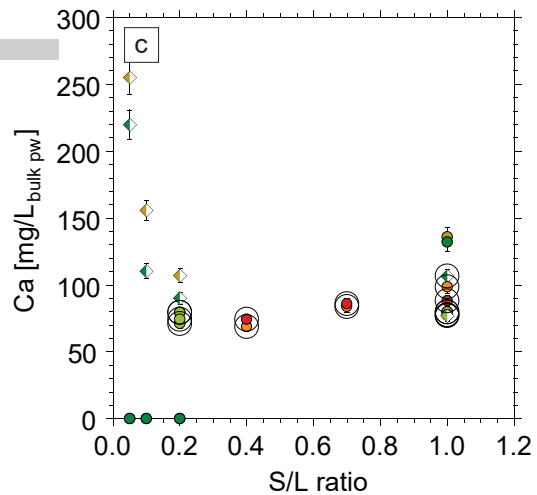
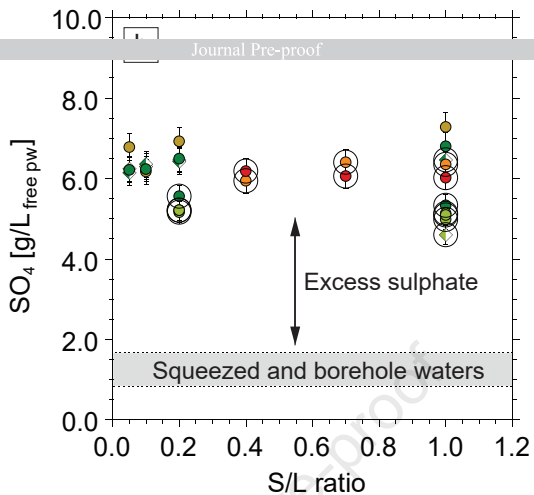
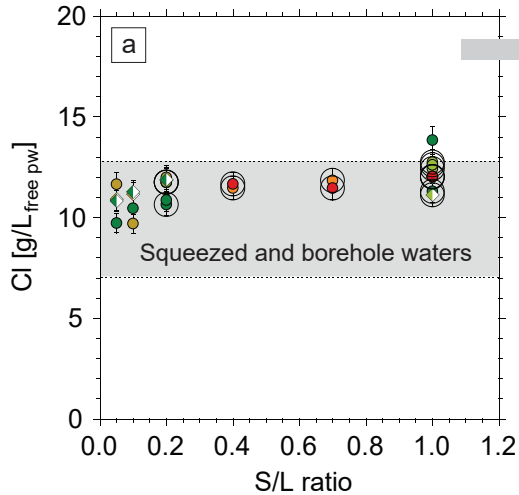


- Borehole waters (Pearson et al., 2003)
- Borehole waters (newer data)
- △ Leachates (Person et al., 2003)
- ▲ Leachates (newer data)



- Squeezed waters (Pearson et al., 2003)
- Squeezed waters (newer data)
- Groundwaters & seepages





Brown symbols: BCI-21A-296-319

Dark green symbols: BCI-21-550-600

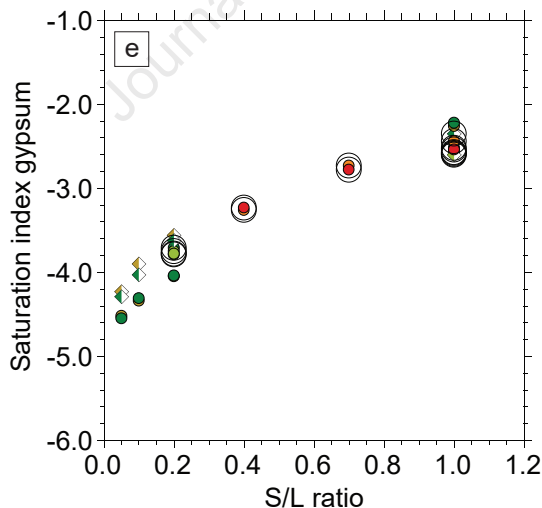
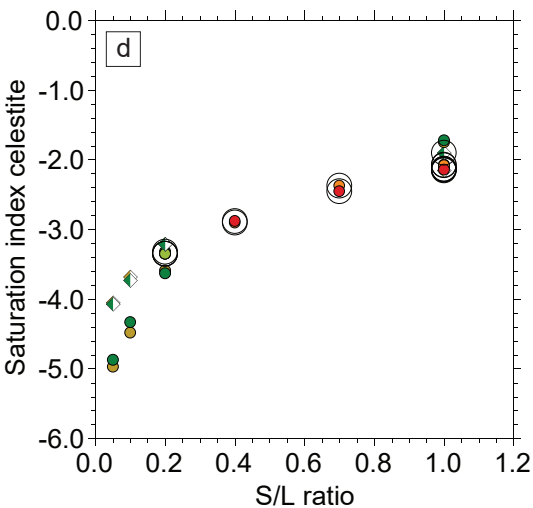
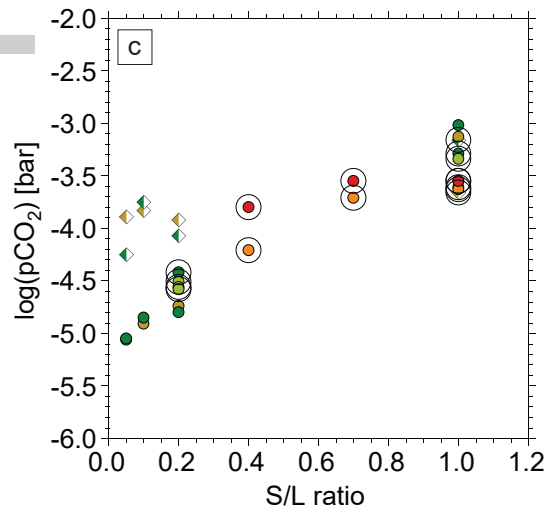
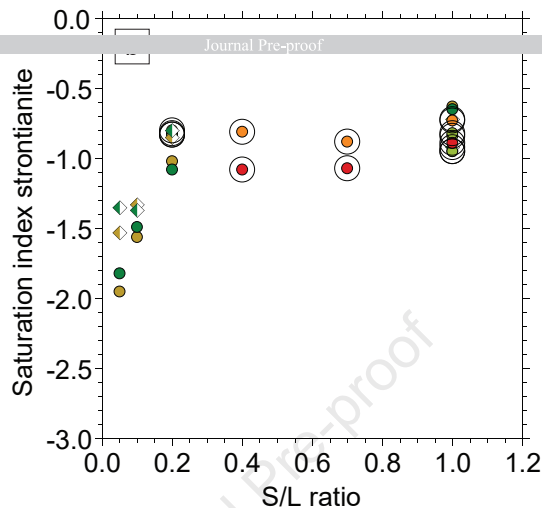
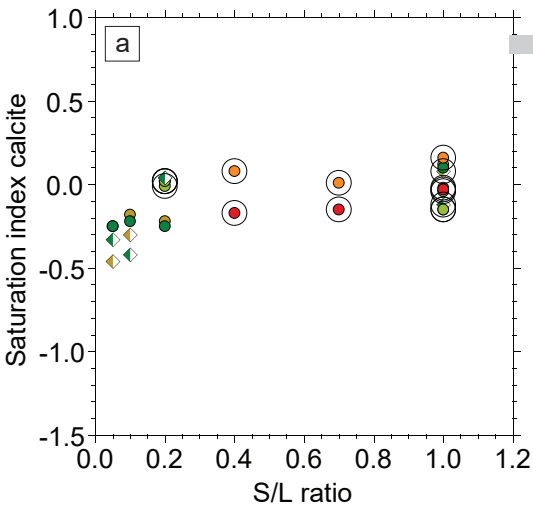
Light green symbols: BCS-7

Orange symbols: BPF1-4.30m

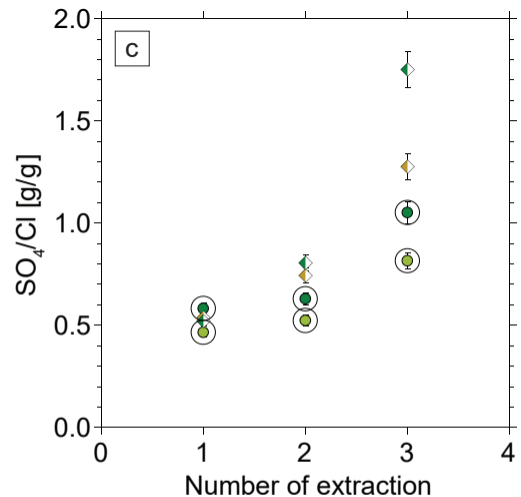
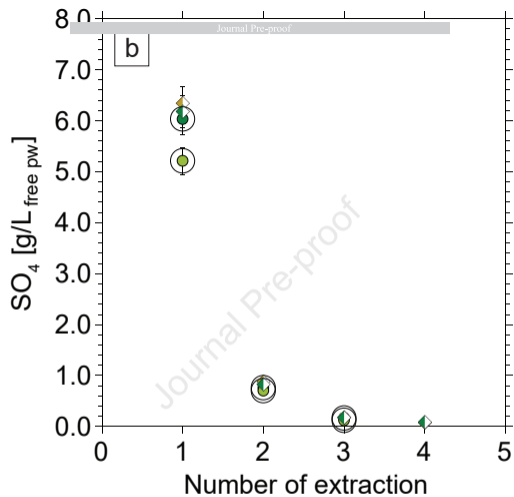
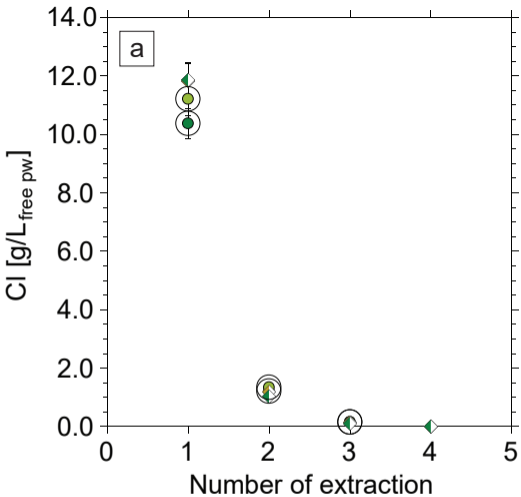
Red symbols: BPF1-3.90m

◊ Milled sample

● Crushed sample



- Brown symbols:** BCI-21A-296-319
- Dark green symbols:** BCI-21-550-600
- Light green symbols:** BCS-7
- Orange symbols:** BPF1-4.30m
- Red symbols:** BPF1-3.90m
- ◊ Milled sample**
- Crushed sample**



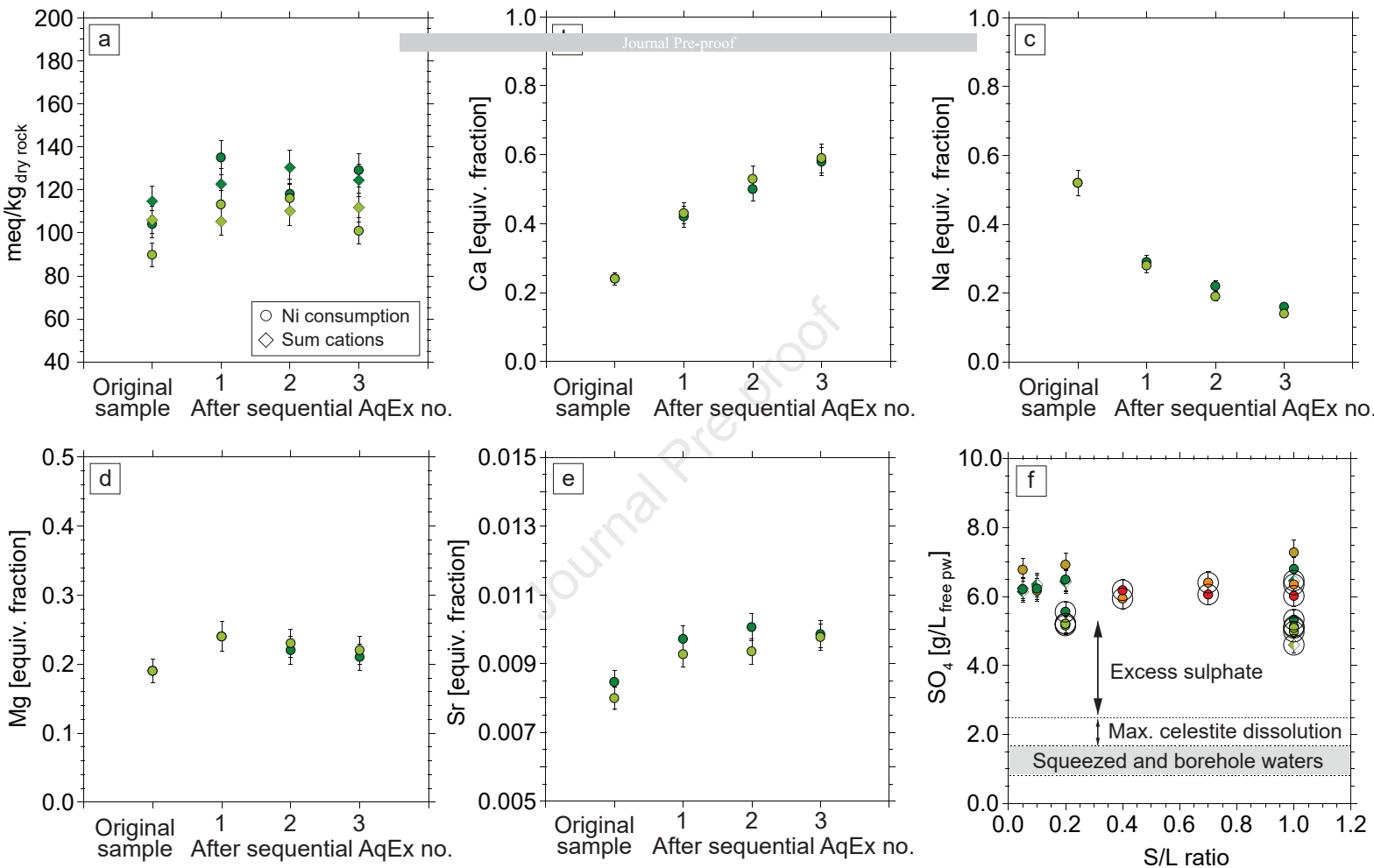
Brown symbols: BCI-21A-296-319

Dark green symbols: BCI-21-550-600

Light green symbols: BCS-7

◆ Milled sample

● Crushed sample



Brown symbols: BCI-21A-296-319

Dark green symbols: BCI-21-550-600

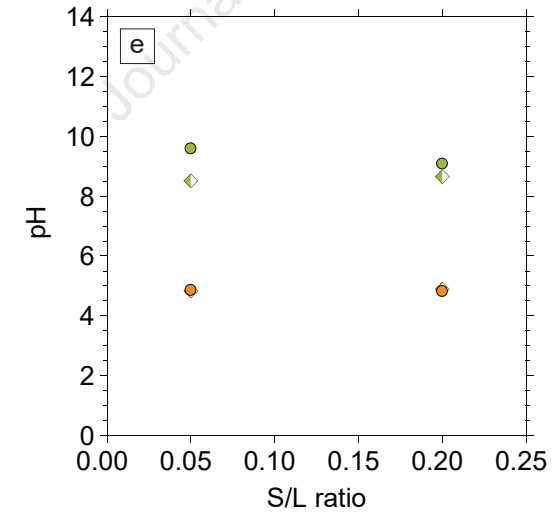
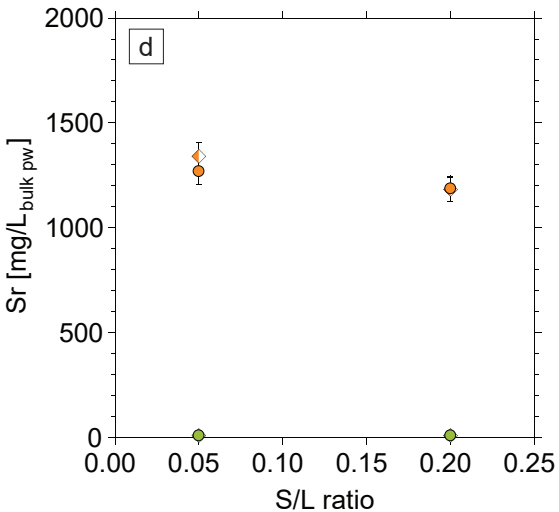
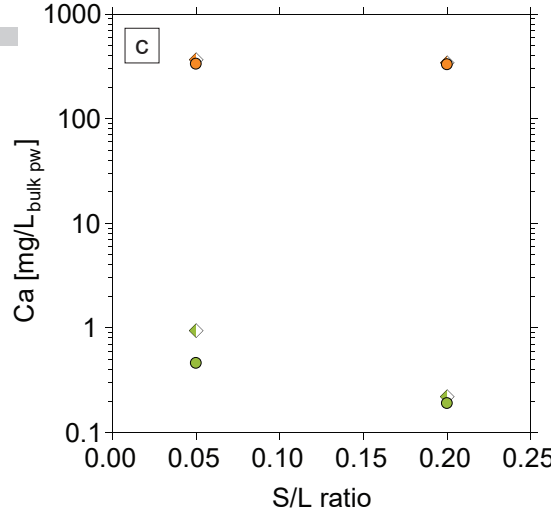
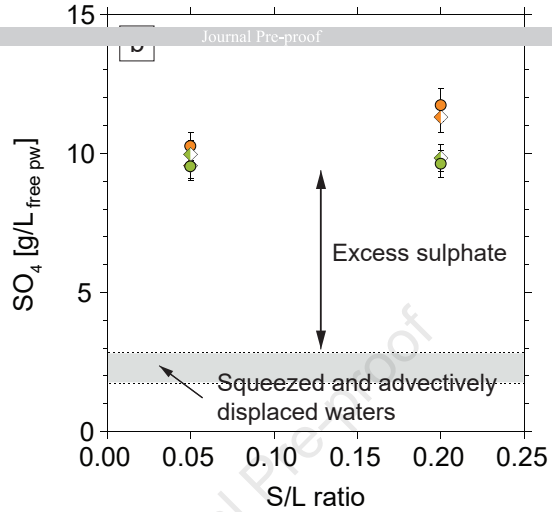
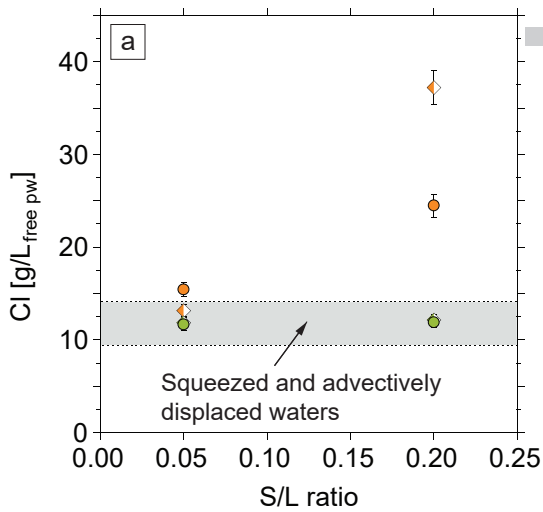
Light green symbols: BCS-7

Orange symbols: BPF1-4.30m

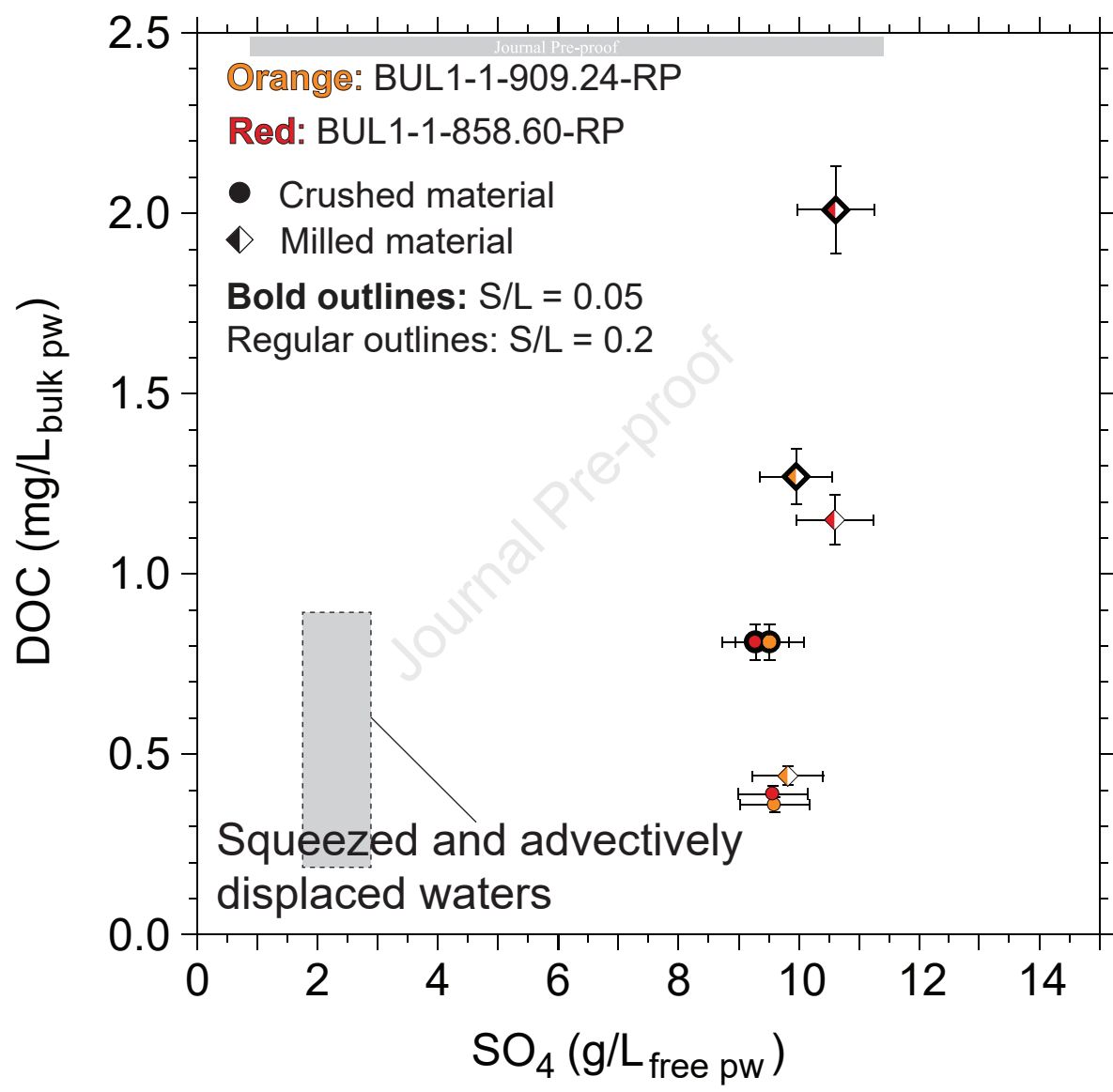
Red symbols: BPF1-3.90m

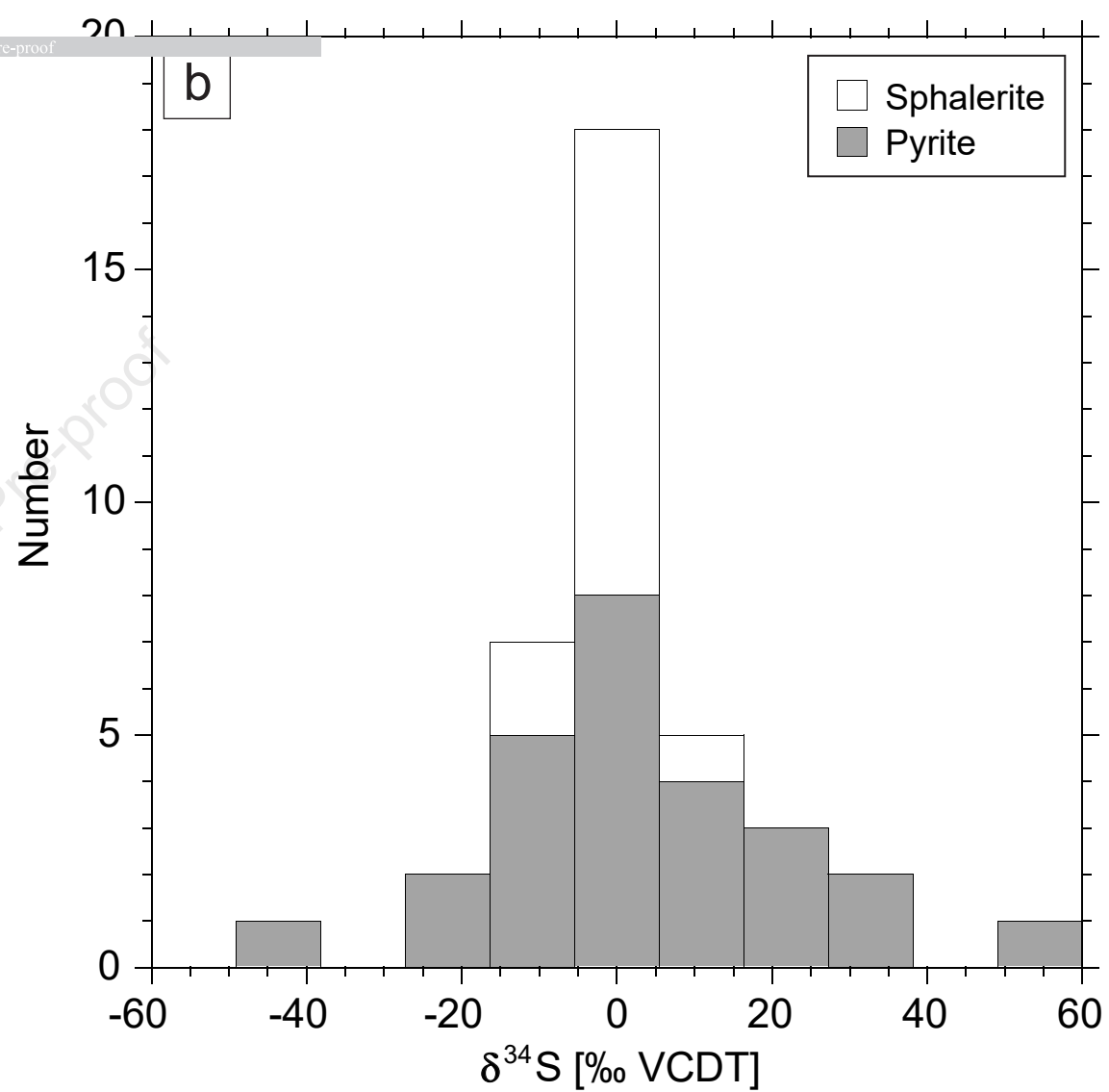
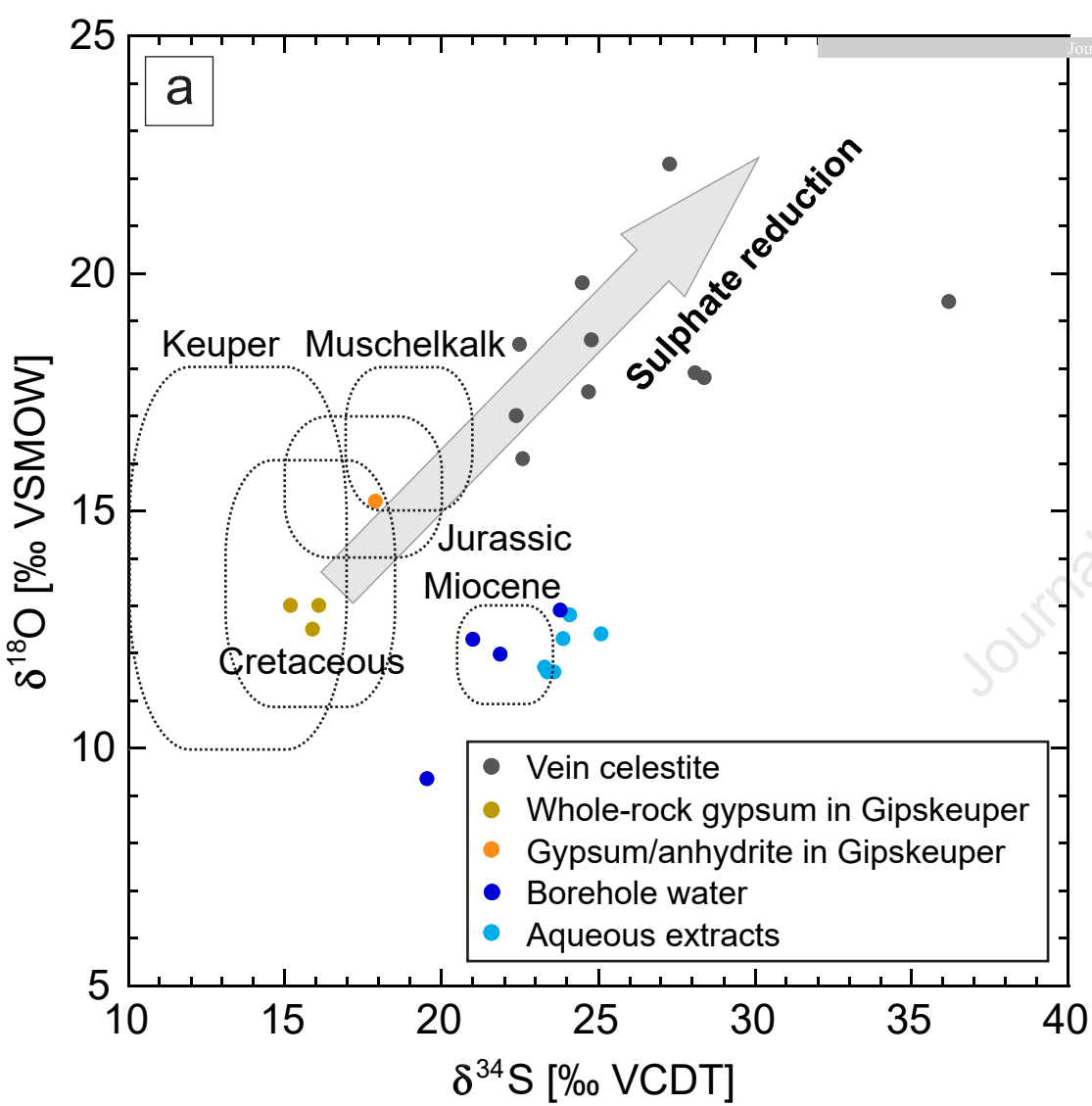
◆ Milled sample

● Crushed sample



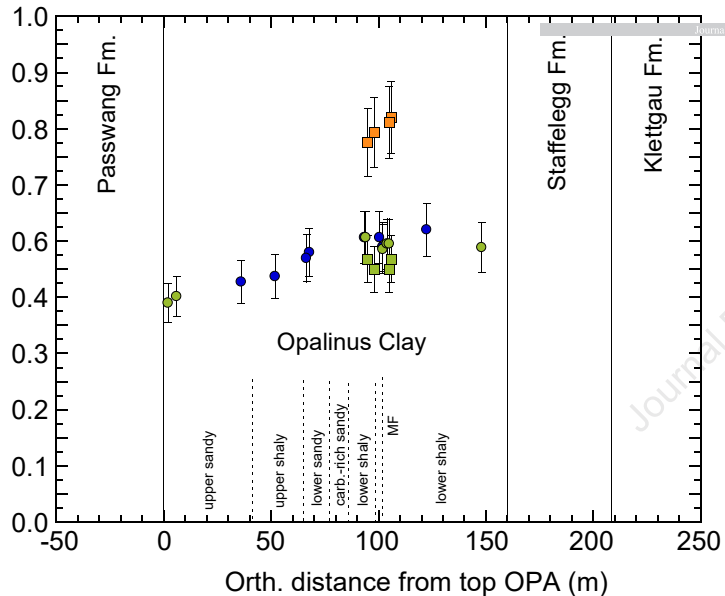
Bright green symbols: Aqueous extracts
Orange symbols: Acid extracts
● crushed samples
◊ milled samples





a)

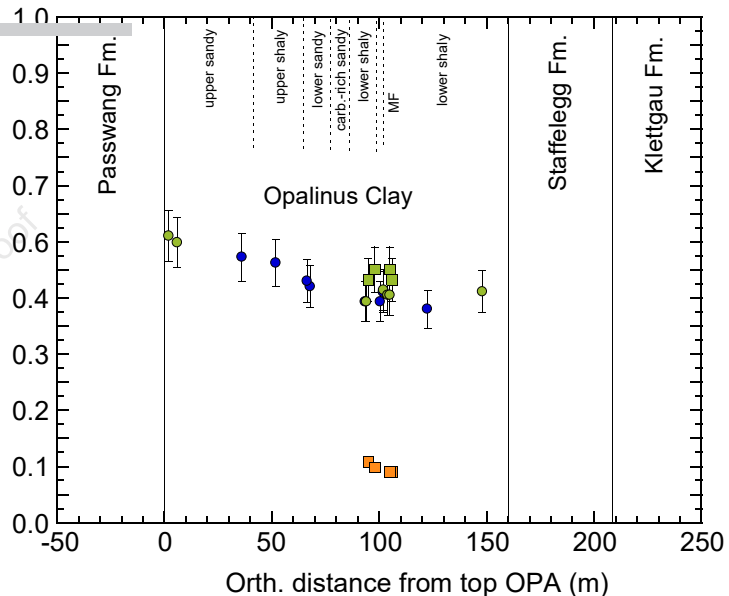
Exchangable Na (equiv. fraction)



- Modelled borehole waters (Wersin et al., 2022)
- Calculated from aqueous extracts (this study)

b)

Exchangable Ca + Mg (equiv. fraction)



- Ni-en extracts (Wersin et al., 2022)
- Ni-en extracts (this study)

Highlights

- Excess SO_4 in aqueous extracts of Opalinus Clay samples
- Experimental study of water-extractable sulphate in Opalinus Clay
- Obvious sulphate sources fail to explain excess SO_4 in aqueous extracts
- Dissolved SO_4 in aqueous extracts and borehole water is isotopically similar
- Possibly, some sulphate is weakly bound to mineral surfaces

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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