

1 **Origin of silica in rice plants and contribution of diatom earth fertilization: insights**
2 **from isotopic Si mass balance in a paddy field**

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16
17 **Abstract**

18 *Background and aims*

19 The benefits of Si for crops is well evidenced but the biogeochemical cycle of Si in
20 agriculture remains poorly documented. This study aims at identifying and quantifying the Si
21 sources (primary and secondary soil minerals, amorphous silica, irrigation, Si-fertilizer) to
22 rice plants.

23 *Method*

24 Field experiments were carried out with and without application of diatomaceous earth (DE)
25 under rice and bare conditions to determine the water and dissolved mass balance in paddy
26 fields (Karnataka, Southern India). The fate of the Si brought by irrigation (DSi) (uptake by
27 rice, uptake by diatoms, adsorption) was assessed through a solute mass balance combined
28 with silicon isotopic signatures.

29 *Results*

30 Above the ground-surface, about one third of the DSi flux brought by borewell irrigation (545
31 mmol Si.m⁻²) to bare plots and half of DSi in rice plots were removed from solution within
32 minutes or hours following irrigation. Such rate is consistent with the rate of DSi adsorption
33 onto Fe-oxyhydroxides but not with diatom blooms. In rice and rice+DE experiments, the

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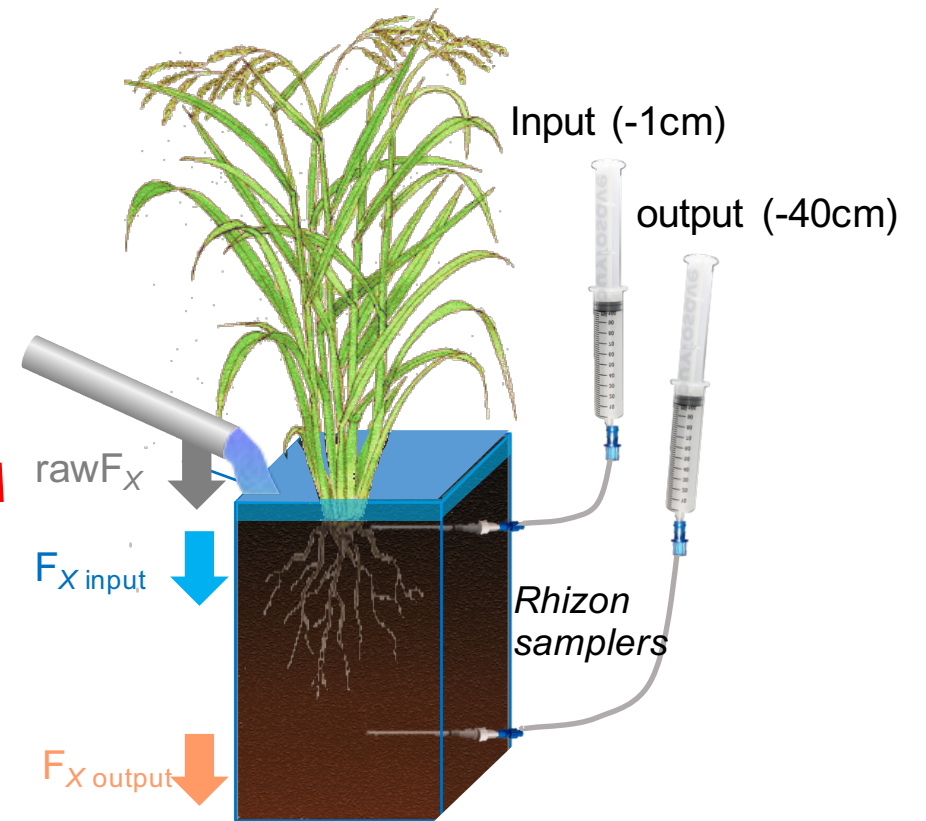


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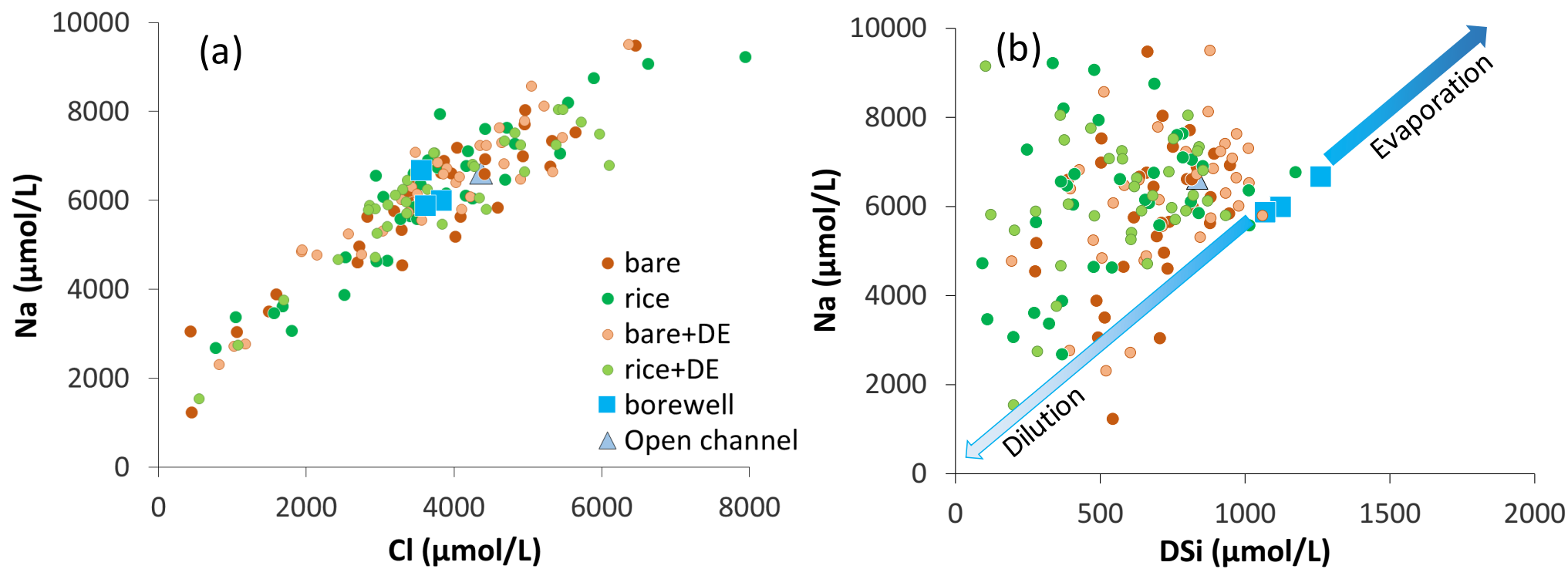


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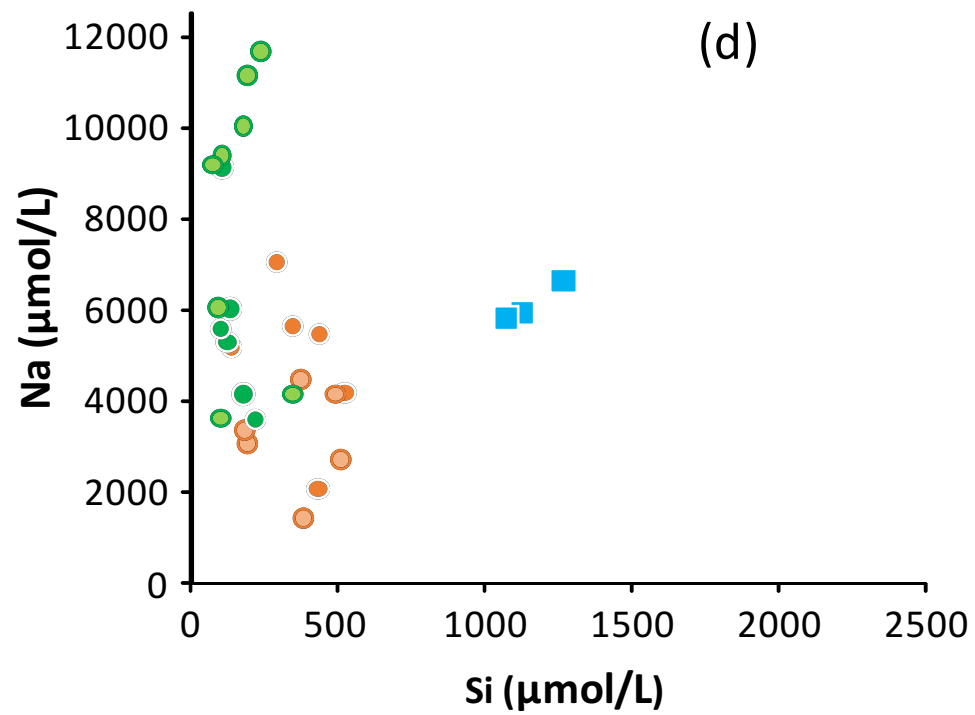
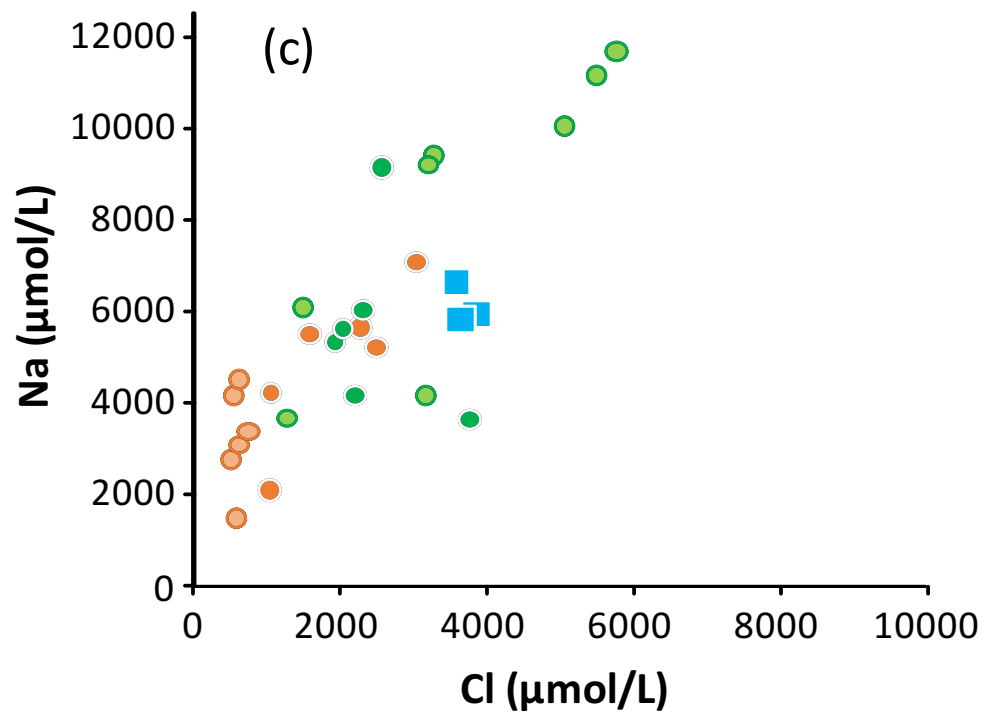


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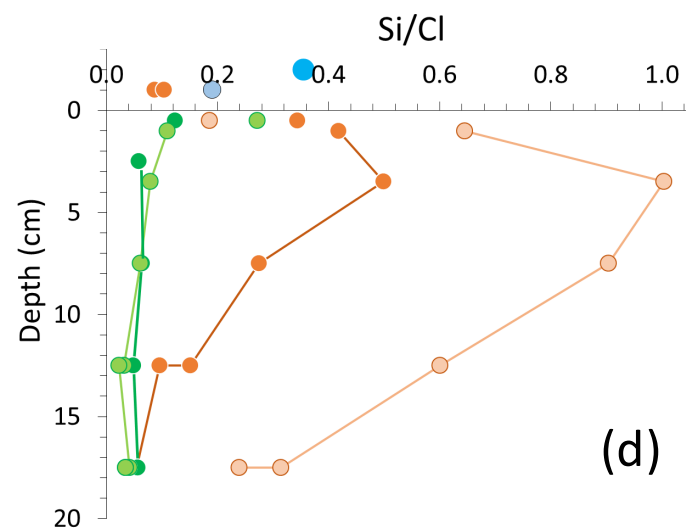
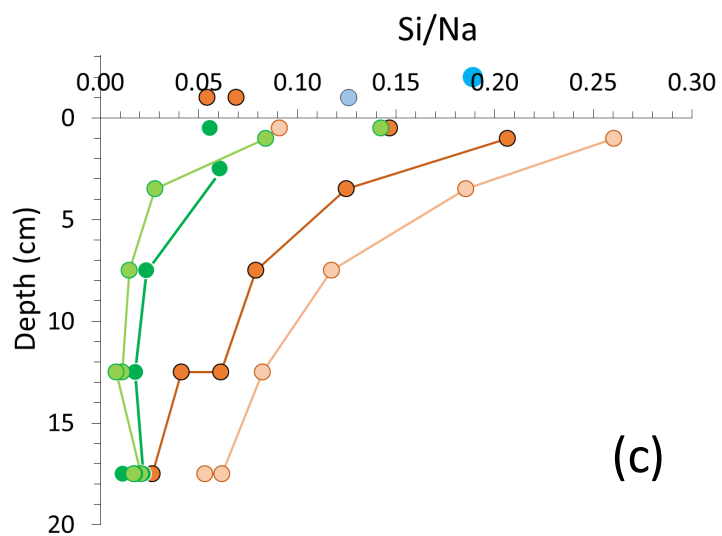
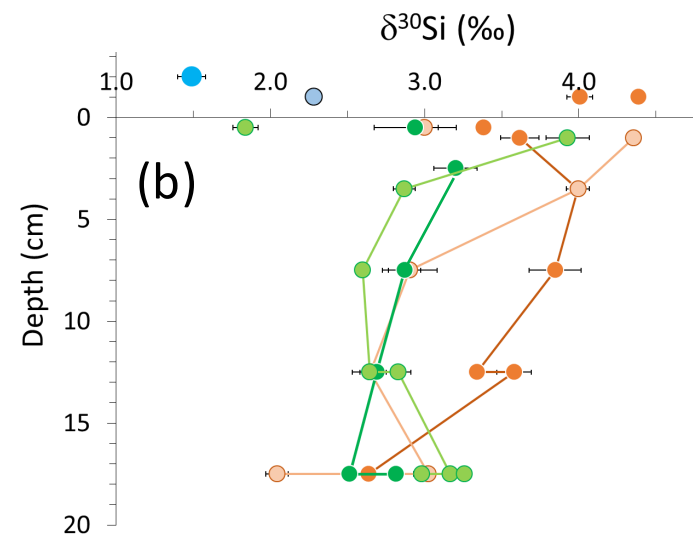
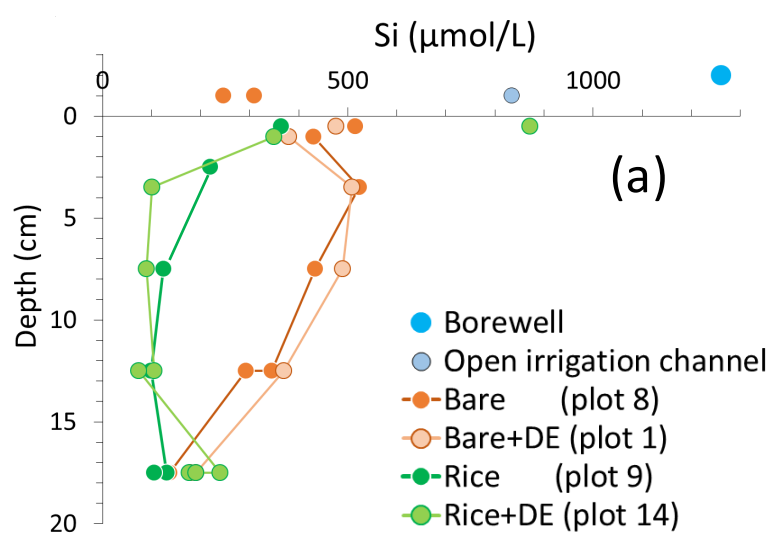


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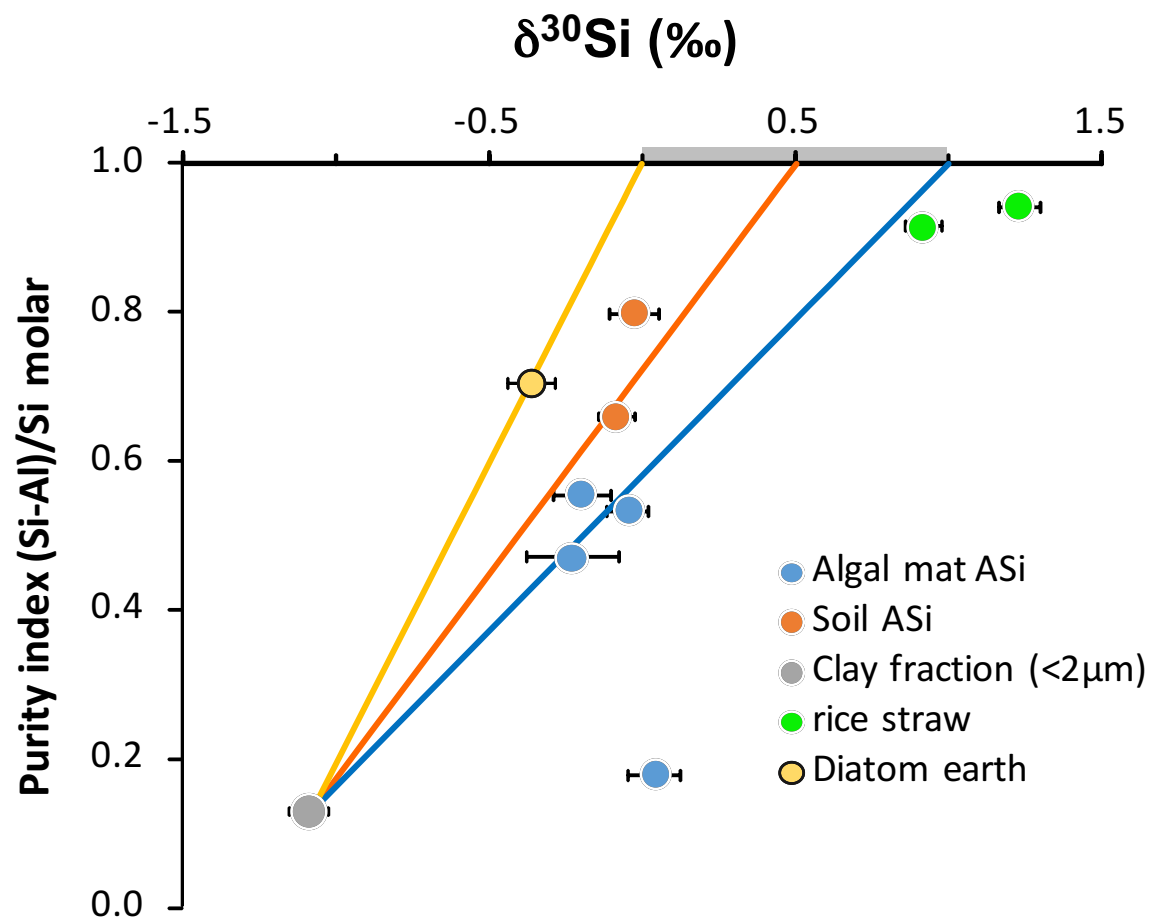


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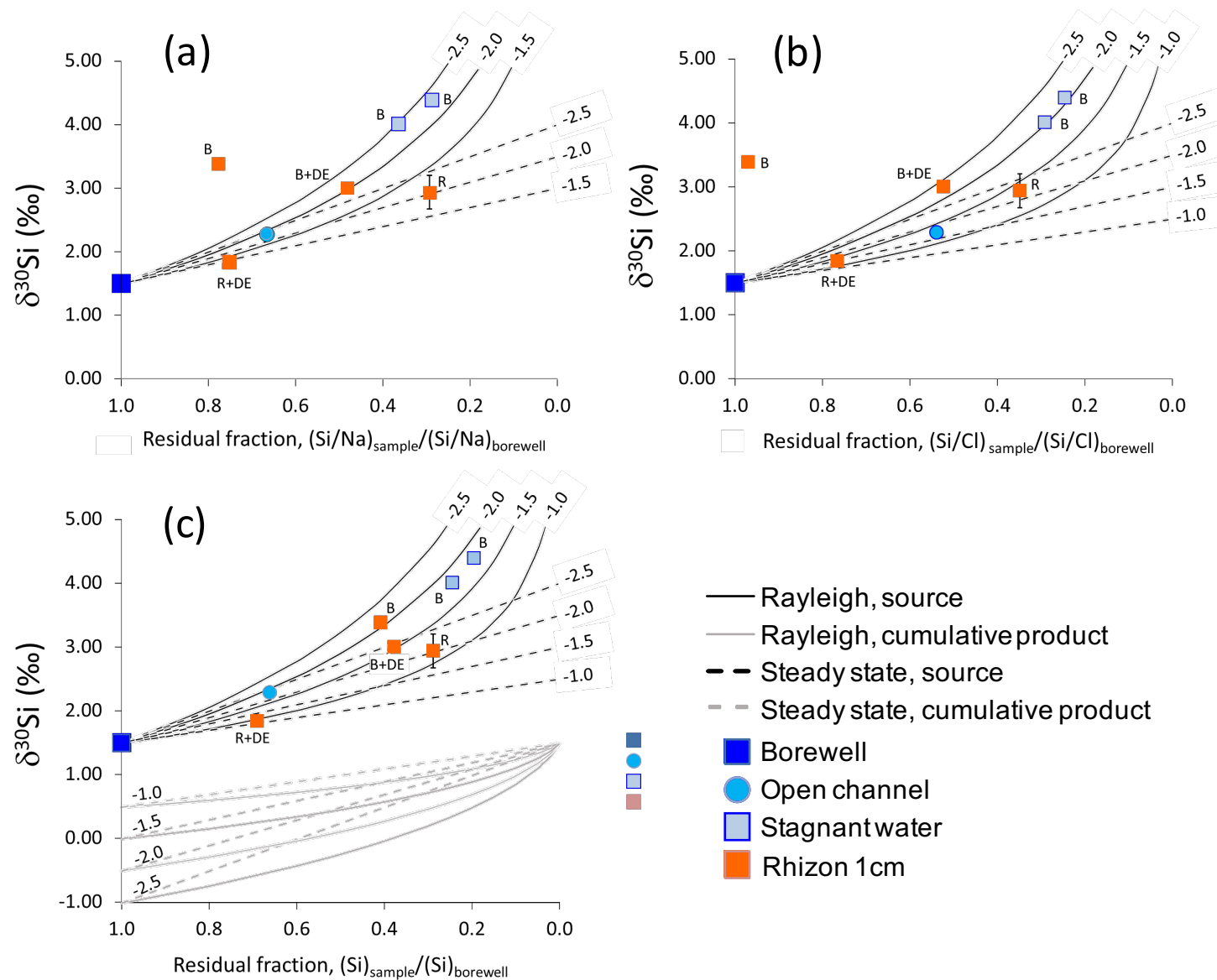


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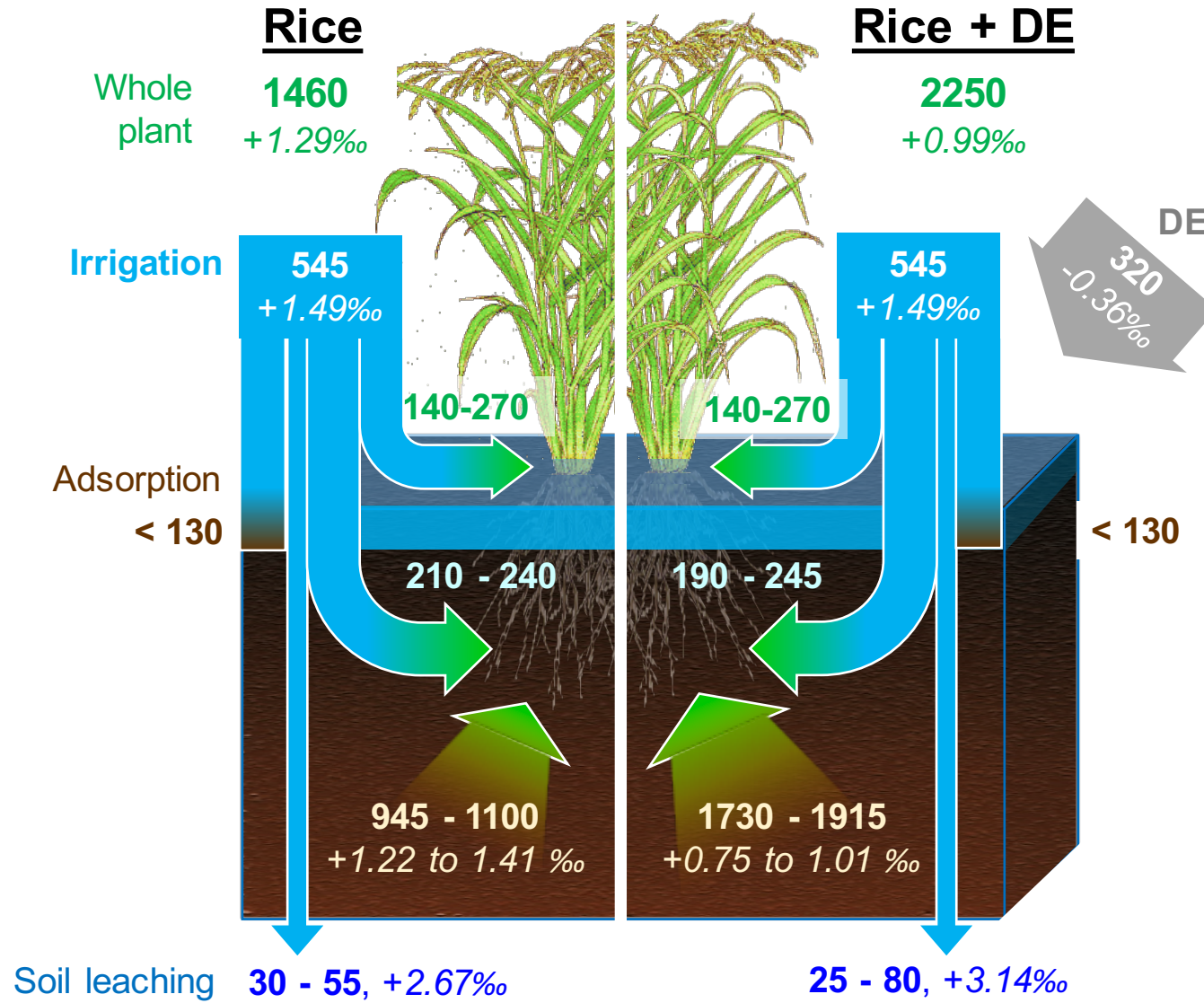


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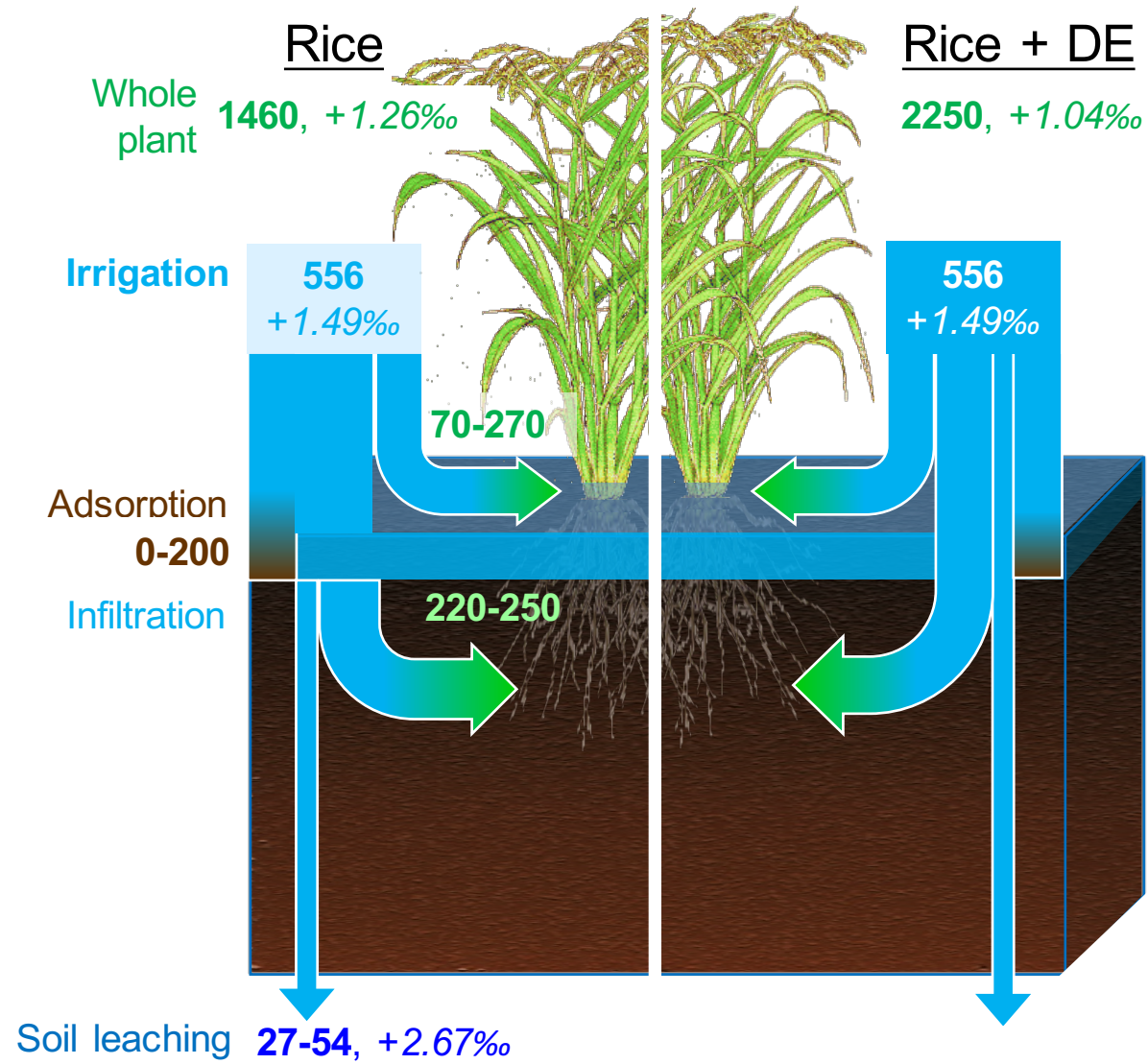


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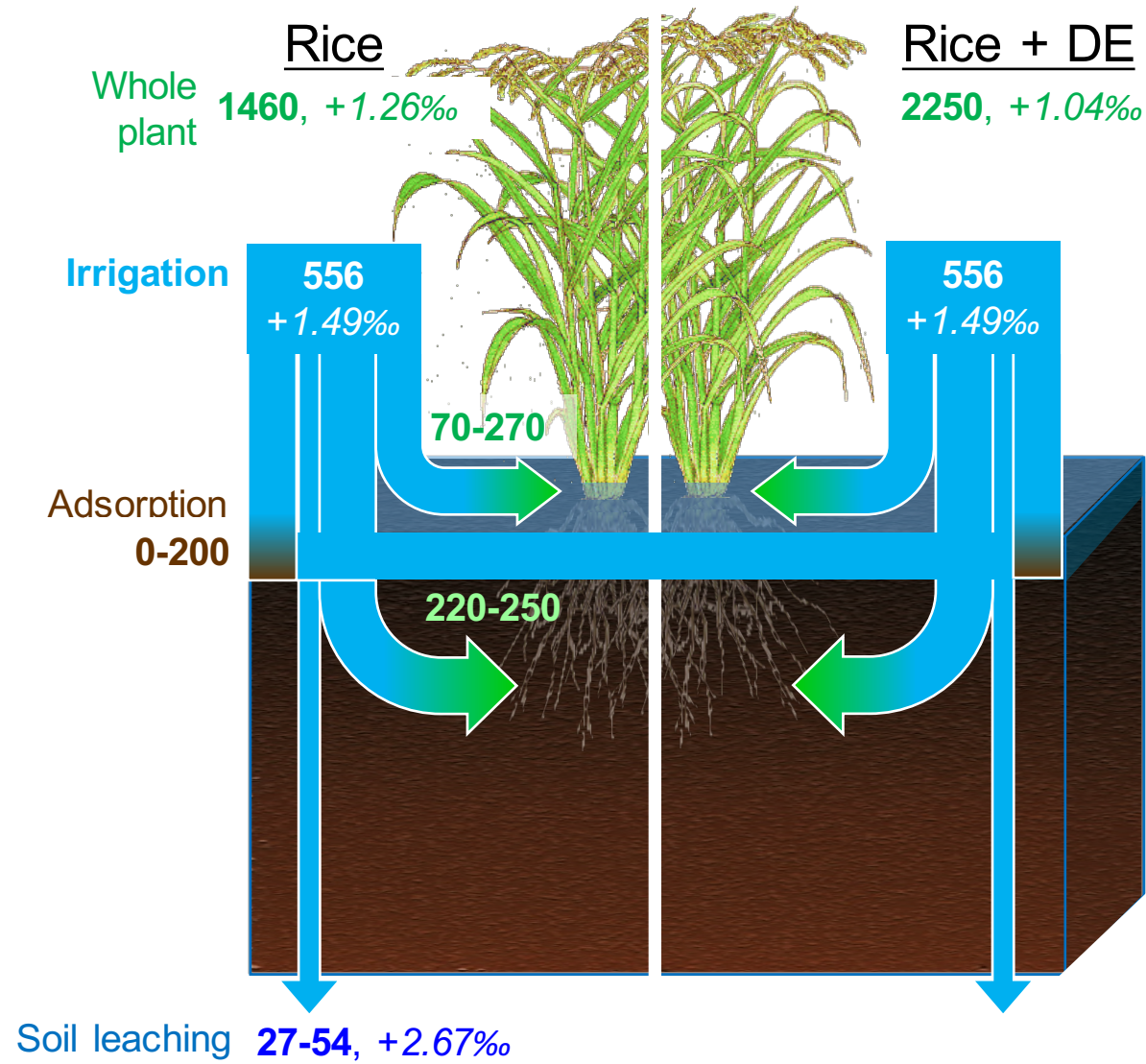
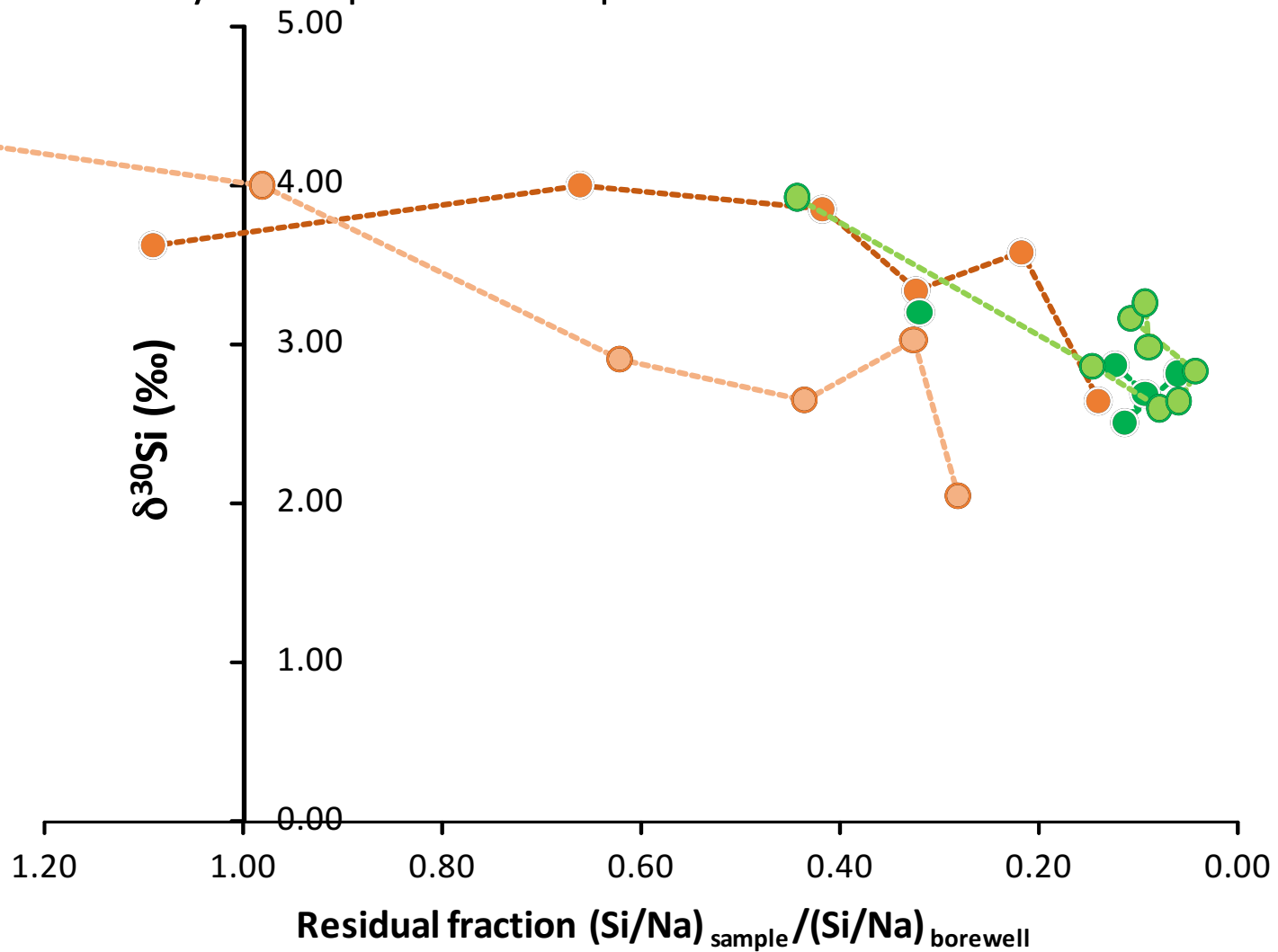
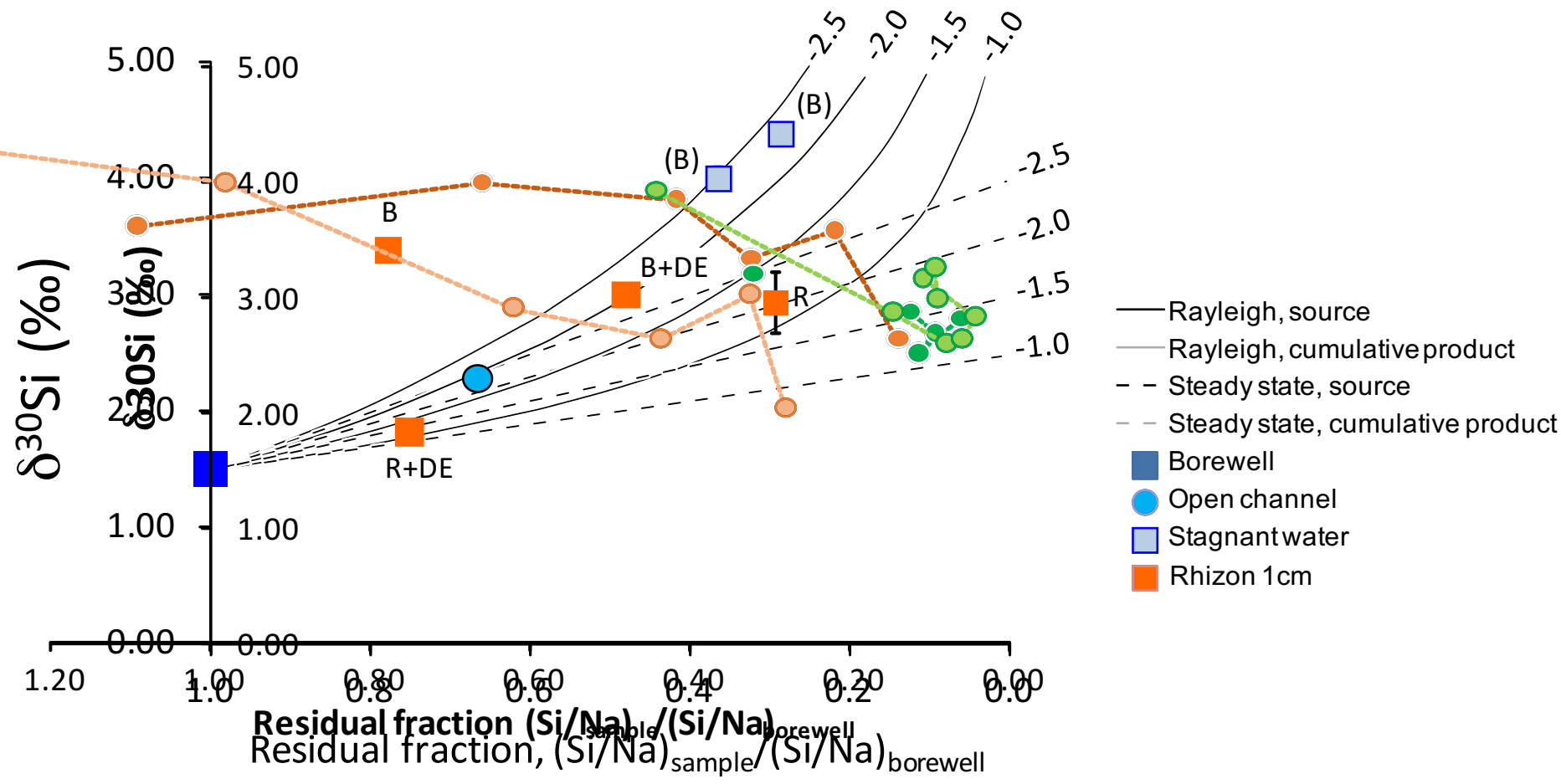
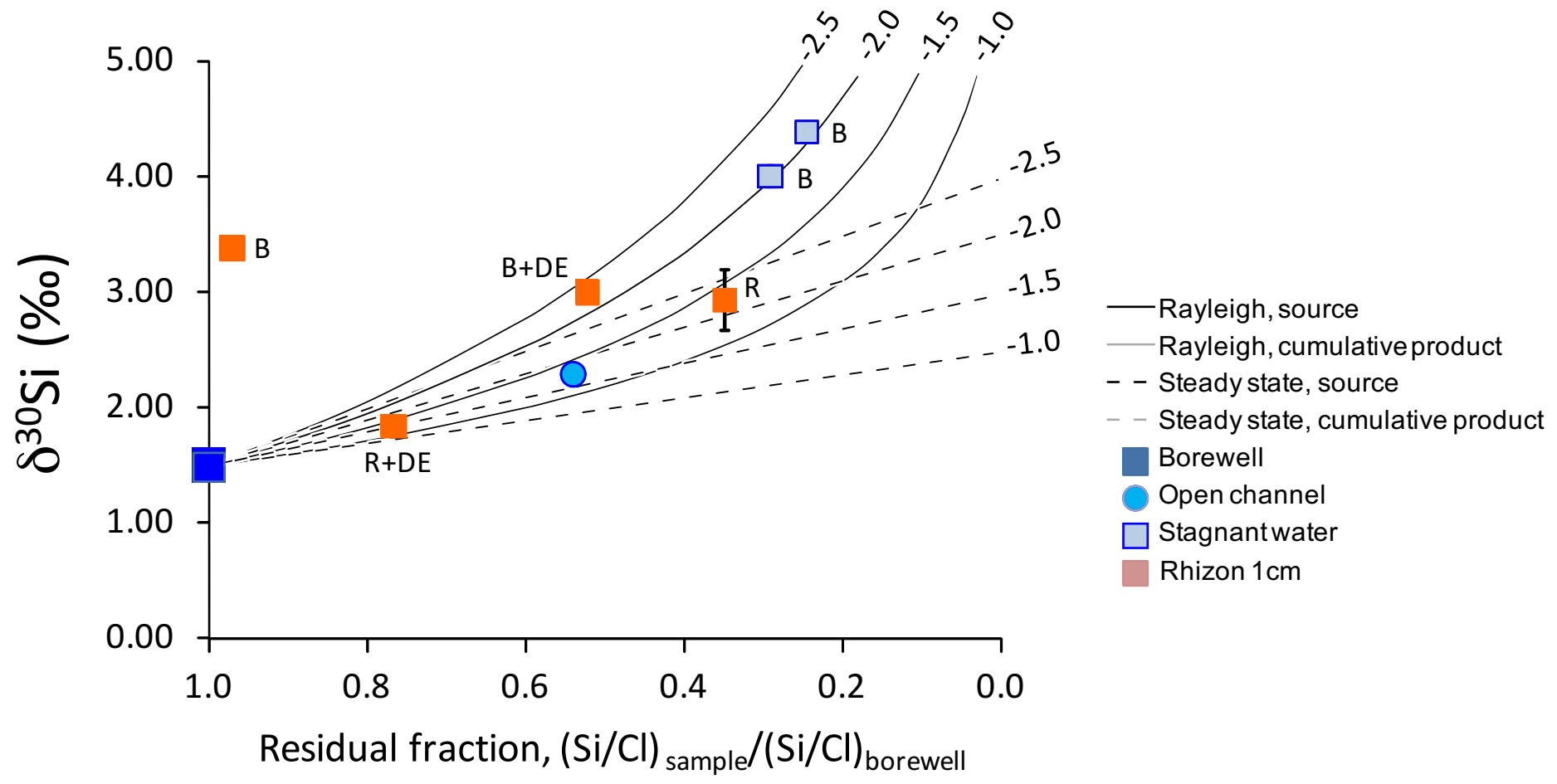
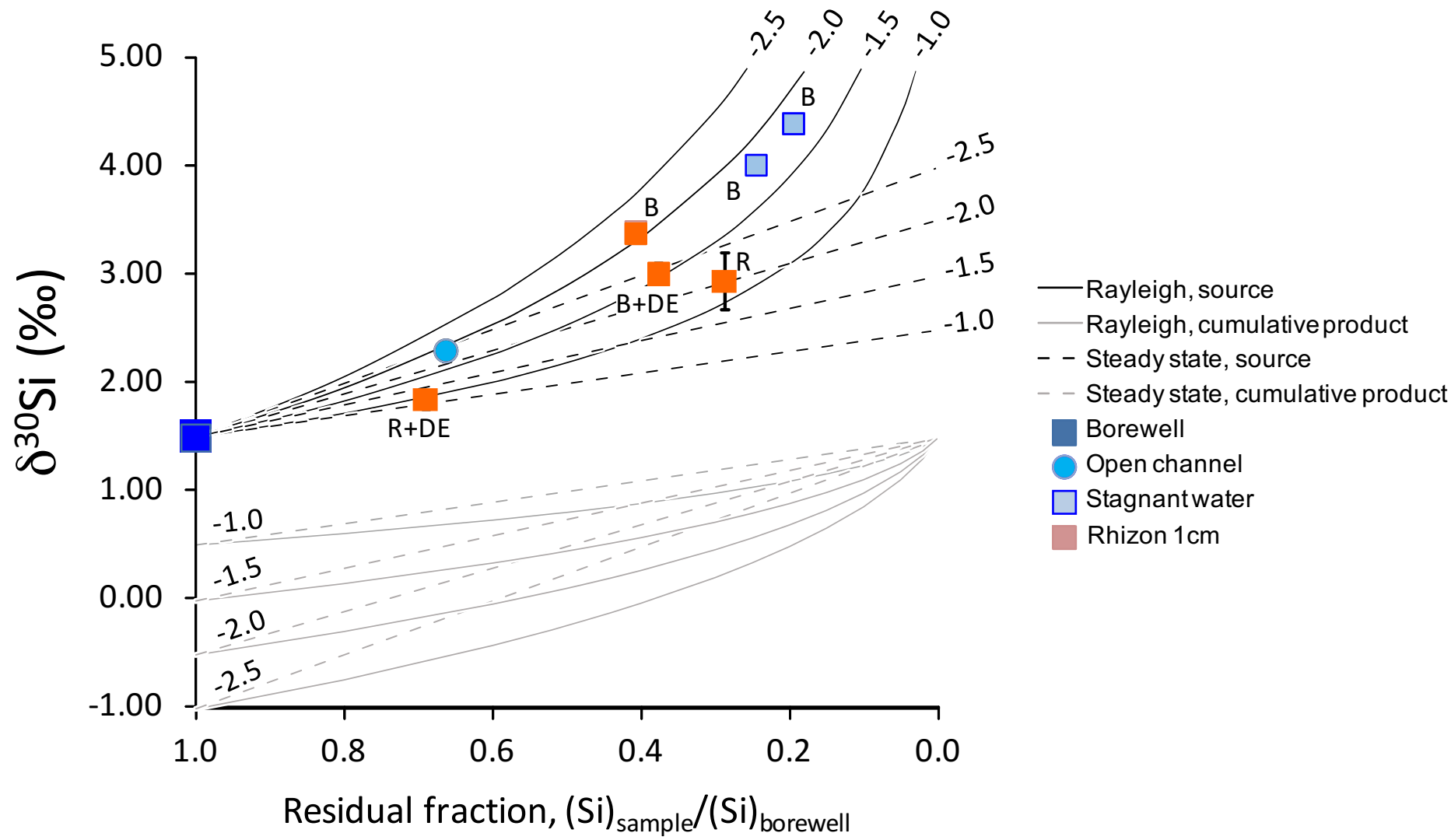


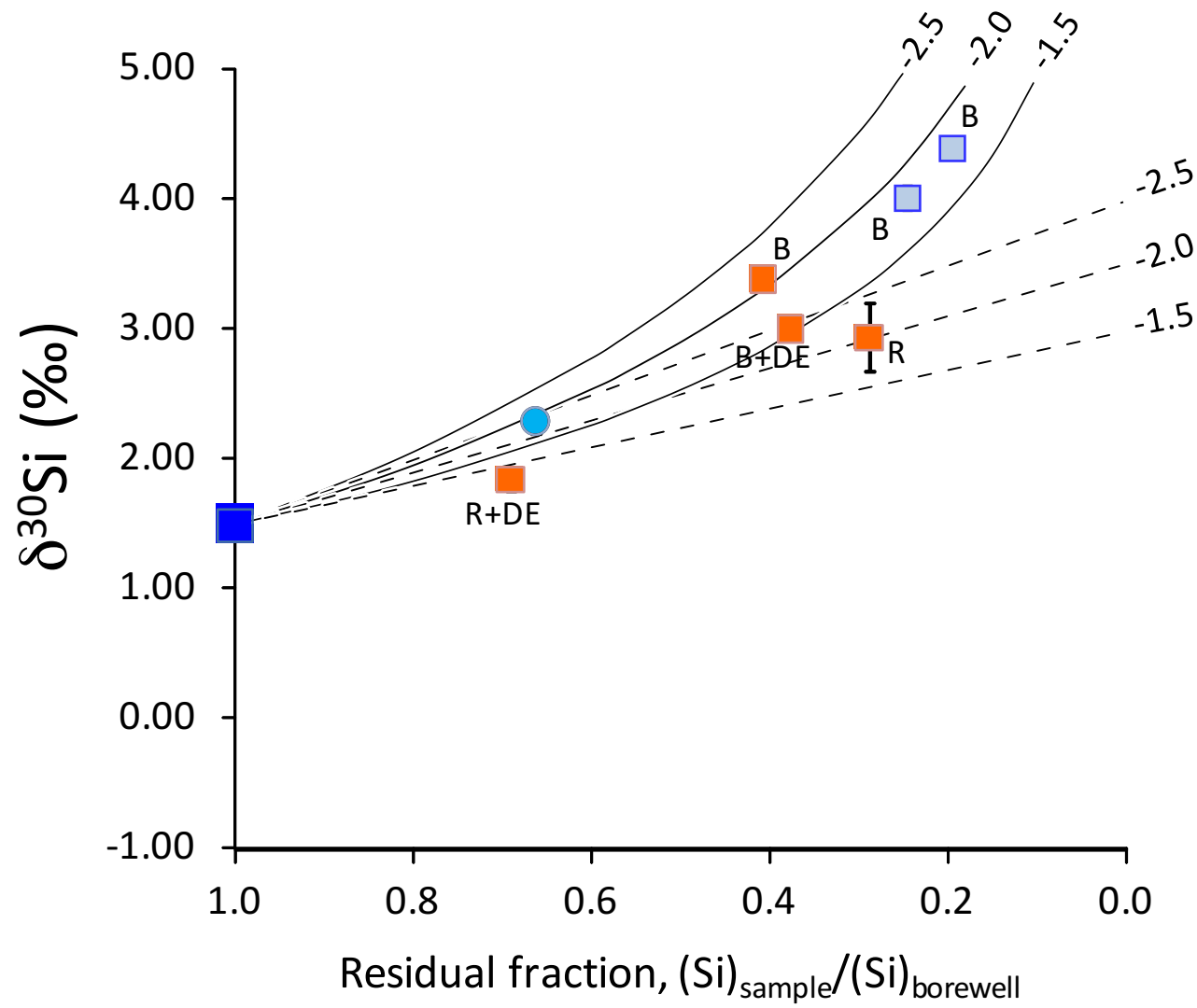
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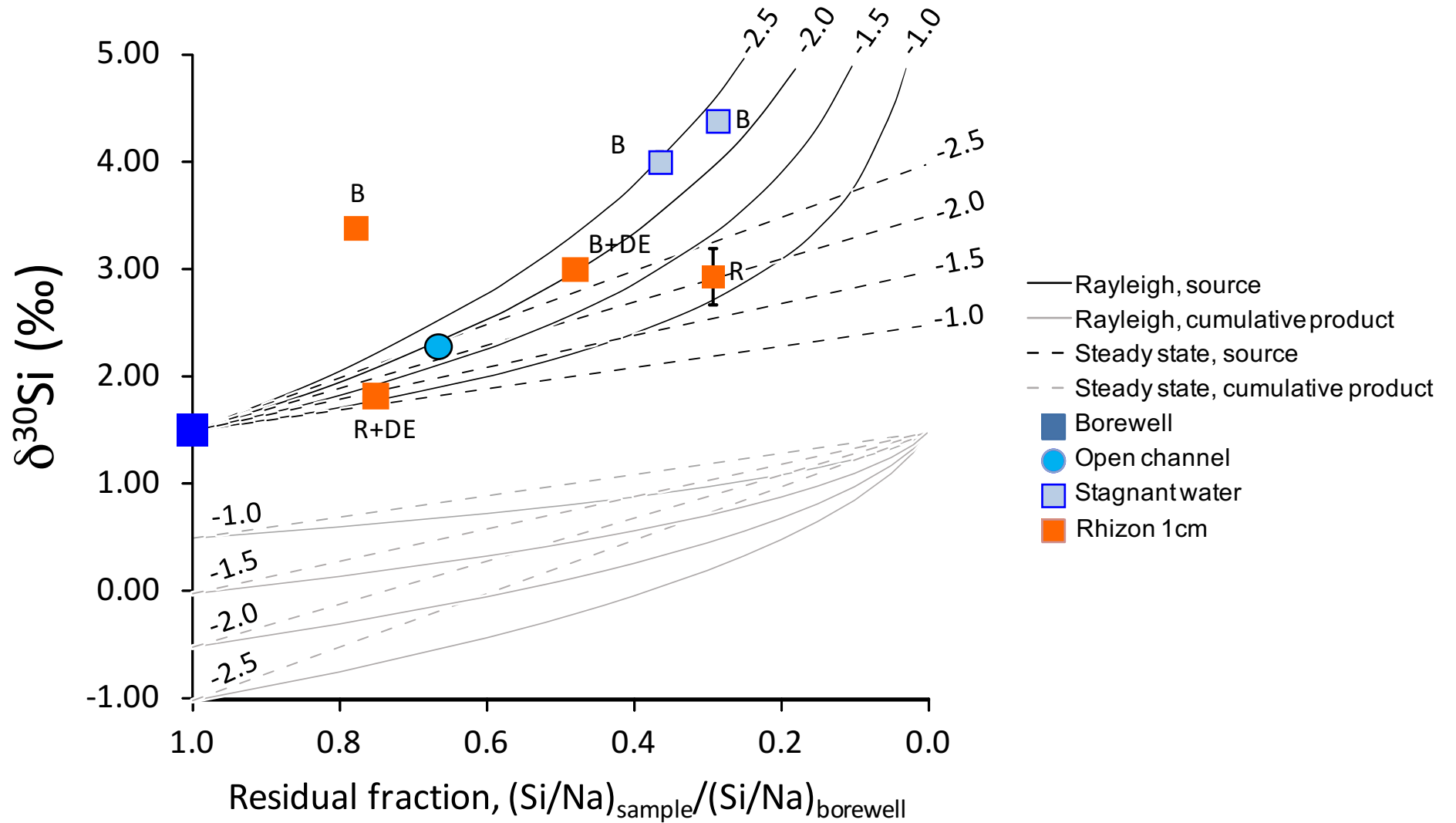


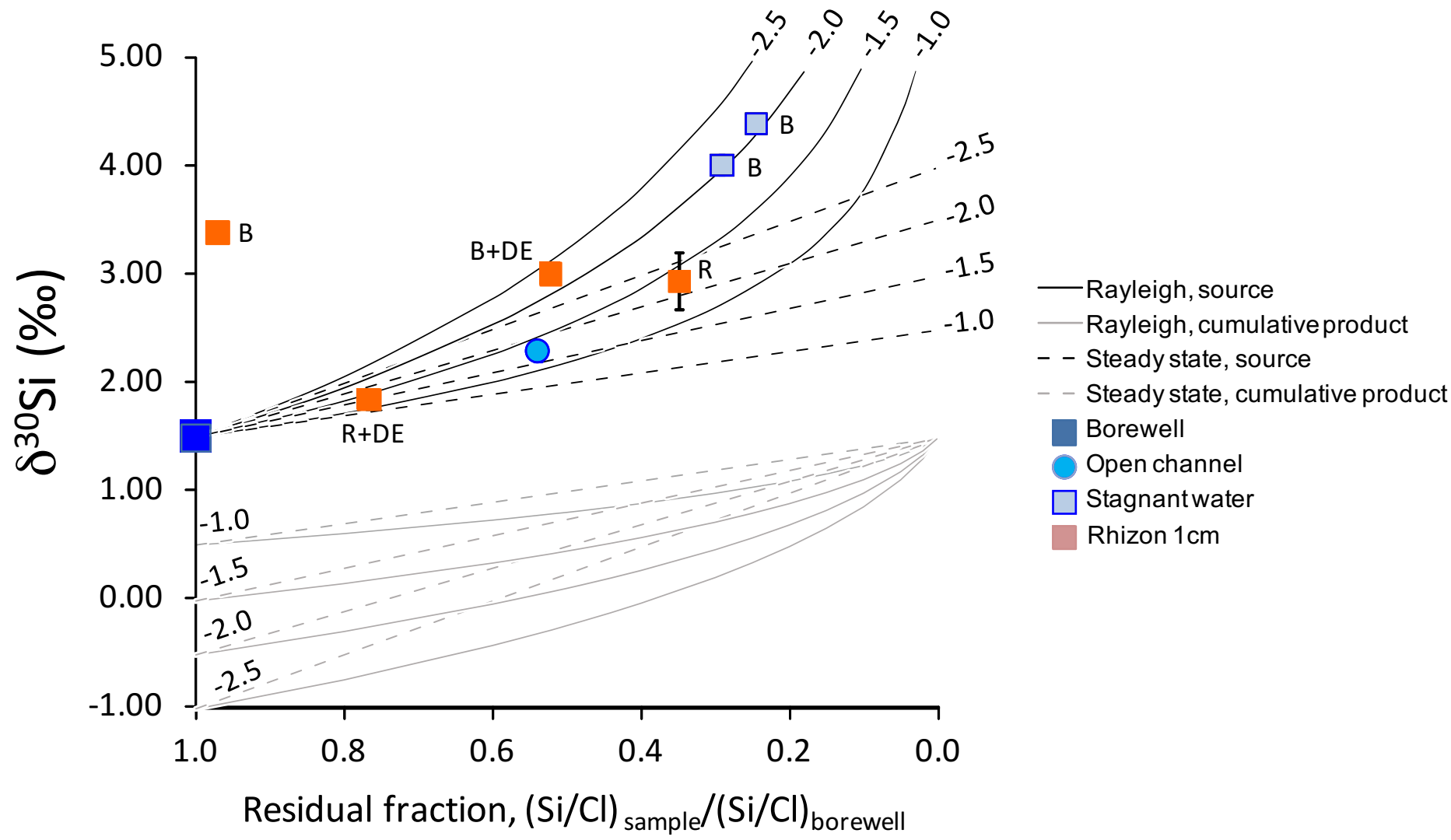


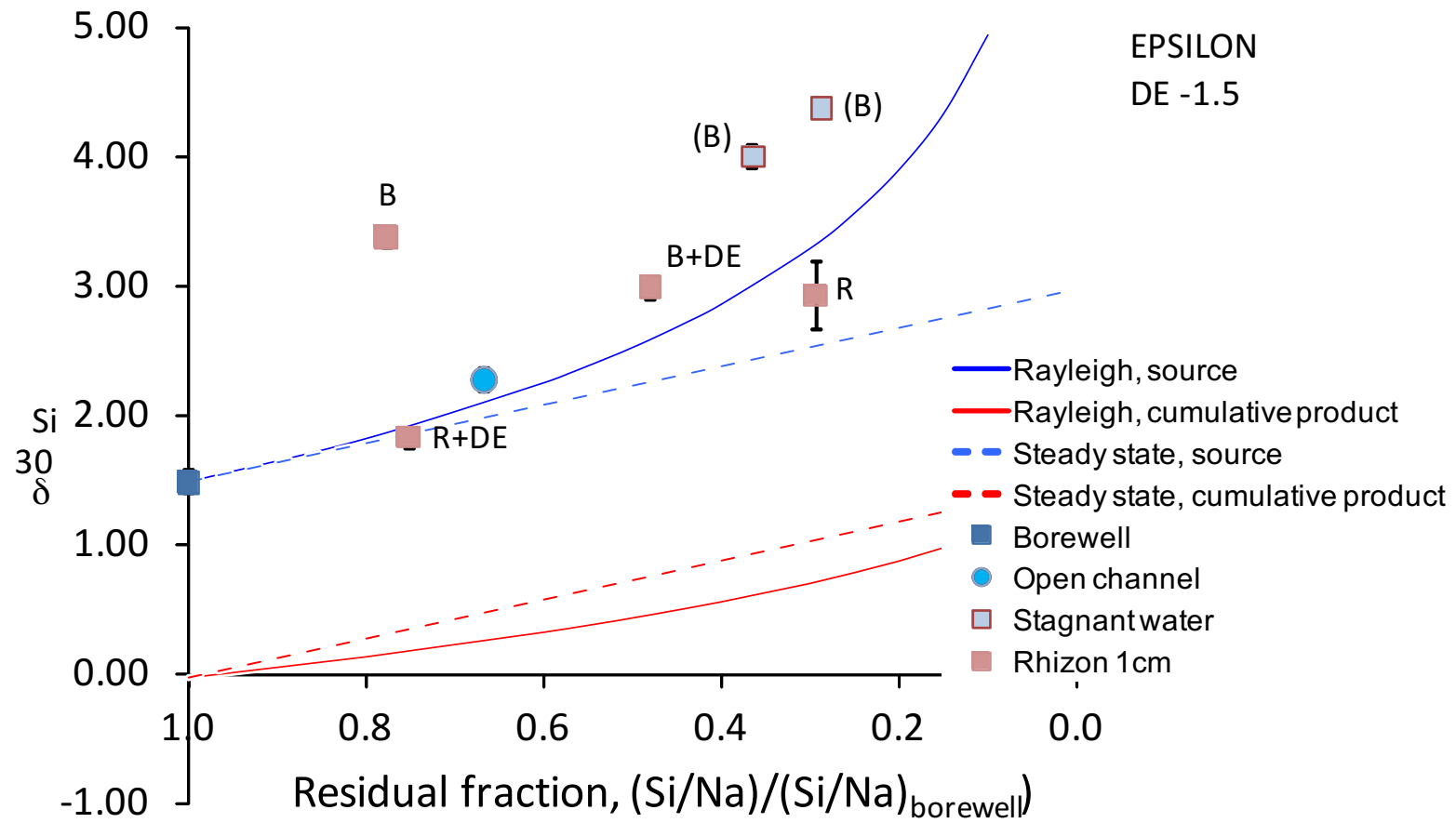


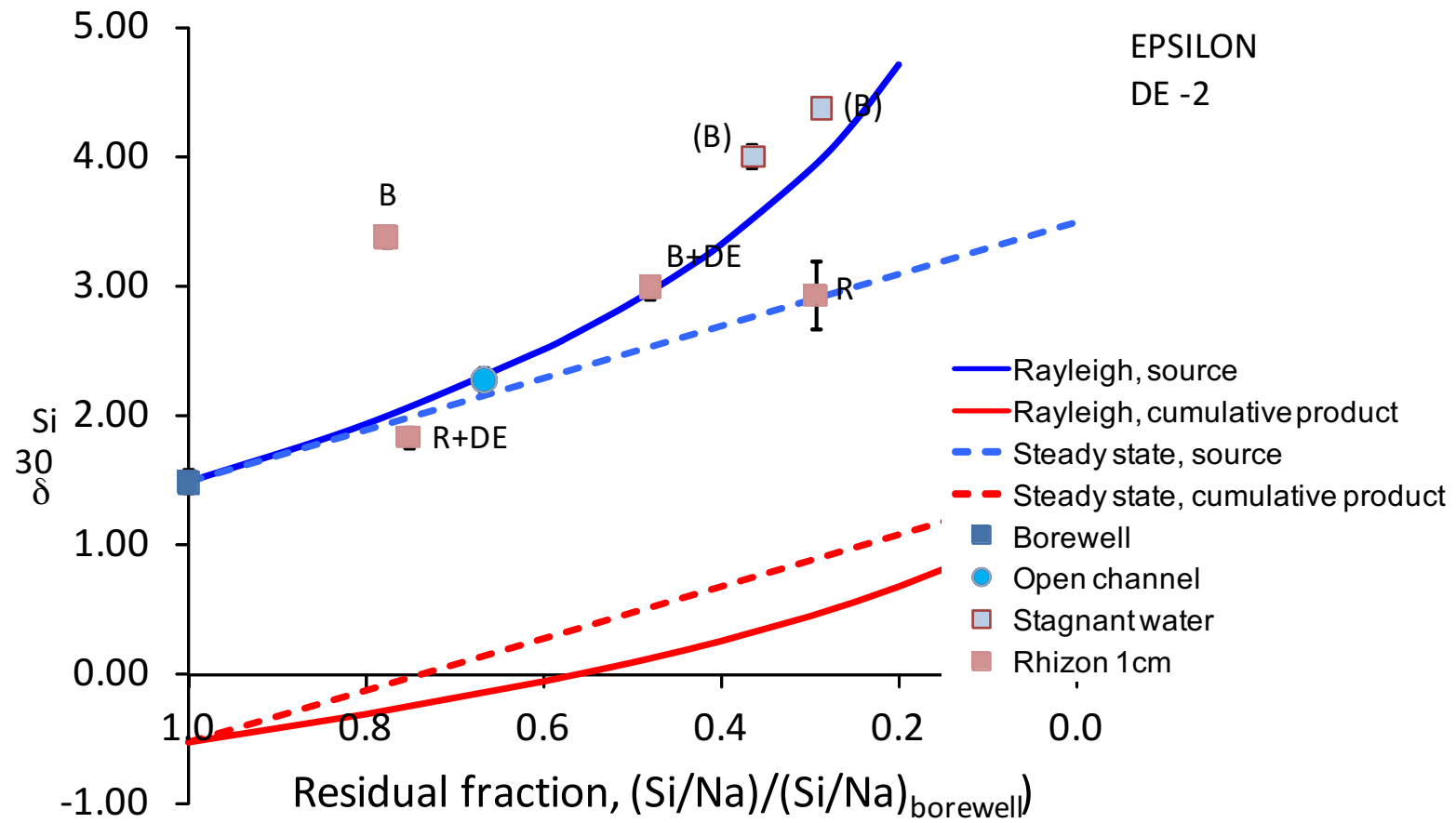


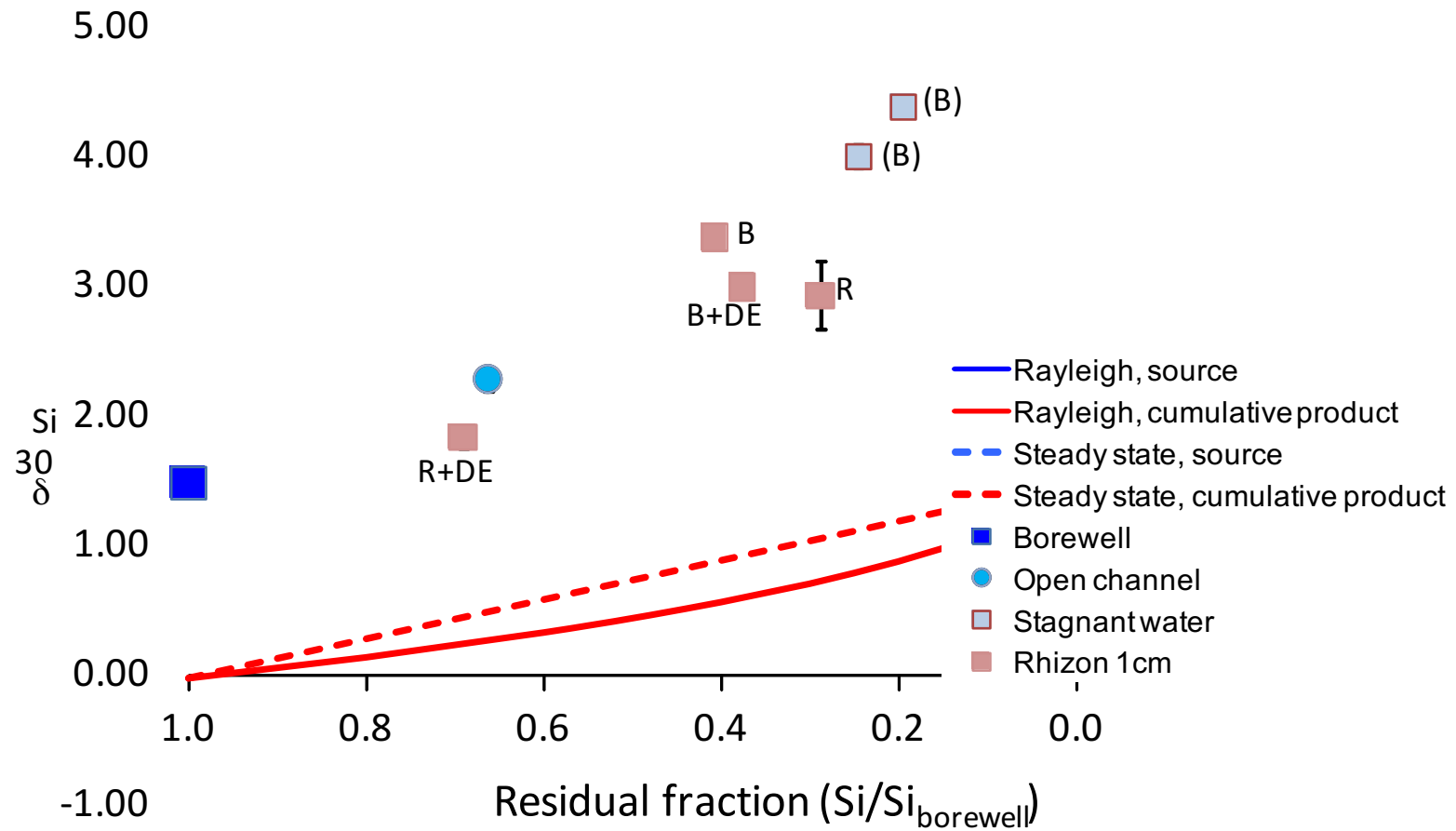


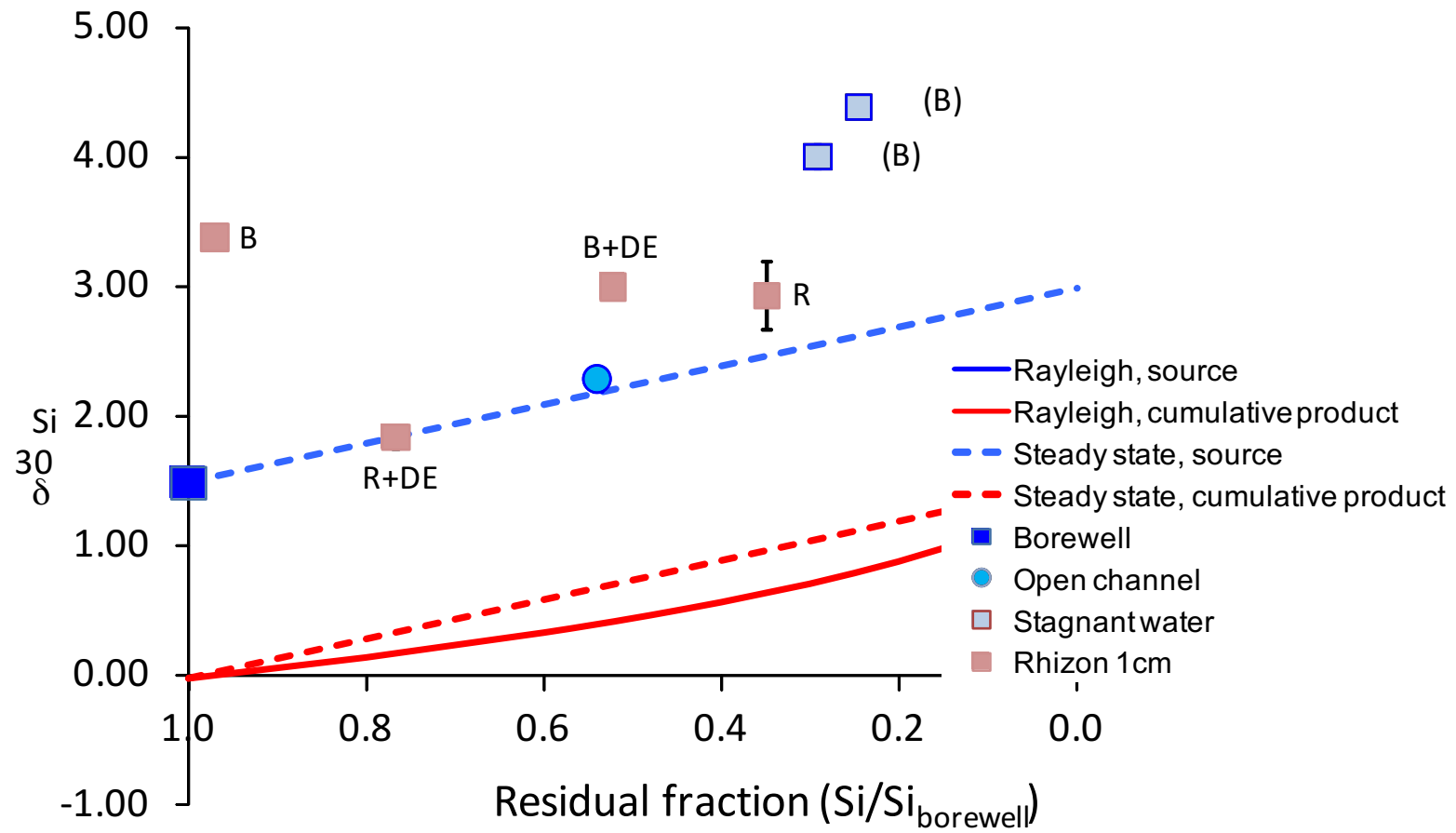


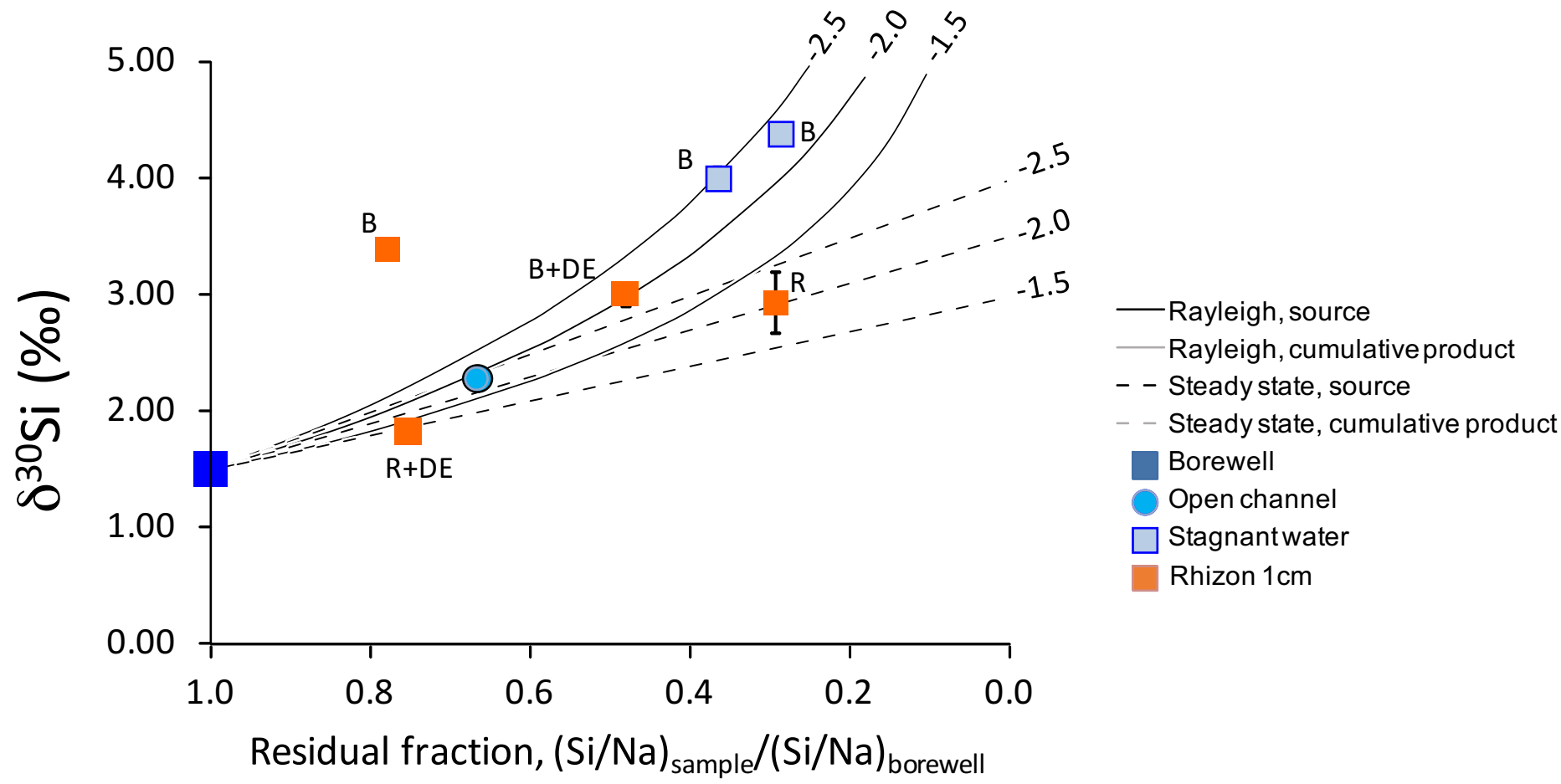


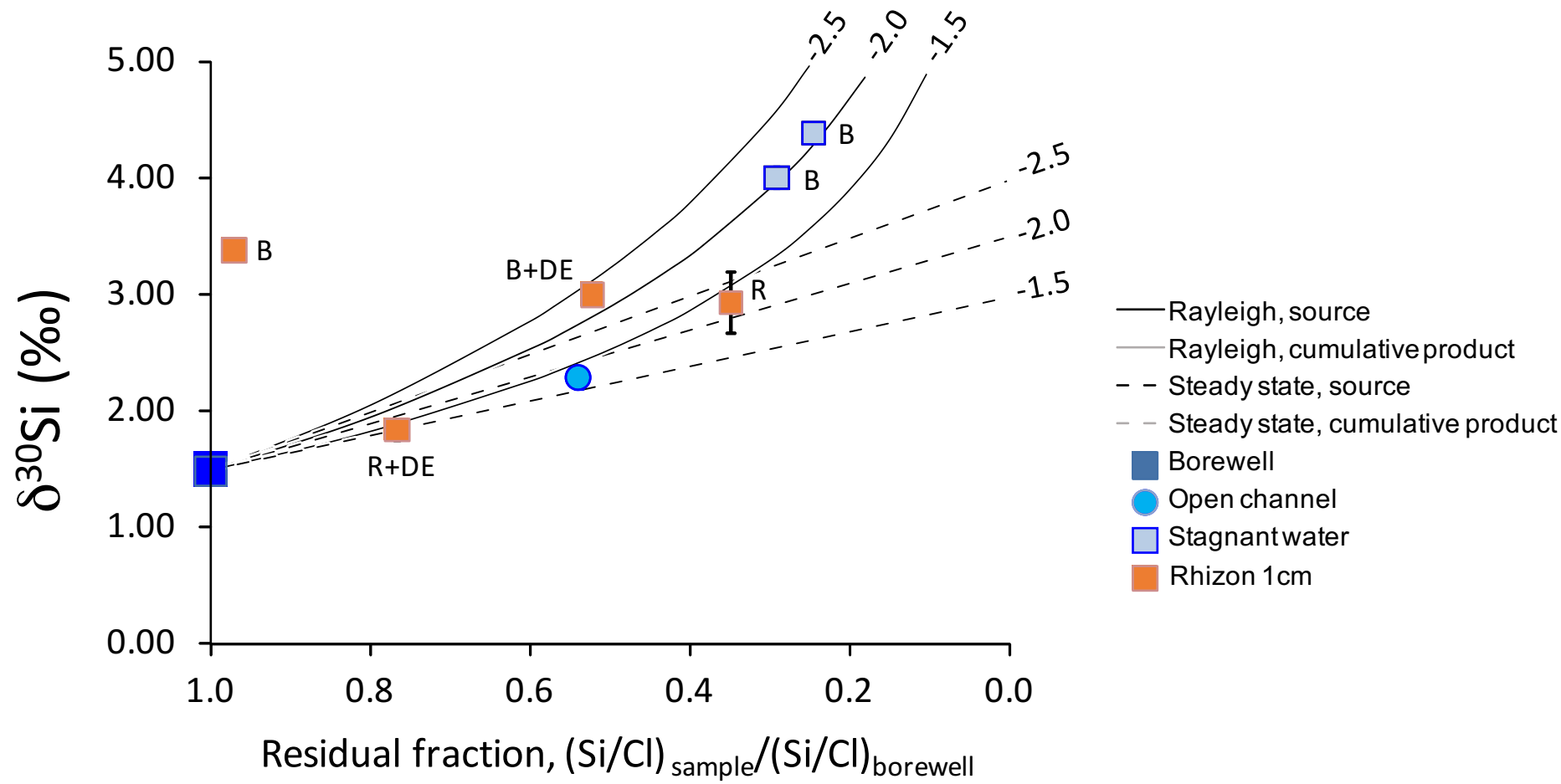


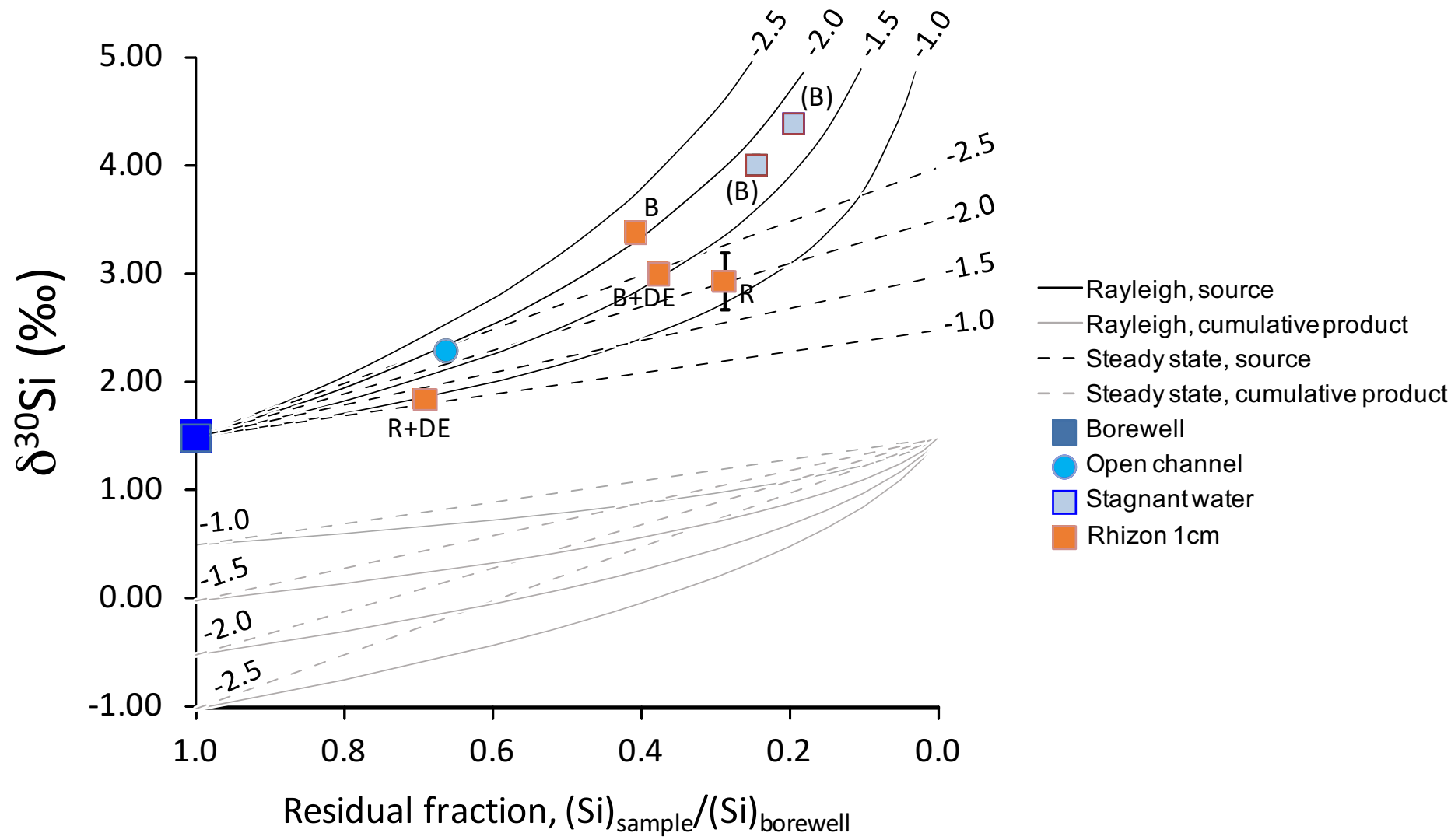


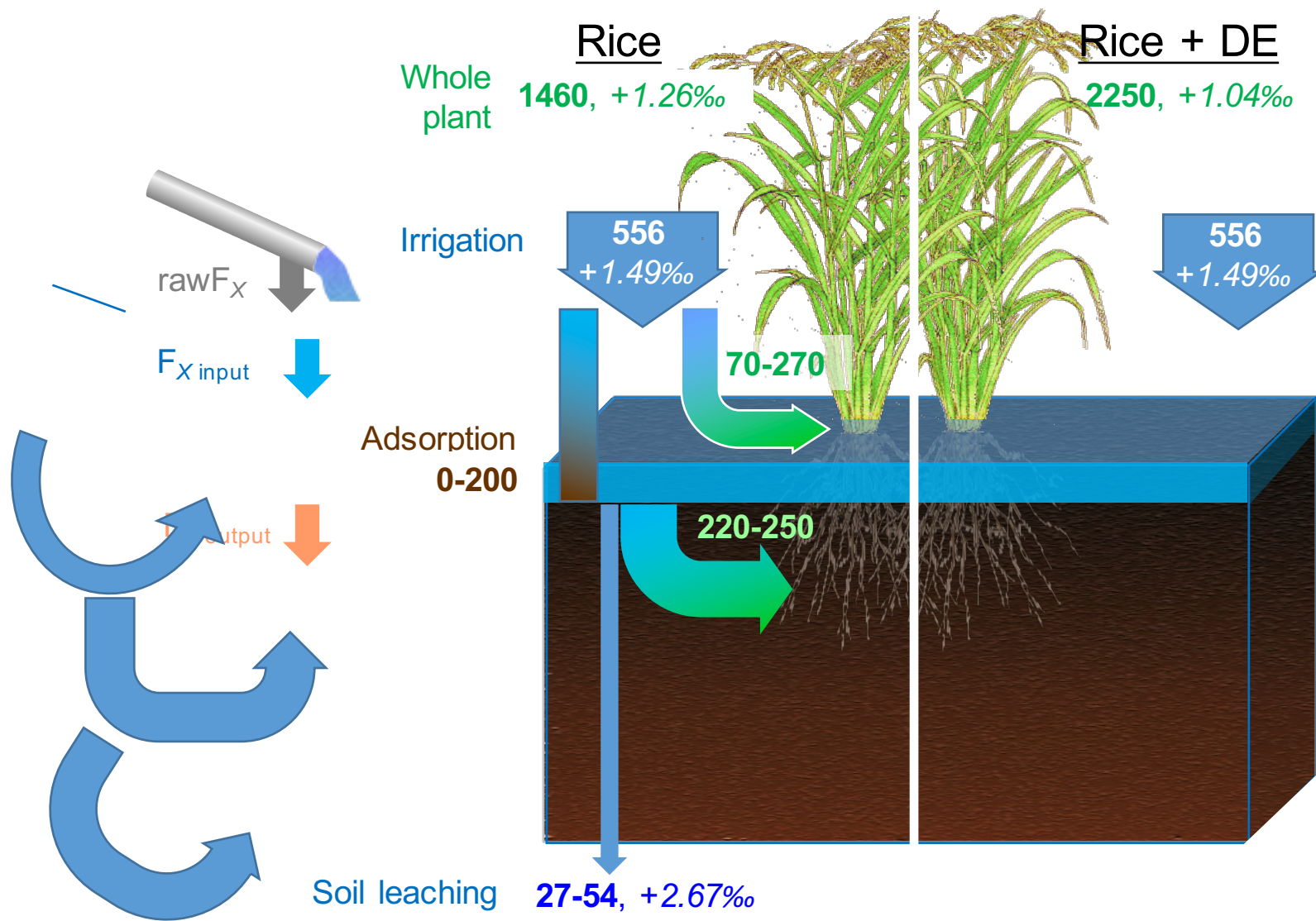


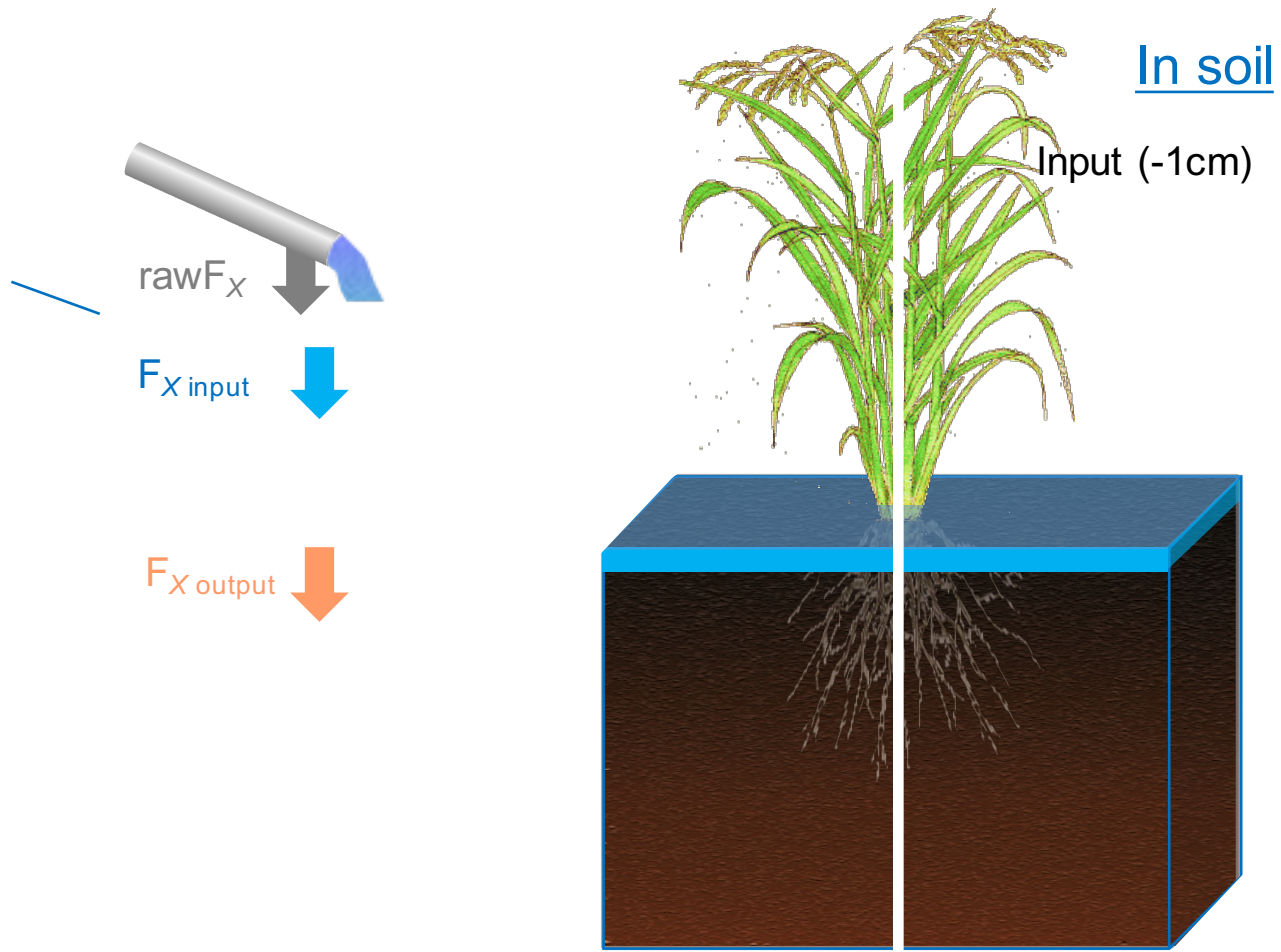


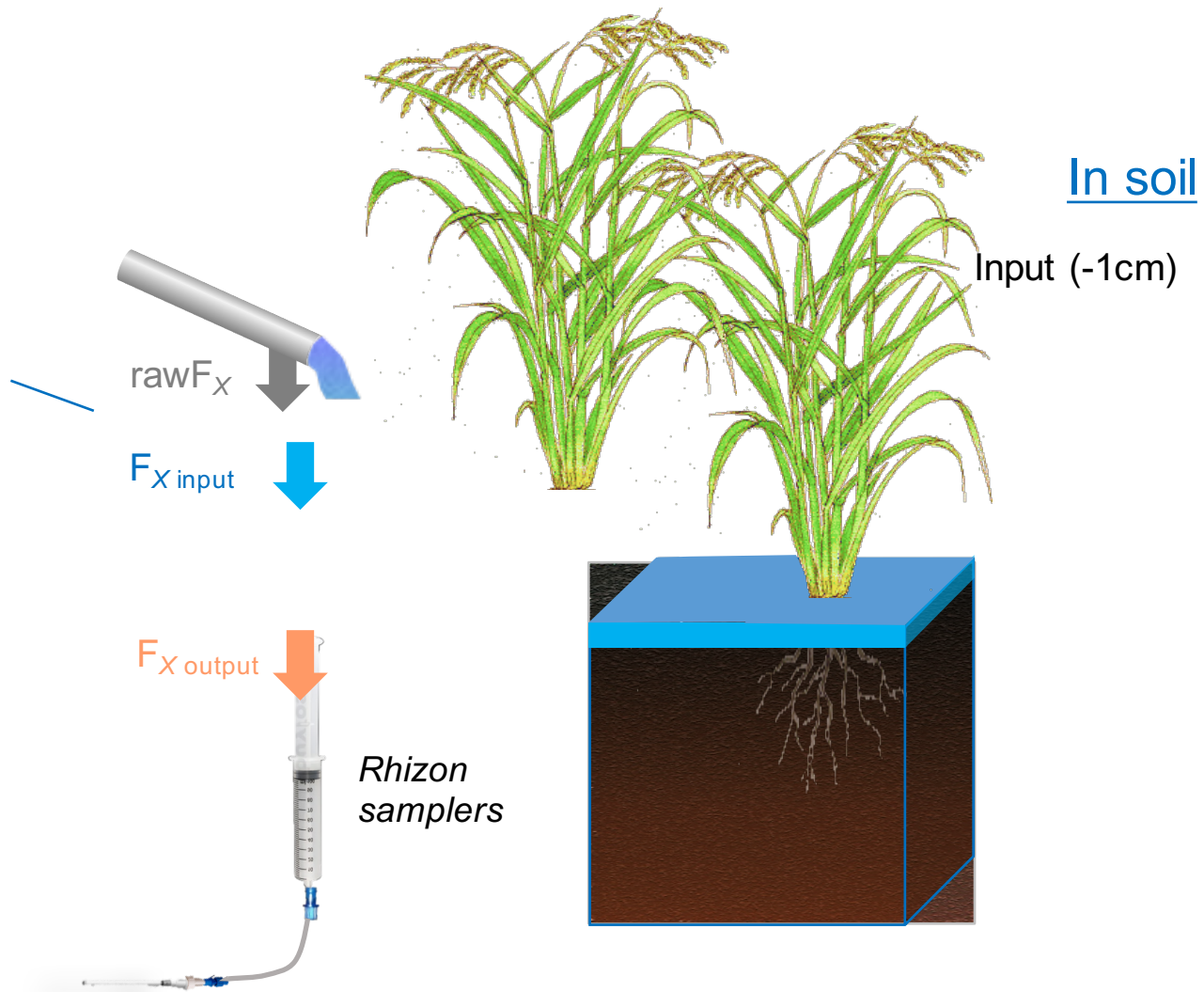












34 isotopic fractionation factor ($^{30}\epsilon$) between bore well and stagnant water compositions is close
35 to -1 ‰, i.e. the isotopic fractionation factor known for rice, indicating that above-ground DSi
36 removal would be dominated by plant uptake upon adsorption. Within the soil layer, pore
37 water DSi decreases much faster in rice experiments than in bare ones, demonstrating the
38 efficiency of DSi rice uptake upon adsorption.

39 Total irrigation-DSi to plant-Si would then represent 24 to 36 % in rice experiments (over
40 1460 ± 270 mmol Si m⁻² in biomass) and 15 to 23 % in rice+DE ones (over 2250 ± 180
41 mmol Si m⁻²). The $\delta^{30}\text{Si}$ signature of whole plants was significantly different in the rice+DE
42 plot analyzed, 0.99 ± 0.07 ‰, than in the rice one, 1.29 ± 0.07 ‰. According to these $\delta^{30}\text{Si}$
43 signatures, the main Si source from the soil would be the amorphous silica pool (ASi). A
44 slight contribution of DE to the rice plant could be detected from the Si isotopic signature of
45 rice.

46 *Conclusions*

47 The $\delta^{30}\text{Si}$ signatures of the various soil-plant compartments, when associated to Si mass
48 balance at scale, constitute a reliable proxy of the Si behavior in paddy fields. The solute Si
49 balance is controlled by rice uptake in rice plots and by adsorption and diatom uptake in bare
50 ones. The main Si sources for the rice plants were soil ASi, irrigation Si and to a lesser extent
51 Si fertilizer when it was applied.

52

53 *Introduction*

54 There is an increasing body of evidences showing that Si is playing a beneficial role for the
55 development of crops (Guntzer et al., 2012; Liang et al., 2015). The Si concentration in plants
56 depends primarily on the concentration of silicic acid in the soil solution (Ding et al. 2005;
57 Henriot et al., 2008) and is not correlated to the total Si concentration of the soil (Brenchley
58 and Maskell, 1927). However, correlations were observed between the Si concentration in rice
59 and the percentage of clay in soils (Cheng, 1982), and between the Si concentration in rice or
60 banana and the stock of weatherable minerals (Henriot et al., 2008; Makabe et al., 2009) but
61 the contribution of the potential Si sources remain to be quantified. The geochemical cycle of
62 Si in natural ecosystems such as forest and grassland is first controlled by silicate rock
63 weathering which constitutes the primary source to hydro and ecosystems. Depending on
64 weathering intensity, Si can be partitioned between a dissolved phase (DSi) and secondary
65 clay minerals such as smectite (bisilialitisation, i.e. slight weathering) or kaolinite
66 (monosialitisation, i.e. moderate to intense weathering), or dissolved congruently in case of

67 extreme weathering (allitisation) (e.g. Allen, 1997). The dissolved silica taken up by plants
68 precipitates as amorphous silica (ASi) particles called phytoliths (Piperno 1988; Meunier et
69 al., 2017). Because of its higher rate of dissolution in soil solution (Frayse et al., 2009) Si
70 from phytoliths can be preferentially recycled by plants (Alexandre et al. 1997; Lucas, 2001)
71 or leached out of the soils and control the flux delivered to oceans by rivers as DSi and ASi
72 (Derry et al., 2005; Riotte et al., 2014; Cary et al., 2005; Hughes et al., 2011; Frings et al.,
73 2014).

74 The biogeochemical cycle of Si in cultivated land is poorly documented. According to
75 Vandevenne et al. (2012) agriculture may have disturbed the natural cycle of Si because plant
76 materials do not return to the field and are injected into the urban cycle. Several perturbations
77 have been documented in the surface soil horizons: depletion of the phytolith pool (Struyf et
78 al., 2010; Clymans et al., 2011; Guntzer et al., 2012; Vandevenne et al., 2015a) and a decrease
79 of crystallinity of clays (Irfan et al., 2017). Besides, repeated crop removal can reduce the
80 concentration of potentially available Si to the extent that Si fertilization is necessary (Datnoff
81 and Rodrigues, 2005; Meunier et al., 2008; Savant et al., 1997). Desplanques et al. (2006)
82 showed in a rice field of Camargue (France) that if soil ASi would be the only source of Si for
83 plants, this stock would be exhausted after five years of cultivation. Another potential cause
84 of Si-depletion in rice cropping systems is DSi leaching from the soil. According to the
85 estimation made by Nguyen et al, (2016) from an hydrological modelling in Viet-Nam, the
86 potential loss could reach 10 tons Si ha⁻¹ yr⁻¹ (350.10³ mol Si ha⁻¹ yr⁻¹), i.e. ten times the Si
87 taken up by rice plants in this system. Therefore, there is a need for better documenting the Si
88 budget in the cultivated land. In a recent rice cropping experiment in California where straw
89 was incorporated into the soil prior to cultivation, Seyffert et al. (2013) monitored the Ge/Si
90 ratio in soil pore water and observed an increase of Ge/Si during the fallow season and a
91 decrease during the cropping season. These authors assigned these relative variations to the Si
92 release from the straw and its further uptake by the rice crop. Improving the quantification of
93 Si-fertilizer's contribution for adjusting the doses applied to the plant requirements would
94 require not only a thorough Si mass balance in paddy fields (quantifying the Si sources and
95 sinks of Si, including Si-fertilizers contribution), but also a proxy of Si sources.

96

97 Studying the silicon isotopic compositions of the various soil-water-plant compartments of
98 rice cropping experiments could bring new insight for the Si mass balance at soil-plant scale
99 and particularly about the nature of the Si sources to the rice. Silicon has three natural (stable)
100 isotopes, ²⁸Si, ²⁹Si, ³⁰Si which fractionate during water-soil interactions and plant uptake

101 (reviews in Opfergelt et al., 2012; Frings et al., 2016). The partition of Si between dissolved
102 load and clay minerals during silicate weathering induces preferential allocation of the light Si
103 isotopes in clay minerals and subsequent enrichment of heavy Si isotopes in the solution
104 (Ziegler et al., 2005; Georg et al., 2007). As a consequence, primary bedrock silicates,
105 secondary clay minerals and soil pore water often exhibit distinct isotopic signatures.
106 Similarly, Si adsorption onto ferrihydrite or goethite favors light isotopes (Delstanche et al.,
107 2009) according to an isotopic fractionation factor ($^{30}\epsilon$) varying between -1.1 ‰ for
108 ferrihydrite to -1.6 ‰ for goethite. Such isotopic fractionation also occur between plant and
109 solution. The first studies of the Si isotopic signatures in rice plants highlighted a $^{30}\epsilon$ between
110 the soil or the hydroponic solution and the rice plants of -1 ‰ (Ding et al., 2008), a value
111 similar to the few other plants measured up to now: banana, wheat or bamboo (Opfergelt et
112 al., 2012 and references therein). Recently, hydroponic experiments (Sun et al., 2016)
113 revealed that the Si isotopic fractionation factor between the external solution and the whole
114 plant could indeed range from -0.4 ‰ to -1.13 ‰ according to the DSi concentration of the
115 solution (here 0.17 to 8.5 mmol Si L⁻¹). Sun et al. deduce from these experiments that the rice
116 plant takes up most of the silica through an active mechanism and that the preferential uptake
117 of light Si isotopes occurs via a passive mechanism. The respective $\delta^{30}\text{Si}$ signatures of rice
118 and feeding solution are then expected to clarify the Si accumulation processes in the plant.
119 To our knowledge, the only study which reported Si isotopes on cultivated soils solution
120 showed a shift to heavier values, attributed to a decrease of the phytolith source for DSi
121 (Vandevenne et al., 2015b).

122 The objective of this study is to perform a rice cropping experiment for identifying and
123 assessing the contributions of the various Si sources to the plant and the possible contribution
124 of a Si-fertilizer, diatomaceous earth (DE). DE have proven to be a good fertilizer in India as
125 measured by the increased Si concentration in the shoots and the grain yield (Crooks and
126 Prentice, 2016; Pati et al., 2016). Indeed, DE contains relics of diatom tests that are made of
127 amorphous silica. Amorphous silica particles (phytoliths and diatoms) are highly soluble
128 compared to the other soil silicates minerals around neutral pH (Frayse et al., 2009). We
129 combined a solute budget at soil-plant scale for estimating the contribution of irrigation with
130 the Si isotopic compositions ($\delta^{30}\text{Si}$) of the various soil, plant and water compartments for
131 assessing the complementary Si sources. In order to decipher the plant-driven processes from
132 the water-soil interactions, the solute budget was performed in four different conditions: bare
133 plot, bare plot with addition of DE, rice plot and rice plot with DE addition.

134 **1 Materials and methods**

135 **1.1 Experimental set up**

136 The study took place at the VC Farm (Experimental farm of Mandya, Southern India which
137 depends on the University of Agricultural Sciences, Bengaluru, 12°34'22"N, 76°49'38.5"E).
138 The soil is categorized as Typic Rhodustalfs, has a sandy loam texture, a pH of 7.1 and
139 contains quartz, feldspar, goethite, kaolinite and illite clay minerals (see also Sandhya K. 2016
140 for further information for the soil composition). A paddy field was divided into 16 plots of 4
141 by 5m (20m²), isolated from each other by furrows (Fig. 1) to prevent any drainage
142 input/output from adjacent plot.

143
144 Each plot was inundated and ploughed. Then, four different experiments were set up, each
145 with four replicates: (1) barren soil (further referred as "bare"), (2) barren soil with
146 application of 30 g m⁻² of diatom earth from Agripower Australia Ltd. (DE; further referred as
147 "bare+DE") (3) planted with rice (further referred as "rice"), and (4) rice planted with
148 application of 30 g m⁻² of DE before planting (further referred as "rice+DE"). In rice and
149 rice+DE plots, twenty one days old rice seedlings of species KMP-101, locally called Thanu,
150 were transplanted with a spacing of 20 cm by 10 cm. The total fertilizer applied was 27.2 g m⁻²
151 of urea (CH₄N₂O), 39 g m⁻² of single superphosphate (SSP, Ca(H₂PO₄)₂) and 10.4 g m⁻² of
152 muriate of potash (MOP, KCl), corresponding respectively to 910 mmol N m⁻², 248
153 mmol P m⁻² and 140 mmol K m⁻². The entire dose of SSP, half dose of MOP and urea were
154 applied prior to transplanting. Remaining MOP and urea were given as two splits at 30th and
155 60th days after transplanting. All plots were irrigated once in a week with the local borewell
156 water for the 100 days duration of the experiment (22nd August to 16th December 2015). The
157 applied DE (Agripower Australia Ltd) contains amorphous silica particles (diatom frustules)
158 and crystalline minerals (quartz, smectite, kaolinite).

159

160 **1.2 Water and plant sampling**

161 Water from the bore well used for irrigation was collected four times from March 2015 to
162 November 2016 for checking the stability of its chemical composition. Two soil pore water
163 samplers (Rhizon®) were installed in the center of each plot: one just below soil surface at
164 1 cm depth to collect infiltration water (considered as soil water input), the other at 40 cm
165 depth to collect soil leaching (considered as soil output water). Samplers at 40 cm were
166 installed prior to ploughing and their connection tube buried. To avoid disturbance of local

167 soil properties, particularly preferential infiltration, connection tube was unearthed the day of
168 transplanting, after ploughing. Shallow Rhizon samplers were inserted horizontally after
169 transplanting. Soil pore waters were collected twice in a month (n=6-9 per plot, 33 to 36
170 samples per experiment) by suction with a 50 ml syringe and stored in polypropylene bottles.
171 Volume collected each time ranged from few ml to 50 ml. Unfortunately, we observed from
172 chemical analyses that Rhizon samplers at 40 cm were collecting the local shallow
173 groundwater, which composition is very close to the canal irrigation water used in the
174 command area of the KRS dam (Meunier et al., 2015), instead of collecting soil leaching. As
175 an alternative, four plots (one per experiment) were cored up to 20 cm depth to sample soil
176 pore water not impacted by the local groundwater in November 2015, i.e. about one month
177 before harvest. Cores were sliced in five sections (0-2.5 cm, 2.5-5 cm, 5-10 cm, 10-15 cm and
178 15-20 cm) and soil pore water extracted by centrifugation and/or hydraulic press when pore
179 water content was too low for extraction by centrifugation. Few additional samples of
180 stagnant water, from a previous experiment were also analyzed for comparison with Rhizon
181 and core samples. Water chemistry was determined at the Indo-French Cell for Water
182 Sciences, Indian Institute of Sciences, Bengaluru. Major anions and cations were analysed
183 with an ion chromatograph (Metrohm) and silica using the molybdate blue method and a UV-
184 visible Knauer detector. The overall precision obtained for the concentration measurements
185 was better than 10%. The reference materials used for the quality check was ION 96.4 and
186 PERADE (Environment Canada). Plant biomass was harvested at plant maturity and weighed.
187 Straw (leaves and stems) and grains with husk were dried and preserved for further chemical
188 and isotopic analyses. Finally, one algal mat per experiment was collected to assess the
189 presence of diatoms and check the isotopic composition of ground-surface soil ASi.
190 All of the data were analyzed statistically using one-way ANOVA with XLSTAT (Addinsoft)
191 at a significance level of $P < 0.05$ via the Tukey test.

192

193 ***1.3 Determination of plant Si and soil ASi***

194 Si concentration in plants was measured following the method described in Ma and Takahashi
195 (2002). Briefly the rice plants were washed in distilled water before oven dried at 70°C for 2-
196 3h and finely grounded. Samples were digested in concentrated HNO₃, H₂O₂ and HF using a
197 microwave digestion system before dilution in 4% boric acid. The Si was determined using
198 the molybdenum blue method at 600nm. The ASi soil pool was separated from the soil matrix
199 (5g aliquot) using heavy liquid flotation. Carbonates were first removed with HCl (at 37 %

200 overnight), then the organic matter (OM) was oxidized with H₂O₂ 33 % at 50–70 °C. The clay
 201 fraction was removed by decantation with sodium hexametaphosphate to ease deflocculation
 202 and the heavy minerals by flotation using ZnBr₂ dense liquor set at d=2.3 g cm⁻³. ASi_{zb}
 203 fraction should theoretically be composed of pure amorphous silica. However, this fraction
 204 may contain some impurities, typically clays, which could impact the estimation of ASi stock
 205 in soil and also alter the δ³⁰Si signature of phytoliths. In order to assess the purity of ASi_{zb}
 206 samples and to correct if necessary ASi_{zb} and δ³⁰Si values, we used an index based on the
 207 chemical composition of ASi_{zb} fraction that considers Al as a proxy of clay contamination
 208 (kaolinite or smectite) according to the equation:

209

$$210 \quad \text{ASi}_{zb} \text{ purity} = (\text{Si} - \text{Al}) / \text{Si} \quad (1)$$

211

212 With Si and Al contents in mol kg⁻¹. The ASi_{zb} purity of pure silica fraction should be one,
 213 pure kaolinite zero and Ca-smectite around 0.58. The concentration of Si from ASi can be
 214 calculated considering a mean water content in opal of 10 % (Bartoli & Wilding, 1980)
 215 equivalent to 0.37 moles of H₂O for 2 moles of SiO₂ and the purity index following the
 216 equation:

217

$$218 \quad \text{ASi} = \text{ASi}_{zb} \cdot \text{ASi}_{zb} \text{ purity} \cdot 0.42 \quad (2)$$

219

220 With 0.42 the conversion factor from opal to Si.

221 **1.4 Solute mass balance at soil-plant scale**

222 The objective of solute Si mass balance at soil-plant scale is to assess where and how much
 223 dissolved silica (DSi) is removed from the system, which first requires a water budget. The
 224 total input water flux (Q_{total}) is composed of irrigation and rainfall. Irrigation flux (I) was
 225 quantified by measuring the yield of the borewell pump and by irrigating all plots for a same
 226 known duration. Rainfall (R) was measured with the manual rain gauge of the VFS farm.
 227 Estimation of the DSi flux leached from the soil requires estimating the leaching water flux
 228 ($Q_{soil \ output}$) which depends on the intensity of local evapotranspiration (ET). $Q_{soil \ output}$ was
 229 assessed following two ways:

- 230 (1) Considering a simplified water balance. In absence of runoff, $Q_{soil \ output}$ can be deduced
 231 from the relation $Q_{soil \ output} \approx Q_{total} - ET = R + I - ET$. In bare soil conditions, ET is
 232 expected to be similar to the potential evapotranspiration (PET). In paddy fields, the

233 actual evapotranspiration (ET_a) is known to exceed PET. For this reason, ET_a is
234 usually estimated by multiplying PET with a crop coefficient. Crop coefficient varies
235 according to the local climatic conditions and along the cropping season. For the
236 simplified water balance, we used the value of 1.15, corresponding to the average crop
237 coefficient of rice for semi-arid and moderate wind conditions, provided by FAO
238 (Allen et al., 1998). This value is consistent with the estimates of Tyagi et al. (2000) in
239 Northern India and more recently of Reddy et al. (2015) in Southern India. The local
240 PET was assessed from solar radiation and temperature data for the 100 days of
241 cropping period (data from the Karnataka State Natural Disaster Monitoring Centre,
242 KSNDMC). This $Q_{soil\ output}$ estimation is independent from chemical data.

243 (2) Using the solute mass balance of a conservative element. It relies on the hypothesis
244 that the soil input flux of a conservative element is equal to the soil output flux (steady
245 state hypothesis). A conservative behavior means that interactions with soil and plant
246 are limited enough to be neglected and then, that its concentration in the soil layer
247 only depends on the evapotranspiration intensity. This approach, classically used for
248 estimating groundwater recharge in pristine watershed (e.g. Maréchal et al., 2009,
249 2011a,b; Fouépé et al., 2011), considers chloride as the conservative element and is
250 then known as the chloride mass balance method (CMB). In most cases Cl is
251 considered to originate only from atmospheric inputs. However, CMB was also
252 applied with success in anthropic systems like urban watersheds (Fouépé Takounjou et
253 al., 2011) or agriculture in a context similar to this study: a winter wheat plot fertilized
254 with KCl for three decades (Tyner et al., 2000). Since in the present study it was not
255 possible to monitor the soil pore water composition at 40 cm depth, CMB was applied
256 for the first 20 cm of soil using the core pore water composition with, as main
257 advantage, being able to assess the above-ground evaporation and to track, once in the
258 soil, the progressive enrichment of Cl with depth by transpiration and compare it with
259 the expected depletion of silica. The small scale CMB provides the opportunity to test
260 the pertinence of sodium as conservative element, since Na is not brought by
261 fertilizers nor involved in plant cycle. Above-ground evaporation was assessed for all
262 four experiments by comparing the average Cl or Na concentration in Q_{total} with the
263 average Cl or Na concentration in the infiltrating solution (1 cm depth Rhizon
264 sampler) according to the relationship:

265

266
$$Q_{AG\ evaporation} = Q_{total} - \frac{[Na,Cl]_{borewell} \cdot I + [Na,Cl]_{rain} \cdot R}{[Na,Cl]_{surface\ porewater}} \quad (3)$$

267

268 With $\overline{[Na,Cl]_{borewell}}$ the average Na or Cl concentration in irrigation water (n=6),

269 $\overline{[Na,Cl]_{rain}}$ the average Na or Cl concentration in rain water, here taken from long term

270 monitoring of the Mule Hole watershed (n ≈ 200; Riotte et al., 2014), and

271 $\overline{[Na,Cl]_{surface\ porewater}}$ the average Na or Cl concentration in the 1cm depth pore water

272 collected with Rhizon sampler (n=8 to 9 per plot, 4 plots per experiment, then 32 to 36

273 samples per experiment). Water fluxes are specific, which means they are expressed per

274 surface unit in mm or L/m². The water flux infiltrating in the soil can be deduced as:

275

276
$$Q_{input} = Q_{total} - Q_{AG\ evaporation} \quad (4)$$

277

278 The specific water flux leached from the soil, Q_{output} , can be approximated for each

279 experiment by simple mass balance, assuming that the soil input flux of the conservative

280 element is equal to the soil output flux, which is the principle of the CMB method. Here, to be

281 consistent with the soil output composition (core pore water at 15-20 cm), the soil input

282 composition considered for the calculation was the shallowest core pore water (0-2.5 cm) of

283 each experiment. Then, Q_{output} can be described as:

284

285
$$Q_{output} = Q_{input} \cdot \frac{[Na,Cl]_{0-2.5cm\ porewater}}{[Na,Cl]_{15-20cm\ porewater}} \quad (5)$$

286

287 Soil input and output DSi fluxes (FSi_{input} and FSi_{output} , respectively) were estimated in a

288 second step, by multiplying DSi concentrations in 1 cm and 15-20 cm pore waters,

289 respectively, with the water fluxes estimated from ET or CMB approaches. The difference

290 between input and output DSi fluxes (ΔFSi) provides an estimate of the apparent removal or

291 addition DSi flux. This flux is considered as “apparent” because it may not account for the

292 entire Si flux mobilized or removed from the soil pore water. However, the $\delta^{30}Si$ signature of

293 this flux is expected to provide constrains on the water-soil-(plant) processes involved in the

294 soil. It can be assessed according to a simple isotopic mass balance equation:

295

296

$$\delta^{30}\text{Si}_{\Delta\text{FSi}} = \frac{\text{FSi}_{\text{output}} \cdot \delta^{30}\text{Si}_{\text{output}} - \text{FSi}_{\text{input}} \cdot \delta^{30}\text{Si}_{\text{input}}}{\Delta\text{FSi}} \quad (6)$$

297

298 **1.5 $\delta^{30}\text{Si}$ measurements**

299 The $\delta^{30}\text{Si}$ signatures were determined on irrigation water, stagnant water (n=3), shallow
300 (1 cm) Rhizon pore water (n=4), core pore water depth profiles (n=25) and on solid silica
301 pools, i.e. DE, clay fraction, ASi of algal mats (n=4), ASi of soils (n=2) straw (n=2) and - rice
302 grains with husk (n=2). Solid samples were first digested by alkaline fusion with NaOH and
303 dissolved in water and diluted HCl, following the procedure of Zambardi and Poitrasson
304 (2011) modified from Georg et al. (2006). Both digested solid and dissolved samples were
305 processes through Bio-Rad AG50-X12 ion exchange resin to remove the cationic matrix and
306 elute the silica fraction. This latter was diluted to 2 mg L⁻¹. Then, 1 mg L⁻¹ of Mg was added
307 as internal standard for online correction of mass bias during the analysis.

308 Isotopic measurements were performed on a Multi-Collector ICP-MS Neptune (Thermo®) at
309 medium resolution and replicated 3 times. The reference material NBS 28, also spiked with
310 1 mg L⁻¹ of Mg, was measured between each sample (bracketing mode). Isotopic data were
311 normalized to the NBS 28 international standard and expressed in per mil (‰) following the
312 relation:

313

$$\delta^{30}\text{Si} (\text{‰}) = \left(\frac{\left(\frac{{}^{30}\text{Si}}{{}^{28}\text{Si}} \right)_{\text{sample}}}{\left(\frac{{}^{30}\text{Si}}{{}^{28}\text{Si}} \right)_{\text{NBS 28}}} - 1 \right) \cdot 1000$$

314

315

316 The uncertainty associated with the $\delta^{30}\text{Si}$ data (2σ) corresponds to the relative standard
317 deviation obtained from the 3 replicates. The reproducibility was checked by regular
318 measurements of the reference material BHVO (a basaltic rock). The average $\delta^{30}\text{Si}$ obtained
319 from 2010 to 2016 measurements, $-0.27 \pm 0.06 \text{‰}$ (n=24), matches the values obtained by
320 Zambardi and Poitrasson (2011), $-0.27 \pm 0.08 \text{‰}$ and Savage et al. (2012), $-0.30 \pm 0.09 \text{‰}$.
321 The standard deviation found for BHVO measurements ($\pm 0.06 \text{‰}$) will be considered as the
322 minimum precision of $\delta^{30}\text{Si}$ data.

323 2 Results

324 2.1 Chemical composition of waters

325 The composition of the borewell water was stable over the whole study period, Cl and Na
326 concentrations ($3484 \pm 383 \mu\text{mol L}^{-1}$; $6215 \pm 360 \mu\text{mol L}^{-1}$, Table 1) being within the range
327 found in the region for groundwater located in semi-arid conditions and impacted by
328 agriculture (Siva Soumya et al., 2013). Borewell water is also particularly rich in DSi, on
329 average $1217 \pm 155 \mu\text{mol L}^{-1}$, as compared for instance to the Kaveri river, between 100 and
330 $300 \mu\text{mol L}^{-1}$ (Meunier et al., 2015) or to the groundwater of a nearby forested watershed
331 (Maréchal et al., 2011b). Such concentration should make irrigation water a significant Si
332 source to plants. Sodium and Chloride concentrations of shallow Rhizon pore waters (n=138)
333 and stagnant water (n=2) stretch on a linear relationship ($R^2 = 0.83$ for all samples, $0.72 < R^2$
334 < 0.93 for the 16 individual plots), on which the borewell composition falls too. This trend
335 reflects the common dilution (by rain) and concentration (by evaporation) cycles of both
336 elements (Fig. 2a). On the contrary, DSi concentrations are always more diluted than the
337 borewell, even at the highest Na concentrations. DSi ranges from $100 \mu\text{mol L}^{-1}$ (Fig. 2b),
338 which correspond to the equilibrium with quartz, to $1000 \mu\text{mol L}^{-1}$.

339
340

341 DSi concentrations in rice and rice+DE experiments are on average lower than in bare and
342 bare+DE ones. Within the soil, the Cl and Na concentrations of core pore water samples
343 increase with depth (Table 2, figure 3). DSi exhibits again a different pattern with sharp
344 decrease to $\sim 100 \mu\text{mol L}^{-1}$ within the upper five centimeters in rice and rice+DE plots, and
345 more regular decrease in bare and bare+DE plots (Fig. 3). Between 15 and 20 cm depth, DSi
346 concentration of rice plots cannot be distinguished from those of bare plots.

347

348 2.2 Water and solute mass balance

349 The total amount of water received by each plot over the cultivation period (from
350 transplantation to harvest) was 889 mm, comprising 473 mm from bore well and 416 mm
351 from rainfall. Considering a PET of 433 mm for this period and a crop coefficient for rice of
352 1.15 (Allen et al., 1998), the actual evapotranspiration in rice plots should be 500 mm. In
353 absence of surface runoff or lateral subsurface flow, the soil leaching flux would be 390 mm
354 beneath rice plots, while it would be slightly higher, 455 mm, in bare soils.

355 Using equations of section 2.4 and either Na or Cl as conservative element, it was possible to
356 distinguish the water and solute budgets both above-ground (in stagnant water, before
357 infiltration) and below-ground (within soil). Above-ground evapotranspiration (Eq. 3) ranges
358 from 370 mm in bare experiment to 410 mm in rice+DE experiment (Table 3). No difference
359 was observed between Cl- and Na-based calculations. Both estimations agree with direct pan
360 measurements made by Siva Sivapalan (2015) in similar climatic conditions and latitude.
361 Water fluxes leached from the soil layer were assessed using Cl and Na concentrations
362 measured in the deepest soil pore waters and Eq. 5. Sodium-based calculations provided
363 homogeneous leaching water fluxes across experiments, from 180 mm (rice + DE) to 230 mm
364 (rice), i.e. twice lower than those estimated from the water balance, while chloride-based
365 leaching water fluxes were more scattered and ranged from 110 (rice + DE) to 460 mm (rice).
366 Since DSi of stagnant water fluctuates over time due to concentration by evaporation or
367 dilution by rain (Figure 2b), deducing the DSi flux removed at the ground surface from the
368 average DSi concentration only would provide a value marred by a large uncertainty.
369 Normalizing DSi to Na or Cl allows overcoming dilution and concentrations effects and then
370 improving the precision associated to calculation of DSi removal. Average Si/Na molar ratios
371 a 1cm depth of bare and bare+DE experiments are 0.128 and 0.124, respectively, while they
372 are slightly but significantly lower in rice and rice+DE experiments, 0.095 and 0.092,
373 respectively according to the Tukey HSD test (Table 1). Standards deviations are about twice
374 larger for Si/Cl, probably because of KCl additions, but remained narrower compared to the
375 DSi fluctuations. The above-ground DSi removal calculated from Na/Si ratios was 210
376 $\text{mmol}\cdot\text{m}^{-2}$ in bare and bare+DE experiments, and 275-280 mmolSi m^{-2} in rice and rice+DE
377 experiments. Similar values were obtained using Si/Cl (Table 3). These results indicate that
378 less than two third of the DSi flux brought by borewell irrigation to bare experiments and
379 about half of DSi in rice experiments infiltrate into the ground; such proportion of above-
380 ground DSi removal was unexpected and has, to our knowledge, never been reported before.
381 By difference with the input DSi flux to each plot, the DSi flux infiltrating into the soil would
382 be 410 mmolSi m^{-2} in bare and bare+DE experiments and 320 mmolSi m^{-2} in rice and
383 rice+DE experiments. Soil leaching DSi fluxes, calculated using the deepest soil pore water
384 compositions and leaching water fluxes, ranged from 27 to 55 mmolSi m^{-2} in rice experiment
385 to 40 to 84 mmolSi m^{-2} in bare+DE experiment. This value is relatively low compared to the
386 Si percolating flux calculated in humid tropical conditions (Philippines; Klotzbücher et al.,
387 2015), because of the high percolating water flux. The DSi removal within the soil layer,

388 calculated as the difference between soil DSi input and leaching fluxes, was slightly lower in
389 rice experiments (190 to 235 mmolSi m⁻²) than in bare ones (250 to 310 mmolSi m⁻²).

390

391 **2.3 $\delta^{30}\text{Si}$ of waters**

392 The $\delta^{30}\text{Si}$ of the bore-well water, 1.49 ‰, falls in the upper part of the range observed up to
393 now in groundwater (Frings et al., 2016), but it is similar to the values found in the
394 groundwater of the Mule Hole watershed (0.81 to 1.49 ‰) located on the same peninsular
395 gneissic complex as Mandya. This signature evolves towards heavy values, up to 4.39 ‰, as
396 water stagnates and DSi drops. With the exception of one sample which exhibits a low $\delta^{30}\text{Si}$
397 value (1.89 ‰) associated to high DSi (849 $\mu\text{mol L}^{-1}$), shallow (1 cm) soil pore water display
398 heavy $\delta^{30}\text{Si}$ ranging from 2.94 to 4.36 ‰ (Fig. 3). These signature slightly decrease with
399 depth, down to 2.04 to 3.26 ‰ at 15-20 cm. The $\delta^{30}\text{Si}$ of these soil pore water are
400 significantly heavier than those ever measured up to now (see review of Frings et al., 2016).
401 On average, $\delta^{30}\text{Si}$ of soil pore water is slightly lower in rice plots than in bare plots, but all
402 pore waters evolve with depth within the same $\delta^{30}\text{Si}$ range, whatever the experiment.

403

404 **2.4 Soil silica pools and $\delta^{30}\text{Si}$**

405 The soils of the sub-humid and semi-arid zones of the Deccan plateau are known to be
406 immature and still contain primary minerals like plagioclases and quartz (e.g. Braun et al.,
407 2009). In Mandya, the <2 μm fraction of the soil, which includes clays *sensus stricto* and clay
408 minerals like Fe-oxyhydroxides, accounts for only 21 % which means that primary minerals
409 and ASi compose about 80% of the soil. The soil ASi_{ZB} fractions in rice and rice+DE plots,
410 when corrected from impurities, are 1.9 and 1.8 % (Table 4). Such ASi values are twice
411 higher than in the Mule Hole forest, located in similar geological settings (~1%), or than in
412 some other paddy fields (Desplanques et al., 2006). Taking into account the ASi_{ZB} fraction,
413 the proportion of Si located in primary silicates would be at least 75%.

414 The $\delta^{30}\text{Si}$ of primary minerals can be assimilated to the whole bedrock signature (-0.34 ‰)
415 determined for the Mule Hole watershed. Soil clays of Mandya display $\delta^{30}\text{Si}$ of -
416 1.09 ± 0.06 ‰, slightly heavier but close to the Mule Hole Ferralsol clays (-1.3 ± 0.15 ‰).
417 This confirms that the fractionation factor ($^{30}\epsilon$) between bedrock and clay in this weathering
418 context is lower than that predicted by models (Meheut et al., 2007) or measured in tropical
419 (Ziegler et al., 2005) or boreal (Georg et al., 2007) soils. The slightly heavier $\delta^{30}\text{Si}$ in

420 Mandya's clay could however be explained by a minor contribution of silica adsorbed onto
421 ferrihydrite in the clay-size fraction, since the granulometric fraction recovered contained
422 more Fe than Si (Table 4). The $\delta^{30}\text{Si}$ of soil ASi_{ZB} fractions were corrected, when needed,
423 from clay contribution using the purity index described in section 2.3. Correction consists in
424 extrapolating the mixing curve between clay and ASi to a purity index of 1 (Fig. 4). Both
425 ASi_{ZB} compositions align on the same mixing curve which tends towards $\delta^{30}\text{Si}$ of 0.5 ‰.

426

427 **2.5 ASi stock and $\delta^{30}\text{Si}$ of rice plants, algal mats and DE**

428 The rice biomass, Si content in rice and its $\delta^{30}\text{Si}$ signature are presented in Table 5. Because
429 root Si accounts for only few percent of the total Si taken up by rice plants (Ding et al., 2005;
430 Sun et al., 2008), straw (stem and leaves) and whole grain (grain and husk) represent the bulk
431 rice Si uptake. Average straw biomass and grain weights harvested in the four rice plots are
432 7.96 ± 0.60 tons ha^{-1} and 6.12 ± 0.26 tons ha^{-1} , respectively. In the rice+DE plots, straw
433 biomass is significantly higher, 10.3 ± 0.5 tons ha^{-1} , for a similar whole grain (grain + husk)
434 yield as rice experiments, 6.33 ± 0.71 tons ha^{-1} . Average straw Si contents in rice and rice+DE
435 experiments are comparable, 4.72 ± 0.72 % and 5.77 ± 0.30 %, respectively. These values fall
436 in the upper side of the range found in China by Ding et al. (2005) but are twice higher than in
437 Camargue (South of France; Desplanques et al., 2006). Whole grain Si contents (including
438 husk), 0.55 ± 0.09 and 0.59 ± 0.04 %, respectively, are also similar to the husk and grain
439 values of Ding et al. (2005) and Sun et al. (2008). The average Si uptake in rice experiments,
440 deduced from biomass and ASi data, are 377 ± 81 kg ha^{-1} (1.34 ± 0.29 molSi m^{-2}) in straw
441 and 33.3 ± 6.3 kg ha^{-1} (0.12 ± 0.02 molSi m^{-2}) in grains, comparable to Desplanques et al.
442 (2006) and in rice+DE experiments 595 ± 54 kg ha^{-1} (2.12 ± 0.19 molSi m^{-2}) in straw and
443 37.5 ± 4.5 kg ha^{-1} (0.13 ± 0.02 molSi m^{-2}) in grains. The Si uptake by the whole plants is then
444 significantly higher in rice+DE experiments, 2250 ± 180 mmolSi m^{-2} , than in rice ones,
445 1460 ± 270 mmolSi m^{-2} . The $\delta^{30}\text{Si}$ in rice compartments evolves from about 1 ‰ in the straw
446 to 2 ‰ in the whole grain (Table), in agreement with the enrichment of heavy isotopes
447 observed in the highest parts of the plant (Ding et al., 2005; 2008, Sun et al., 2008; 2016).
448 Bulk rice $\delta^{30}\text{Si}$ of rice experiments, 1.29 ± 0.07 ‰, is significantly different from the bulk rice
449 of rice+DE experiments, 0.99 ± 0.07 ‰. Both are 1 ‰ higher than the values observed up to
450 now in rice, all close to 0 ‰ (Ding et al., 2005; 2008, Sun et al., 2008).

451 The $\text{ASi}_{\text{ZB corr}}$ fractions of the four algal mats (one per experiment) range between 0.7
452 (rice+DE) to 2.0 % (bare+DE) (Table 4). Although the presence of few diatom frustules in

453 algal mats was attested by scanning electron microscopy, the $ASi_{ZB\ corr}$ contents in algal mats
454 is not significantly different from soils. One reason could be that because soil ASi is high, the
455 algae bloom has little effect on the total ASi at soil surface. Three over the four $\delta^{30}Si$ of algal
456 mat ASi_{ZB} fall within a mixing between clays and a range of ASi end-member from +0.5 to
457 +1.5 ‰ (Fig. 4), encompassing the straw $\delta^{30}Si$ (+1 ‰). In absence of pure algae analysis,
458 some uncertainty remains on the $\delta^{30}Si$ of algal mat $ASi_{ZB\ corr}$.
459

460 **3 Discussion**

461 *3.1 Validation of Na- and Cl-based mass balances*

462 The high DSi and Na concentrations in the bore-well makes irrigation the unique solute
463 source (>99 %) of these elements to the plot (Table 2). Bore-well represents also the dominant
464 source of Cl (93 %) and makes the KCl contribution marginal (~6 %) although this latter is
465 still 12 times higher than the rainwater contribution (0.5 %). Such situation is representative
466 of the intensive agriculture context in Peninsular India, which relies massively on bore-well
467 irrigation since two decades (Shah, 2014) and is responsible for the degradation of
468 groundwater quality (Siva Soumya et al., 2013; Buvaneshwari et al., 2017). Applying CMB
469 method in this context is unusual, as in most systems studied up to now it was considered that
470 Cl originates only from the atmosphere (Dettinger 1989, Maréchal et al., 2009) or from KCl
471 (Tyner et al., 2000). Since bore well water composition was stable over the duration of the
472 experiment, the Si, Cl and Na input fluxes to each plot could be precisely determined. In the
473 stagnant water (above-ground samples and 1cm-deep Rhizons of all experiments), the
474 covariation of Cl and Na concentrations reflects the evaporation/dilution cycles of the
475 irrigation water (Fig. 2a) and cannot be explained by interactions with soil particles nor
476 plants. Then, above the ground the conservative behavior of Cl and Na is validated,
477 confirming their pertinence for estimating the evaporation at the ground surface (Eq. 3) and
478 the DSi removal from stagnant water.

479 Soil pore waters could be recovered only once during the reproducing stage, i.e. when the rice
480 plants had grown up, which is a possible limitation of the approach. Taken as a whole,
481 chemical composition of pore waters displays a Na vs Cl relationship more scattered than for
482 surface waters. Moreover, the deepest pore waters from the rice experiments plot above the
483 area defined by above-ground waters (Fig. 2c). This relative Na-enrichment can be explained
484 by Na addition and/or a Cl removal from pore water combined with high evapotranspiration.

485 Since the main source of Na in local soils is Na-plagioclase (Riotte et al., 2014), Na addition
486 would imply a slight but significant weathering of this primary mineral in rice experiments.
487 Alternatively, a combination of partial Cl removal by plant uptake with high
488 evapotranspiration would be consistent with (1) the evapotranspiration intensity at the period
489 of coring which is known to be maximum at this crop stage III (reproductive; e.g. Tyagi et al.,
490 2000) and (2) the soil-to-plant transfer of chloride of 5% and the Cl concentrations in above-
491 ground rice biomass, from 0.14 g kg⁻¹ dry wt in polished rice to 4.8 g kg⁻¹ in roots (Tsukada
492 and Takeda, 2008). While it was not possible to quantify the extent of Na addition and/or Cl
493 removal, the soil pore water compositions at least indicate that in rice experiments Na and/or
494 Cl are not conservative. The main consequence for the solute mass balance within the soil
495 layer of this experiment should be an underestimation (Na-based) or an overestimation (Cl-
496 based) of soil leaching water flux. Indeed, Cl-based and Na-based soil leaching fluxes, 457
497 and 229 mm respectively, flank the value deduced from actual evapotranspiration, 391 mm.
498 Although the relative uncertainty on the soil leaching water flux is large, the incidence on the
499 Si solute budget is limited because of the low DSi concentrations of deep soil pore waters.
500 According to the calculation of water flux, soil leaching Si flux in the rice experiment range
501 only from 30 to 55 mmolSi m⁻². Then, the DSi flux removed from the soil layer, calculated by
502 difference between DSi soil input and output would only range within 210 and 240
503 mmolSi m⁻², under the conditions which this mass balance was performed, i.e. in absence of
504 monitoring of soil pore water composition. To summarize, Na and Cl exhibit conservative
505 behaviors above the ground but not within the soil layer of rice experiments. Nevertheless,
506 because Na and Cl behave in opposite ways, the former slightly added to the system and the
507 latter slightly removed, they can provide a range for the soil leaching water flux. The
508 precision associated to a solute budget within the soil layer, deduced from Na and Cl mass
509 balance, shall mostly depend on the difference between input and output DSi concentrations.
510

511 ***3.2 Controls of DSi and $\delta^{30}\text{Si}$ - DSi above the ground surface***

512 Solute budgets indicate that above-ground processes affect DSi mass balance of all
513 experiments, with different intensities for bare and rice experiments but no visible influence
514 of DE addition. Two processes could be envisaged for explaining above-ground DSi removal
515 in bare plots, diatom uptake and/or adsorption on Fe-oxyhydroxides. Since soil Si pools are
516 large compared to the DSi flux removed during a cropping season, none of these processes is
517 expected to significantly change the size or the isotopic composition of soil pools. For

518 instance, if DSi removal would only originate from diatom blooms, the algal mat would
519 contain at best 10% more ASi than the soil if the sample collected at the ground surface would
520 be 3mm thick. Such a limited increase lies within the uncertainty of ASi determination and
521 prevents quantification of this process, although few diatom frustules were observed by
522 scanning electron microscope. An alternative way to assess the importance of diatom uptake
523 and/or adsorption on Fe-oxyhydroxides is to consider the kinetics of these processes. In batch
524 experiments with solid/liquid ratio as low as 1/250 and similar initial DSi concentration,
525 Delstanche et al. (2009) observed that 40% of DSi is absorbed onto Ferrihydrite after 72 hours
526 and 25% onto Goethite after 500 hours. In paddy field conditions where the solid/liquid ratio
527 is ten to hundred times higher than in this batch experiment, DSi removal rate should increase
528 in same proportions as the solid/liquid ratio and induce a drop in DSi within few hours after
529 irrigation.

530 During these experiments, the level of DSi in 1cm-Rhizons or above-surface samples was
531 nearly always depleted compared to the borewell, even when waters were collected soon after
532 irrigation. The intensity and rate of DSi removal is visible when DSi is compared to Na
533 concentrations (Fig. 2b): for most samples, DSi drops while Na remains at the borewell
534 concentration. For instance, a 30% DSi depletion was observed within the 100 m-long open
535 channel separating the bore-well from the experimental plots, during a previous experiment
536 (the channel was replaced by a pipe avoid Si depletion by delivering irrigation water directly
537 to the plot, Fig. 2b) which attests that DSi depletion is almost immediate and incompatible
538 with the timescale of diatom growth, typically few days whatever the temperature, nutrient
539 and light conditions (e.g. Litchman et al., 2003; Schabhüttl et al., 2013).

540 The DSi removal above the ground surface fractionates Si isotopes according to an isotopic
541 fractionation factor ($^{30}\epsilon$) that depends upon the process at stake. For instance, $^{30}\epsilon$ induced by
542 diatom uptake ($-1.12 \pm 0.2 \text{ ‰}$, Alleman et al., 2005; $-1.04 \pm 0.08 \text{ ‰}$, Opfergelt et al., 2011)
543 and adsorption onto ferrihydrite ($-1.08 \pm 0.06 \text{ ‰}$, Delstanche et al., 2009) induce smaller
544 isotopic fractionation than Si adsorption onto goethite ($-1.62 \pm 0.24 \text{ ‰}$; Delstanche et al.,
545 2009). Thanks to the solute mass balance (see section 3.2), the residual fraction of DSi in
546 above-ground water could be estimated for each sample and the $^{30}\epsilon$ of above-ground DSi
547 removal deduced graphically using the initial borewell composition, the DSi- $\delta^{30}\text{Si}$ and the
548 residual fractions of DSi. Residual fractions of DSi were calculated by three ways, (1)
549 considering Na as conservative element (Fig. 5a), (2) considering Cl as conservative element
550 (Fig. 5b) and (3) directly from the DSi fraction (Fig. 5c). It can be seen from Fig. 5 that

551 $^{30}\epsilon$ vary slightly according to the way residual fraction is calculated. However, several
552 consistent insights can be drawn from these graphs. First, data fit better a Rayleigh model than
553 a steady state one, particularly bare experiments which display higher DSi- $\delta^{30}\text{Si}$ than rice
554 ones and larger isotopic fractionation factors, between -1.5 to -2.5 ‰ depending on residual
555 fraction calculation (considering the 1cm rhizon of bare experiment (B) as an outlier in Fig.
556 5a and 5b). These values confirm that the evolution of DSi and DSi- $\delta^{30}\text{Si}$ above the ground
557 surface cannot be explained by diatom uptake. Indeed, the fast decrease of DSi above the
558 ground even led in several samples to isotopic fractionations even larger than those expected
559 from adsorption onto goethite. This could be linked to the kinetics itself that would enhance
560 preferential removal of light isotopes compared to ^{30}Si . Second, in rice experiments the
561 apparent isotopic fractionation factors were smaller than in bare ones and ranged between -1
562 (value for rice; Ding et al.; 2008) and -1.5 ‰, which means that in rice and rice+DE
563 experiments both plant uptake and adsorption compete for DSi removal. Since the $^{30}\epsilon$ of DSi
564 removal in rice experiments is close to -1 ‰ (value for rice plant), it is likely that plant uptake
565 dominates DSi removal. Therefore, it will be assumed in the further discussion that above-
566 ground plant uptake ranges from 140 to 270 mmolSi m⁻². Third, in agreement with the above
567 ground-surface DSi solute mass balance (Table 3), the DE application did not impact the DSi
568 above-ground budget nor DSi- $\delta^{30}\text{Si}$ which confirms that above-ground processes do not
569 involve soil particles dissolution.

570

571

572 In regions covered with paddy fields, irrigation water is transported by canal from the river to
573 the paddy fields located at the highest topographical position and then passes by gravity
574 through many terraces before returning to the river. It is then likely that interactions of
575 irrigation water with the succession of soil surfaces should amplify the Si adsorption onto Fe-
576 oxy-hydroxides. According to the batch experiments of Delstanche et al. (2009), the fraction
577 of DSi removed by adsorption onto Fe-hydroxides depends on the initial DSi concentration.
578 In the case of goethite, the fraction adsorbed is inversely proportional to the initial DSi, and
579 can reach >70% when initial DSi is 210 $\mu\text{mol L}^{-1}$ (lowest initial DSi tested by these authors),
580 against 45% for an initial DSi of 1290 $\mu\text{mol L}^{-1}$. Although the trend is less clear for
581 ferrihydrite experiments, DSi adsorption still accounts for more than 60% for the lowest
582 initial DSi concentration. According to the compilation from Gaillardet et al. (1999), DSi of
583 major rivers rarely exceeds 200 $\mu\text{mol L}^{-1}$, the world average being only 127 $\mu\text{mol L}^{-1}$. Low
584 DSi in rivers could then contribute to increase the proportion of adsorbed DSi in regions

585 where paddy fields are irrigated by surface water. In this context, our field experiments and
586 the adsorption experiments of Delstanche et al. (2009) provide an alternative or at least
587 additional explanation for the heavy $\delta^{30}\text{Si}$ observed in Asian rivers like the Yangtze River
588 (Ding et al., 2004), the Nile River (Cockerton et al., 2013) or some tributaries of the Ganga
589 (Fontorbe et al., 2013, Frings et al., 2015) where paddy fields and wetlands are widespread.
590 The extreme $\delta^{30}\text{Si}$ values downstream the Yangtze River for instance, up to 3.7‰, fall within
591 the range observed in the 1cm rhizons and above-surface waters of our experiments. If they
592 were assigned to plant uptake in paddy fields and wetlands by Ding et al. (2004), we suggest
593 here that these $\delta^{30}\text{Si}$ values result at least partly from Si absorption onto soil particles. In these
594 regions, both processes contribute to large DSi removal from aquatic systems, unlike what is
595 observed in temperate climate for instance (Clymans et al., 2011). More detailed studies
596 would be needed to estimate the respective roles of adsorption and plant uptake on extreme
597 riverine $\delta^{30}\text{Si}$ values in basins where paddies and/or wetlands are widespread.

598

599 **3.3 Controls of DSi and $\delta^{30}\text{Si}$ - DSi within the soil**

600 Depending of leaching calculation methods, the DSi flux leached from the 20cm topsoil layer
601 ranges from 30-55 mmolSi m⁻² (rice) to 40-80 mmolSi m⁻² (bare+DE) (Table 3), which
602 overall corresponds to 5 to 15% of the initial DSi supply to each plot. DSi leaching from
603 bare+DE and rice+DE experiments are slightly higher than from bare and rice experiments,
604 indicating that the DE applied may have contributed to DSi budget and plant uptake in the
605 20 cm topsoil layer. Such values are nearly three orders of magnitude lower than those
606 proposed by Nguyen et al. (2016) from HYDRUS modeling in a Vietnamese crop experiment
607 but closer to the solute balance performed by Klotzbücher et al. (2015) in Philippines, i.e.
608 more humid climate than Mandya. The apparent DSi flux removed from the soil layer (ΔFSi ,
609 corresponding to the difference, in Table 3, between soil input and soil output) is
610 paradoxically higher in bare and bare+DE experiments (275-325 and 255-300 mmolSi m⁻²,
611 respectively) than in rice and rice+DE experiments (210-240 and 190-245 mmolSi m⁻²,
612 respectively). However, if one includes the additional 140 to 270 mmolSi m⁻² taken up by rice
613 plant above soil surface (see previous section), the ΔFSi values are equivalent for all
614 experiments. As for the above-ground balance, this does not mean that the processes
615 responsible for the DSi removal in bare and rice experiments are the same.

616 In bare experiments, the smooth decrease of DSi with depth corresponds to a process
617 occurring along with water percolation, such as DSi adsorption and clay minerals

618 precipitation. However, according to the Si isotopic fractionation factors estimated up to now
619 for DSi adsorption ($^{30}\epsilon = -1\text{‰}$; Delstanche et al., 2009; Opfergelt et al., 2009) or clay
620 minerals formation ($^{30}\epsilon = -1$ to -2‰ ; Ziegler et al., 2005; Georg et al., 2007; Méheut et al.,
621 2007), these two processes should have depleted the residual soil pore water in light Si
622 isotopes and then induce an increase of $\delta^{30}\text{Si-DSi}$. Instead, $\delta^{30}\text{Si}$ decreased by about 1‰
623 between soil surface and 15-20 cm depth. The theoretical $\delta^{30}\text{Si}$ associated to the DSi removal
624 ($\delta^{30}\text{Si}_{\Delta\text{FSi}}$, calculated with Eq. 6) in bare and bare+DE experiments would then range from
625 3.70 to 3.84 ‰ and from 4.53 to 4.80 ‰ (Table 3), respectively; i.e. 0.1 to 0.4 ‰ higher than
626 the $\delta^{30}\text{Si}$ of the input flux. Such signatures are incompatible with the signatures measured in
627 the soil silica pools, which suggests that Si removal is not the unique process controlling DSi
628 and $\delta^{30}\text{Si-DSi}$ in the soil. The $\delta^{30}\text{Si-DSi}$ values points to concomitant, isotopically light silica
629 release from soil particles like Si desorption (then partial isotopic exchange during DSi
630 adsorption) or mineral dissolution. Desorption would mean silica exchange with the adsorbed
631 pool of Si of the soil. Since the isotopic signature of the exchangeable pool cannot be
632 determined, the extent of this process cannot be assessed. However, its effect on $\delta^{30}\text{Si-DSi}$
633 was already suspected during an adsorption experiment performed on lateritic soils of
634 Cameroon (Opfergelt et al., 2009). The soil silicates susceptible to weather and release silica
635 encompass primary minerals (quartz, Na-plagioclase), secondary clay minerals and opal
636 (ASi). According to the saturation indexes calculated by PHREEQS, quartz and clay minerals
637 would be stable but soil pore waters would be undersaturated regarding to ASi (-0.5 to -0.7)
638 and Na-plagioclase (-13 to -15 assuming Al concentration of 1 ppm). Na-plagioclase
639 weathering could be consistent with the Na excess observed in soil pore waters (Fig. 2c), but
640 both ASi dissolution and Na-plagioclase weathering are expected to contribute to soil DSi.
641 In rice experiments, the DSi drop just below ground-surface to values as low as $100\ \mu\text{mol L}^{-1}$
642 or less, was also observed in hydroponic conditions (Ding et al., 2008). Both Na and Cl
643 concentrations increase while DSi decreases which confirms that Si uptake by the rice plant is
644 predominantly selective and then occurs via an active mechanism (e.g. Sun et al., 2016).
645 Because of the Si uptake efficiency, the plants could bring pore water DSi concentration low
646 enough to modify the saturation regarding soils minerals. In several samples DSi was for
647 instance lower than saturation with quartz ($100\ \mu\text{mol L}^{-1}$). The few pore waters recovered by
648 hydraulic press (labelled “HP” in Table 2) systematically exhibited lower concentration than
649 centrifuged ones; the water located in the smallest pores, where roots are more susceptible to

650 take up nutrients, are indeed more Si depleted than in macro-pores. It is then possible that the
 651 undersaturation with soil minerals is more pronounced in these pores than in macro porosity.

652 **3.4 Isotopic mass balance of rice and possible Si sources**

653 Estimating the Si sources to rice plant is possible because the cumulated uncertainty
 654 associated to adsorption and soil leaching flux has a little impact on the estimation of DSi
 655 contribution to plant uptake, which ranges from 25 to 35 % in rice experiments and from 15 to
 656 23 % in rice+DE ones. The soil pool contributing to plant uptake can be assessed once
 657 deduced in this latter the contribution of irrigation DSi. If the total silica taken up by the rice
 658 plant (FSi_{plant}) is considered as mix of silica coming from irrigation water (ΔFSi) and from
 659 soil mineral weathering, its isotopic composition can be described as:

$$660 \quad \delta^{30}Si_{plant} = \frac{\Delta DSi \cdot \delta^{30}Si_{F\Delta DSi} + (FSi_{plant} - F\Delta DSi) \cdot \delta^{30}Si_{soil\ pool}}{FSi_{plant}} \quad (7)$$

662 where $\delta^{30}Si_{F\Delta DSi}$ is the $\delta^{30}Si$ of irrigation DSi taken up by plants. This isotopic signature can be
 663 roughly estimated if one assumes that its evolution during uptake follows a Rayleigh model,
 664 which is a working hypothesis, by the relationship:

$$665 \quad \delta^{30}Si_{F\Delta DSi} = \delta^{30}Si_{borewell} - {}^{30}\epsilon_{rice} \cdot f_{F\Delta DSi} \cdot \frac{\ln(f_{F\Delta DSi})}{1 - f_{F\Delta DSi}} \quad (8)$$

668 Where $f_{F\Delta DSi}$ is the fraction of DSi remaining in soil pore water after plant uptake:

$$670 \quad f_{F\Delta DSi} = \frac{FDSi_{borewell} - FDSi_{plant\ uptake}}{FDSi_{borewell}} \quad (9)$$

672 According to the ranges of DSi uptake estimated for each experiment, $f_{F\Delta DSi}$ of rice
 673 experiment would span from 0.06 to 0.34 and $f_{F\Delta DSi}$ of rice+DE from 0.05 to 0.39. The
 674 $\delta^{30}Si_{F\Delta DSi}$ associated to DSi uptakes (Eq. 8), using the ${}^{30}\epsilon_{rice}$ range from -0.4 to -1 ‰ (Sun et
 675 al., 2016), would be equivalent for rice and rice+DE experiments, from 0.93 to 1.42 ‰ and

677 from 0.89 to 1.43 ‰, respectively. Then, the isotopic signature of the complementary soil
678 source to the plant ($\delta^{30}\text{Si}_{\text{soil pool}}$) can be estimated according to the equation:

679

$$680 \quad \delta^{30}\text{Si}_{\text{soil pool}} = \frac{F\text{Si}_{\text{plant}} \cdot \delta^{30}\text{Si}_{\text{plant}} - \Delta F\text{Si} \cdot \delta^{30}\text{Si}_{\Delta F\text{Si}}}{F\text{Si}_{\text{plant}} - \Delta F\text{Si}} \quad (10)$$

681

682 The $\delta^{30}\text{Si}_{\text{soil pool}}$ of rice and rice+DE experiments would then range from 1.22 to 1.41 ‰
683 and from 0.75 to 1.01 ‰, respectively. Accordingly, the complete isotopic mass balance of Si
684 at the soil-plant scale can be summarized (Fig. 6).

685 These heavy isotopic signatures confirm that clay and primary minerals do not significantly
686 contribute to plant-Si. Without discarding a slight contribution of particle desorption, of
687 which the $\delta^{30}\text{Si}$ cannot be measured or assessed, the closest $\delta^{30}\text{Si}$ among soil Si pools and
688 most likely soil source would then be soil ASi. This finding is indeed consistent with the
689 saturation index of soil pore water regarding to opal (see previous section) and with the
690 dissolution rate of ASi; According to batch experiments performed by Fraysse et al, (2009),
691 phytolith dissolution rates at circum neutral pH are several order of magnitude higher than
692 those of kaolinite or plagioclase. It is then likely that the relative excess of Na compared to Cl
693 in soil pore water would rather correspond to a slight Cl depletion. The isotopic fingerprint of
694 ASi in rice plant confirms the role of this specific soil pool as source of Si in rice, as proposed
695 by some authors from solute mass balance (e.g. Desplanques et al., 2006). However, it should
696 be stressed that contrary to Camargue or other places where irrigation DSi is low and rice
697 straw removed from field, leading to ASi depletion in these soils, the soil ASi contents in soils
698 of our study were remarkably high because of local practices. In our context, the risk of ASi
699 depletion in soils is limited, although rice cultivation is intensive. The $\delta^{30}\text{Si}$ of rice plants is
700 sensitive to the most available Si of the soil, as illustrated by the $\delta^{30}\text{Si}_{\text{soil pool}}$ of both
701 experiments that do not overlap with values in rice+DE experiment about -0.3 ‰ lower than
702 those of rice one. The amount of Si applied by DE corresponds to only 14% of biomass-Si in
703 rice+DE and does not explain the 54% difference with rice experiment. But the $\delta^{30}\text{Si}$ of DE, -
704 0.36 ‰, was contrasted enough to slightly influence the isotopic signature of biomass in
705 rice+DE. Then, it is likely that DE was at least partly incorporated by the plant as a
706 supplementary source of Si and played a role of priming effect, as for N fertilizer (e.g.
707 Jenkinson et al., 1985; Kuzyakov et al., 2000), which induced a higher Si uptake by the plant.

708 The main implication of this isotopic mass balance is that rice could be able to take Si from a
709 solid source (ASi) without significant isotopic fractionation. Finally, replicating such
710 experiments in conditions of low silica availability (ASi-poor soils and irrigation with low
711 DSi water) would probably reveal a different distribution of silica sources to the plant.
712

713 **4 Conclusion**

714 By combining data on water, soil and plants we have shown that Si isotopic signatures are
715 useful for constraining the dynamics of Si in a paddy fields. A significant DSi removal
716 occurred very soon after plot irrigation consistent with adsorption in bare soils. Within the soil
717 layer, pore water DSi and $\delta^{30}\text{Si}$ exhibited a sharp decrease in rice experiments which
718 illustrated the active DSi uptake by rice within the soil. The DE application was also traced by
719 a slightly lighter Si isotope signature in the soil solution. At the field scale, our results puts
720 constraints for a better understanding on the effects of soil Si application. At the global scale,
721 the results highlight a possible DSi sink in wetlands, even in not vegetated areas, that could be
722 responsible of the high $\delta^{30}\text{Si}$ observed in some tropical rivers.
723

724 *Acknowledgements*

725 The study was supported by the Indo-French Centre for the Promotion of Advanced Research
726 (IFCPAR/CEFIPRA; Project n°5109-1) and the French Institute for Research and
727 Development (IRD, France) which funded deputation of J. Riotte and long duration stays of
728 J.D. Meunier. The authors thank the two anonymous reviews for their useful comments on the
729 manuscript. Hemanth Moger and Jean-Louis Duprey are thanked for the chemical analyses,
730 Jonathan Prunier and Manuel Henry for their support in clean room and the personnel of VC
731 farm at Mandya for their help during the rice cropping experiment.

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