

1 **Ca isotope constraints on chemical weathering processes:**
2 **Evidence from headwater in the Changjiang River, China**

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19 **Manuscript submitted to *Chemical Geology* (14-June-2019)**

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27 **Abstract**

28 This study aims to clarify the relationship between chemical weathering of
29 rocks and the carbon budget of rivers and to better understand the weathering
30 mechanisms of plateau watersheds. We chose to study the Jinsha River, which
31 originates from the Tibetan Plateau and also is in the upper reaches of the
32 Changjiang River. Analysis of hydrochemistry, radiogenic strontium isotope and
33 stable calcium isotopes were conducted of the Jinsha River water samples,
34 which were collected along its mainstream and main tributaries in the summer.
35 The results show that the water chemistry of the mainstream is dominated by
36 evaporite weathering, which has a low $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7098 to 0.7108) and wide
37 range of Sr contents (2.70 to 9.35 $\mu\text{mol/L}$). In contrast, tributaries of the Jinsha
38 River have higher $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7090 to 0.7157) and lower Sr contents ($\sim 1\mu\text{mol/L}$).
39 Moreover, the Ca isotopic compositions in the mainstream (0.87-1.11‰) are
40 heavier than the tributaries (0.68-0.88‰) and could not attribute to the
41 conventional mixing of different sources. We suggest that secondary carbonate
42 precipitation fractionates Ca isotopes in the Jinsha River, and fractionation
43 factors are between 0.99935 and 0.99963. At least 66% of dissolved Ca is
44 removed in the mainstream of the Jinsha River through secondary mineral
45 precipitation, and the average value is $\sim 35\%$ in the tributaries. The results
46 highlight that evaporite weathering results in more carbonate precipitation
47 influencing Ca transportation and cycling in the riverine system constrained by
48 stable Ca isotopic compositions and water chemistry.

49 **Key words:** Ca isotopes, Chemical weathering, Secondary carbonate
50 precipitation, Isotope fractionation.

51

52 **1. Introduction**

53 Calcium is the fifth most abundant element in the earth's crust and can
54 migrate easily between major geochemical reservoirs at the Earth's surface
55 ([Rudnick and Gao, 2014](#); [Tipper et al., 2016](#)). As one of major components of
56 rock and minerals, Ca is participant in many critical processes related to the co-
57 evolution of earth and life, including carbon cycling, the evolution of marine
58 chemical components and long-term climate change ([Berner and Berner, 2012](#);
59 [Berner, 2003](#); [Berner et al., 1983](#); [Walker et al., 1981](#)). Chemical weathering of
60 rocks and minerals plays a key role in those processes, in which rocks and
61 minerals react with dissolved acidic gases (such as CO₂ and SO₂) and water in
62 the atmosphere, releasing dissolved metal ions and forming secondary
63 minerals. Solutes are transported to the ocean through rivers, regulating the
64 chemical balance of seawater and absorbing CO₂ in the atmosphere to bury
65 them in the form of carbonate ([Gaillardet et al., 1999](#); [Schmitt et al., 2003](#); [West
66 et al., 2005](#); [White and Blum, 1995](#)). Other products of rock weathering, such
67 as clay minerals, will be accumulated to the floodplain along the river, forming
68 an important part of soil ([Tipper et al., 2006](#); [Torres et al., 2015](#); [West et al.,
69 2005](#)).

70 Riverine input of Ca is a key component in the global Ca model, where

71 oceans impact climate through regulation of atmospheric CO₂ ([Gaillardet et al.,](#)
72 [1999](#)). The study of Ca fluxes and their isotopic compositions in rivers could
73 help understand whether Ca in the ocean is in equilibrium ([DePaolo, 2004;](#)
74 [Schmitt et al., 2003;](#) [Tipper et al., 2010;](#) [Zhu and Macdougall, 1988](#)). This also
75 determines whether the Ca isotopes can be used as an indicator for the study
76 of the paleo-ocean to explore paleo-sea surface temperature (SST) and its
77 corresponding P_{CO2}, which are closely related to long-term climate change
78 ([DePaolo, 2004;](#) [Fantle, 2010, 2015;](#) [Fantle and DePaolo, 2005;](#) [Pogge von](#)
79 [Strandmann et al., 2013;](#) [Pogge von Strandmann et al., 2012;](#) [Rocha and](#)
80 [DePaolo, 2000](#)). On the other hand, riverine Ca fluxes produced by rock
81 weathering are an important part of the ocean Ca budget, which has a
82 significant impact on the global carbon cycle together with the precipitation of
83 carbonate in the ocean ([Schmitt, 2016;](#) [Tipper et al., 2016](#)). Many studies have
84 focused on the behavior of Ca isotopes during rock weathering and material
85 transport by rivers ([Cenki-Tok et al., 2009;](#) [Fantle and Tipper, 2014;](#) [Hindshaw](#)
86 [et al., 2013;](#) [Hindshaw et al., 2011;](#) [Jacobson et al., 2015;](#) [Lehn et al., 2017;](#)
87 [Marie-Laure Bagard et al., 2013;](#) [Marie-Laure Bagard et al., 2011;](#) [Moore et al.,](#)
88 [2013;](#) [Schmitt, 2016;](#) [Schmitt et al., 2003;](#) [Tipper et al., 2006;](#) [Tipper et al., 2010;](#)
89 [Tipper et al., 2008;](#) [Tipper et al., 2016;](#) [Wiegand and Schwendenmann, 2013](#)).
90 Ca isotopes could not only trace the Ca cycle directly but also be a potential
91 tracer in mineral carbonation and the C cycle ([Pogge von Strandmann et al.,](#)
92 [2019a](#)).

93 Previous studies show that Ca isotopes in rivers may mainly controlled by
94 different factors across different scales. For small rivers, a variety of factors
95 result in changeable Ca isotopic compositions ($\delta^{44/40}\text{Ca}$) which exhibit a wide
96 range from 0.27 to 1.70‰. Ca isotopic compositions are not only controlled by
97 mixing of different sources, such as lithology, underground water and soil water
98 ([Hindshaw et al., 2011](#); [Jacobson et al., 2015](#); [Jacobson and Holmden, 2008](#);
99 [Jacobson and Wasserburg, 2005](#)), but also by secondary processes, such as
100 the uptake of plants ([Brazier et al., 2019](#); [Cenki-Tok et al., 2009](#); [Farkaš et al.,](#)
101 [2011](#); [Hindshaw et al., 2012](#); [Holmden and Bélanger, 2010](#); [Schmitt et al., 2017](#)),
102 the neoformation of secondary mineral phases (soil carbonates, travertines and
103 Ca-bearing clays) ([Hindshaw et al., 2013](#); [Tipper et al., 2006](#)) and the
104 adsorption by clays ([Brazier et al., 2019](#); [Ockert et al., 2013](#)). With regards to
105 world rivers, although complex lithology and variable climate and vegetations
106 result in different hydrochemistry and Sr isotopic compositions, the ratios of Ca
107 isotopes are quite homogeneous ([Schmitt, 2016](#)). Samples collected at river
108 mouths show small $\delta^{44/40}\text{Ca}$ variations of 0.56‰, ranging from 0.69 to 1.25‰
109 with an average of 0.86‰ ([Schmitt et al., 2003](#); [Tipper et al., 2010](#); [Zhu and](#)
110 [Macdougall, 1988](#)). The main controlling factors of Ca isotopes in world rivers
111 are still controversial. Fantle and Tipper ([2014](#)) calculated the average Ca
112 isotopic composition of carbonate and silicate as 0.6‰ and 0.94‰ respectively.
113 Combined with the global riverine Ca flux, the mean theoretical Ca isotope ratio
114 of the riverine flux is 0.63 to 0.69‰, which is lower than the measured value of

115 continental runoff ($0.86 \pm 0.06\%$) ([Tipper et al., 2016](#)). Therefore, they
116 suggested that secondary processes, such as the plant uptake, secondary
117 mineral formation and clay adsorption, play an important role in the riverine Ca
118 isotopic composition. However, Jacobson et al. ([2015](#)) analyzed riverine Ca
119 isotope values in Iceland, and demonstrated that the dissolution of
120 hydrothermal calcite in basalt dominates the Ca isotopic ratios of river in Iceland.
121 They also suggested that conventional mixing processes stemming from
122 mineral dissolution dominates the Ca isotopic compositions of global rivers.
123 These studies suggested riverine Ca behavior relating with geological
124 characteristics were not well explored and the dominant factors controlling
125 riverine Ca isotopes still need to be further clarified.

126 Overall, the monitoring of Ca isotope behavior along rivers is still lacking
127 ([Schmitt et al., 2003](#); [Tipper et al., 2010](#); [Zhu and Macdougall, 1988](#)). Although
128 the factors affecting the Ca isotope value of rivers can be evaluated qualitatively,
129 some critical isotope signals may be overprinted ([Hindshaw et al., 2013](#)),
130 meaning that it is difficult to fully understand and interpret Ca isotope ratios.

131 Moreover, abundant previous studies focus on silicate weathering ([Cenki-](#)
132 [Tok et al., 2009](#); [Hindshaw et al., 2013](#); [Hindshaw et al., 2011](#); [Holmden and](#)
133 [Bélanger, 2010](#); [Marie-Laure Bagard et al., 2013](#); [Nielsen and DePaolo, 2013](#);
134 [Schmitt et al., 2003](#); [Wiegand and Schwendenmann, 2013](#)), and several
135 researchers have studied the effect of sedimentary rocks weathering on carbon
136 budget ([Gaillardet et al., 2018](#); [Lehn et al., 2017](#); [Moore et al., 2013](#); [Tipper et](#)

137 [al., 2006](#); [Tipper et al., 2008](#)), but studies on evaporite weathering are very rare
138 ([Wang et al., 2018](#); [Wellman and Wilson, 1965](#)). As a common rock in the earth-
139 surface, evaporites are often accompanied by sedimentary rocks, such as
140 limestone, dolomite and mudstone. Although the total amount of evaporites is
141 less than that of silicates and carbonates, it has great influence on water
142 chemistry owing to its high solubility and fast dissolution rate ([Wang et al., 2018](#);
143 [Wellman and Wilson, 1965](#)). For example, the dissolution of gypsum releases
144 a large amount of Ca into the water, which to a certain extent increases the
145 absorption of CO₂ by the river and affects the overall carbon budget ([Farkaš et](#)
146 [al., 2007](#)). Previous studies on the Ca isotopes of evaporites have been focused
147 on evaporites from seafloor hydrothermal precipitation ([Amini et al., 2008](#);
148 [Blättler and Higgins, 2014](#); [Galy and France-Lanord, 1999](#); [Hensley, 2006](#);
149 [Holmden, 2009](#)) and several laboratory precipitation experiments of anhydrite
150 ([Harouaka et al., 2014](#); [Hensley, 2006](#); [Lemarchand et al., 2004](#)), which were
151 used to assess the impact of seafloor hydrothermal input on marine Ca isotopic
152 compositions. However, evaluations of the influence of continental evaporite
153 weathering on water chemistry and even Carbon budget are still rare ([Jacobson](#)
154 [and Holmden, 2008](#); [Jacobson and Wasserburg, 2005](#); [Russell et al., 1978](#)).

155 In this study, we collected water samples from the mainstream and main
156 tributaries of the upper Jinsha River. Water chemistry in the mainstream is
157 mainly dominated by evaporates dissolution ([Chetelat et al., 2008](#); [Gaillardet et](#)
158 [al., 1999](#); [Noh et al., 2009](#); [Wu et al., 2008](#); [Zhao et al., 2019](#); [Zhong, 2017](#)).

159 Through analyzing data of hydrochemistry, Ca and Sr isotopes in the Jinsha
160 River Basin, the dominant factors controlling the calcium transportation of the
161 Jinsha River are evaluated, then the influence of evaporite weathering on
162 carbon transportation is assessed, which could lay a foundation for further
163 exploring the mechanism of solute transportation impacted by secondary
164 processes in the rivers origin from the Tibetan Plateau.

165

166 **2. Regional setting**

167 The Jinsha River Basin is located in the eastern Tibetan Plateau,
168 Southwest China. As the headwaters of the Changjiang River, the Jinsha River
169 originates at the end of the ice tongue of the Gladandong Mountains in the
170 middle of the Tanggula Mountains in Qinghai Province at an elevation of 6621
171 m. The source river of the Changjiang River is mainly composed of Dangqu
172 (south source), Tuotuo River (the main source) and Chumar River (north
173 source). They converge as the Tongtian River, which flowed southeast to accept
174 the Batang River near Yushu County, Qinghai Province, after which it is called
175 the Jinsha River ([Su and Chen, 2016](#); [Wu et al., 2011](#); [Wu et al., 2009a](#); [Wu et al., 2008](#); [Zhang et al., 2016](#); [Zhao et al., 2019](#)) (Fig. 1a). The Jinsha River has
176 a basin area of 473,640 km² with a mainstream river length of over 2316 km,
177 accounting for 2/3 of the length of the upper reaches of the Changjiang River
178 ([Su and Chen, 2016](#)). The upper, middle, and lower reaches of the river are
179 divided by Shigu and Panzhihua stations. Significant differences in topography
180

181 and geomorphology are observed in the Jinsha River Basin, leading to great
182 differences in regional climate and water cycle processes in the upper, middle
183 and lower reaches ([Xie et al., 2018](#)). The source region of the Jinsha River is
184 located in the southeast of the Qinghai-Tibet Plateau, with an average altitude
185 of more than 5000 m, showing typical plateau landscape where climate is cold
186 and dry. Runoff of source river is mainly supplied by ice and snow melt water
187 and permafrost, so that water cycle is significantly affected by air temperature.
188 The upper reach of the Jinsha River is accompanied by significant topographic
189 differences changing from plateau to typical dry-hot valley. Surrounded by
190 mountains, external water vapor rarely enters, leading to rare precipitation and
191 significant evaporation. The middle reaches of the Jinsha River flow between
192 the deep canyons. The average annual precipitation increases from northwest
193 to southeast, mostly ranging from 600 mm to 1000 mm, and reaches 1300mm
194 in some areas. As to the lower reach of the Jinsha River, terrain changes from
195 canyon to hilly and plain. The average annual precipitation is 600 - 1500 mm
196 and in some areas more than 1800 mm, and the evaporation is small. The water
197 cycle in this area is different from that in the upper and middle reaches on
198 account of the great influence of human activity ([Liu, 2016](#); [Lu et al., 2016](#); [Xie
199 et al., 2018](#); [Zhang et al., 2016](#); [Zhang et al., 2018](#)).

200 The upper and middle reaches of the Jinsha River were selected as our
201 research area because of little anthropogenic impact ([Zhao et al., 2019](#)) (Fig.
202 1). Evaporites weathering significantly affect the Jinsha River mainstream

203 ([Chetelat et al., 2008](#); [Gaillardet et al., 1999](#); [Noh et al., 2009](#); [Zhao et al., 2019](#);
204 [Zhong, 2017](#)). Mesozoic clastic rocks and evaporites are mainly exposed in the
205 source area, and the research area in this study is mainly composed of Triassic
206 low-grade metamorphic rocks, Paleozoic carbonate rocks and basalts,
207 accompanied with scattered Mesozoic granitoids and Mesozoic ophiolitic
208 mélanges along the upper reach valley ([Wu et al., 2009a](#); [Wu et al., 2008](#); [Wu](#)
209 [et al., 2013](#); [Zhang et al., 2016](#); [Zhao et al., 2019](#)).

210

211 **3. Method**

212 **3.1 Water samples**

213 Water samples were collected in June 2016, corresponding to the high flow
214 season. Temperature, electrical conductivity and pH of the water samples were
215 measured in the field. Alkalinity was determined by HCl titration. Water samples
216 were filtered through 0.45 µm cellulose-acetate filters into a series of pre-
217 cleaned HDPE bottles for analysis. Major cations (Ca, Mg, Na, K) and Si
218 concentrations were measured by ICP-OES with a precision better than 5% (2
219 δ_{mean}). Anions (Cl, SO₄) were determined by ionic chromatography Dionex 90
220 with a precision of 5%. The values of partial pressure of CO₂ (P_{CO2}) and calcite
221 saturation index (CSI) were calculated by the programmer PhreeqC ([Parkhurst](#)
222 [and Appelo, 1999](#)).

223

224 **3.2 Sample preparation for isotopic analysis**

225 Both Ca and Sr are recovered together from the AG50 X12 columns.
226 Because Ca is isotopically fractionated by this resin, quantitative recovery is
227 necessary. River samples were dried down and re-dissolved in 1ml ultrapure
228 HNO₃ on a hot plate at 120°C for 24 h They were then dried and cooled down
229 to room temperature, and then re-dissolved in 1ml ultrapure HNO₃ with 100 µL
230 H₂O₂ on a hot plate at 90°C for 1 h to remove organic matter. Note that then
231 these samples also need to be dried down no higher than 90°C to prevent H₂O₂
232 from exploding when heated. After that, they were re-dissolved in 1 ml ultrapure
233 HCl for 1 h and then dried down at 120°C. They were finally dried and re-
234 dissolved in 1ml 2N HCl for chemical purification.

235 The protocols for Ca and Sr separation in this study are modified from ([Chu](#)
236 [et al., 2006](#); [Nan et al., 2015](#); [Owen et al., 2016](#)). The column used a 30mL
237 Teflon® micro-column with 6.4mm ID × 9.6mm OD (Savillex®), filled with 2mL
238 AG50W-X12 resin (200-400 mesh, Bio-Rad, USA). Columns were precleaned
239 with 20mL 6 mol/L HNO₃ and 3mL 6 mol/L HCl, and then conditioned with 3mL
240 18.2 MΩ H₂O, before sample loading.

241 1mL sample solutions containing ~100ug Ca were loaded and 19mL 2
242 mol/L HCl was used to elute the matrix elements including Na, Mg, K, Fe and
243 Mn. Ca was then collected with 18mL 2 mol/L HCl. Following Ca collection, 2mL
244 3 mol/L HCl was used to elute the tailing of trace Ca. Sr was then collected with
245 10mL 3 mol/L HCl. Both 2mL aliquots before and after the Ca-cut were collected

246 and measured for their Ca contents to test whether the Ca elution curve drifted
247 during the chromatographic process. After the column protocols, Ca and Sr
248 collections were dried and dissolved in concentrated HNO₃, evaporated to
249 dryness three times, and finally dissolved in 0.3 mol/L HNO₃ before isotope
250 analysis ([Sun et al., 2019](#)).

251 Ca isotopic analysis was undertaken using the Nu Instruments MC-ICPMS
252 at the Laboratory of Isotope Geology, Institute of Geology, Chinese Academy of
253 Geological Sciences, Beijing, China. Isotopes of ⁴²Ca, ⁴³Ca and ⁴⁴Ca were
254 measured at low-resolution. The standard-sample bracketing (SSB) approach
255 ([Belshaw et al., 2000](#)) was used to correct the mass discrimination, using NIST
256 915a or NIST 915b as the reference standard, and with sample and standard
257 solutions being matched to give ⁴²Ca intensities with differences less than 10%.
258 All samples were normally repeatedly analyzed for 3~5 times for one session.
259 The external precision of Ca isotope ratios (⁴⁴Ca/⁴²Ca) during the measuring
260 period is better than 0.07‰ (2SD) based on the repeated measurements of
261 standard NIST 915b. Calcium isotope values can be converted using:

$$262 \quad \delta^{44/40}\text{Ca} = 2.048 \times \delta^{44/42}\text{Ca} \quad (\text{Heuser et al., 2016}). \quad (1)$$

263 Data in this study are presented as $\delta^{44/40}\text{Ca}$ relative to the NIST SRM915a
264 standard:

$$265 \quad \delta^{44/40}\text{Ca} (\text{‰}) = 1000 \left\{ \frac{\left(\frac{^{44}\text{Ca}}{^{40}\text{Ca}} \right)_{\text{sample}}}{\left(\frac{^{44}\text{Ca}}{^{40}\text{Ca}} \right)_{\text{SRM915a}}} - 1 \right\} \quad (2)$$

266 Sr isotopic analysis was undertaken at the Institute of Surface-Earth

267 System Science, Tianjin University. The Sr isotope composition were measured
268 using MC-ICPMS and the instrumental mass fractionation was corrected by
269 internally normalizing the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio to 0.1194. The average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio
270 for NBS 987 was 0.710271 ± 0.000030 (2SD, n = 34).

271

272 **4. Results**

273 **4.1 Water chemistry**

274 The pH of the river water samples ranges from 8.06 to 8.66 with an average
275 of 8.35 (Table 1). The temperature of river water is 12.7 to 22.4°C with an
276 average of 16.3°C. The chemical compositions for the Jinsha River waters vary
277 significantly ([Chetelat et al., 2008](#); [Gaillardet et al., 1999](#); [Noh et al., 2009](#); [Wu](#)
278 [et al., 2008](#); [Zhao et al., 2019](#); [Zhong, 2017](#)), with the total dissolved solids
279 (TDS = Ca + Mg + Na + K + Cl + HCO₃ + SO₄ + SiO₂) ranging from 88 to 689
280 mg/L. The range of TDS values in the mainstream (301~689 mg/L) is higher
281 than tributaries' values (88~268 mg/L), and decrease from the upper reach to
282 the lower reach. The total cationic charges (TZ⁺ = 2*Ca + 2*Mg + Na + K) vary
283 dramatically ranging from 1130 μeq/L to 10,120 μeq/L. Ca²⁺ and Mg²⁺ are the
284 dominant cations in tributaries accounting for 59-96% of the total cationic
285 budget. In the mainstream, Na⁺ is the dominant cation, accounting for 37-56%
286 for the total cationic budget. Besides, the dominant anions are HCO₃⁻ and Cl⁻ in
287 the main river water. Cl⁻ value of the mainstream samples gradually decrease
288 from upstream to downstream, HCO₃⁻ in tributaries show large variations and is

289 the dominant anion. Ca/Na ratios of the main river ranging from 0.24 to 0.59,
290 which are lower than that of tributaries ranging from 4.50 to 11.39. Similarly, the
291 range of Mg/Na ratios of mainstream is from 0.16 to 0.29 while that of tributaries
292 is from 1.61 to 3.54.

293 In addition, to evaluate the calcite saturation state for river waters, calcite
294 saturation indices (CSI) were calculated based on alkalinity, pH, temperature
295 and ionic strength using the PHREEQC program ([Parkhurst and Appelo, 1999](#)).
296 Results show that nearly all the Jinsha river waters are supersaturated for
297 calcite ([Table 2](#)).

298

299 **4.2 Strontium and its isotopic composition in the Jinsha River**

300 The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations of waters from the Jinsha River
301 Basin are given in [Table 1](#). The range of $^{87}\text{Sr}/^{86}\text{Sr}$ in the mainstream is similar
302 to source rivers ([Fig. 2](#)) ([Noh et al., 2009](#); [Wu et al., 2009a](#); [Zhao et al., 2003](#)).
303 Moreover, the median value of the source rivers is similar to that of the main
304 stream and tributaries of the Jinsha River, which are close to 0.7100. However,
305 the $^{87}\text{Sr}/^{86}\text{Sr}$ range of the Jinsha River sediments (JS sediment) is 0.7110 -
306 0.7147 ([Wu et al., 2009b](#)), which is higher than that of the source area, the
307 tributaries and mainstream of the Jinsha River.

308 The mainstream of the Jinsha River (JS mainstream) has low variation in
309 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with a narrow range of 0.7098 to 0.7108 and an average value
310 of 0.7105, but shows significant changes in Sr contents from 2.70 $\mu\text{mol/L}$ to

311 9.35 $\mu\text{mol/L}$ with a general decrease from the upper reach to lower reaches
312 ([Table 1](#), [Fig. 3a](#)). However, Sr contents of tributaries are almost constant
313 ($\sim 1\mu\text{mol/L}$). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the tributaries have a wider range, from 0.7090
314 to 0.7157 with an average of 0.7121 ([Table 1](#); [Fig. 3a](#)).

315 Moreover, $1/\text{Sr}$ shows the strong positive correlation with Si/TZ^+ ([Fig. 3b](#)),
316 which implies a trend of mixing endmembers. Low $1/\text{Sr}$ and Si/TZ^+ signatures
317 in the waters could be related to carbonate and/or evaporite weathering in the
318 Jinsha River Basin. Moreover, silicate weathering will lead to high $1/\text{Sr}$ and
319 Si/TZ^+ signature in the waters. While the main stream also shows a simple
320 mixing relationship when plotting Sr isotopes against $1/\text{Sr}$, the tributaries do not
321 have such a clear relationship ([Fig. 3a](#)), suggesting additional endmember
322 contributions.

323

324 **4.3 Ca isotopic compositions of the Jinsha River waters and gypsums**

325 The $\delta^{44/40}\text{Ca}$ of the dissolved load in the Jinsha River ranges from 0.68‰
326 to 1.11‰ with an average of 0.87‰, within the range of other large global
327 rivers (0.42-1.62 ‰) ([Schmitt et al., 2003](#); [Tipper et al., 2006](#); [Zhu and](#)
328 [Macdougall, 1988](#)).

329 The highest $\delta^{44/40}\text{Ca}$ value (1.11‰) is observed in the upstream reach of
330 the main stream (JS-1) and the lowest value (0.68‰) in a tributary in the upper
331 reach (JS-9). There is no systematic change trend of $\delta^{44/40}\text{Ca}$ from upstream
332 to downstream. In general, the mainstream generally has a higher $\delta^{44/40}\text{Ca}$

333 than the tributaries. Furthermore, $\delta^{44/40}\text{Ca}$ values have a significant positive
334 relationship with SO_4/Ca (Fig. 4a), and a slight negative correlation with Si/Ca
335 (Fig. 4b).

336 Moreover, rivers draining different lithological sources show a considerable
337 spread in Ca isotopic compositions based on literature compilations of data (Fig.
338 5). As a regional river originating from the Tibetan Plateau, the Jinsha River has
339 the same Ca isotopic range as rivers from the High Himalayan Crystalline
340 Series (HHCS) (0.69-0.92‰), which is lower than some Ca isotopic values in
341 rivers draining dolostone from Lesser Himalayan Series (LHS) (0.99-1.41‰),
342 but higher than some values in rivers draining limestone from Tethyan
343 Sedimentary Series (TSS) (0.50-1.30‰) (Tipper et al., 2008). The $\delta^{44/40}\text{Ca}$
344 values of the Jinsha River are also consistent with greywacke-draining rivers
345 from the Southern Alps, New Zealand (0.50-1.40‰) (Moore et al., 2013; Pogge
346 von Strandmann et al., 2019b). When compared with other small monolithologic
347 river catchments, the Ca isotopic composition of the Jinsha River is lower than
348 rivers draining granite in La Ronge (1.16-1.33‰) (Holmden and Bélanger, 2010)
349 and parts of the $\delta^{44/40}\text{Ca}$ values in basaltic rivers from Iceland (0.95-1.37‰)
350 (Hindshaw et al., 2013; Jacobson et al., 2015). Moreover, the $\delta^{44/40}\text{Ca}$ values
351 of the Jinsha River are higher than that in rivers draining granite in Exmoor
352 (0.50-0.99‰) (Chu et al., 2006) and Strengbach (0.27-0.86‰) (Schmitt et al.,
353 2003).

354 As a Ca-bearing mineral, gypsum, which is distributed widely in the source

355 area of the Changjiang River (Fig. 1a), is an important endmember for river
356 dissolved Ca. Five gypsum samples, collected from the source area of the
357 Changjiang River, show variable $\delta^{44/40}\text{Ca}$ values from 0.24‰ to 0.95‰ with
358 an average of 0.61‰ (Table1). Among them, two gypsum samples collected
359 near the Dangqu River (G1 in Fig. 1a) have lower $\delta^{44/40}\text{Ca}$ values (0.24-
360 0.27‰). Other three gypsum samples collected near the Tuotuo River (G2 and
361 G3 in Fig. 1a) have higher $\delta^{44/40}\text{Ca}$ values (0.80-0.95‰).

362

363 5. Discussion

364 5.1 Sources of dissolved calcium in the Jinsha River

365 In the Jinsha River basin, potential sources of dissolved Ca are rain water
366 and dissolution of evaporite, silicate and carbonate. And the Ca budget
367 equation of the Jinsha River can be written as follows:

$$368 \quad (Ca)_{river} = (Ca)_{rain} + (Ca)_{eva} + (Ca)_{sil} + (Ca)_{cab} \quad (3)$$

369 5.1.1 Atmospheric input

370 Sample JS-6 has the lowest chloride concentration of 5.8 $\mu\text{mol/L}$ in all river
371 waters, which is consistent with the Cl concentration of local long-term
372 precipitation (0.9-32.7 $\mu\text{mol/L}$) (Zhang et al., 2012) and also similar to that of
373 rain water in the Gula area at the middle reach of the Jinsha River (7.9 $\mu\text{mol/L}$)
374 (Zhao et al., 2019). Atmospheric input was corrected, assuming that the sample
375 with the lowest chloride concentration (JS-6) obtained its dissolved Cl
376 exclusively from rain water. Elemental ratios in precipitation from (Zhang et al.,

377 [2012](#)) were used to calculate the concentrations of other major ions (Ca, Mg,
378 Na, K) in rain water. Rain percentages (P_{rain}) are calculated by:

$$379 \quad P_{rain} = \frac{\sum cation_{rain}}{\sum cation_{river}} \quad (4)$$

$$380 \quad \sum cation_{rain} = Ca_{rain} + Mg_{rain} + Na_{rain} + K_{rain} \quad (5)$$

381 Results are shown in [Table 3](#). Cations from atmospheric sources account
382 for <5% of total riverine cations. In addition, the long term average Ca/Cl molar
383 ratio in rain waters is 4.34 ([Zhang et al., 2012](#)), and the Ca concentration of rain
384 water is 25.2 $\mu\text{mol/L}$, then the proportion of Ca derived from rain water to the
385 total of riverine Ca is 2-6%. Previous studies suggested $\delta^{44/40}\text{Ca}$ values of rain
386 water ranging from -0.34 to 1.30‰ with an average value of $0.70 \pm 0.16\text{‰}$
387 ([Han et al., 2019](#); [Schmitt, 2016](#)). The corrected riverine $\delta^{44/40}\text{Ca}$ are elevated
388 by less than 0.08‰ or lowered by less than 0.02‰, within the long term
389 external precision ($\pm 0.14\text{‰}$). Therefore, atmospheric precipitation has little
390 effect on riverine Ca isotopes.

391 **5.1.2 Rock weathering**

392 Based on the lithological distribution in the Jinsha River basin ([Fig. 1a.](#)),
393 silicate 1 (plutonic acid rock), silicate 2 (basaltic volcanic rock), carbonate, and
394 evaporite were chosen as the four main end-members. Meanwhile, strontium
395 isotopes suggest that water chemistry could be controlled by evaporite and
396 silicate as well as carbonate dissolution in agreement with the previous study
397 ([Wu et al., 2011](#)). From upstream to downstream of the Jinsha River, owing to
398 the increasing weathering input from silicates, concentration of dissolved Si in

399 both mainstream and tributaries increases, which is generally contrary to the
 400 decreasing Ca and SO₄ concentration (Fig. 6). However, there is no systemic
 401 change of δ^{44/40}Ca along the river. Hence, the Ca isotopic composition of the
 402 Jinsha River is not fully controlled by simple mixing between Ca signals of
 403 different rock end-members.

404 The Ca contribution of different rock sources could be calculated by an
 405 forward method (Chetelat et al., 2008). Na from silicates of Jinsha tributaries
 406 can be obtained by equation as follows:

$$407 \quad (Na)_{sil} = (Na)_{river}^* - (Cl)_{river}^* \quad (6)$$

408 Where (Na)_{sil} represents Na from silicate, and (Na)_{river}^{*} and (Cl)_{river}^{*} are
 409 dissolved Na and Cl in river collected from rain water. However, due to the
 410 diverse composition of evaporites (halite, mirabilites, sylvites, borates and
 411 sodium carbonate) in the salt lakes near the source area of the Jinsha River
 412 (Yu and Tang, 1980), Na from silicates of Jinsha mainstream cannot be
 413 obtained based on Eq. (6). A substitute method from (Wu et al., 2008) is
 414 conducted to obtain (Na)_{sil} of mainstream. Assuming that the mainstream and
 415 its adjacent tributary have the similar dissolved (Na)_{sil}/Si ratio, then

$$416 \quad (Na)_{sil-m} = ((Na)_{sil-t} / (Si)_t) \times (Si)_m \quad (7)$$

417 Where (Na)_{sil-m} and (Na)_{sil-t} are Na from silicate in Jinsha mainstream and
 418 tributaries, and (Si)_t and (Si)_m represent dissolved Si from Jinsha mainstream
 419 and tributaries. Then, dissolved Ca from silicate can be acquired as follows:

$$420 \quad (Ca)_{sil} = (Na)_{sil} \times (Ca/Na)_{sil} \quad (8)$$

421 Where $(Ca)_{sil}$ represents the dissolved Ca from silicate, and $(Ca/Na)_{sil}$
 422 represents the Ca/Na ratio of silicate widely distributed in the Jinsha river basin.
 423 Here 0.49 ± 0.3 was used as the value of $(Ca/Na)_{sil}$, which is consistent with
 424 the data of the silicate fraction of sediments in the Jinsha River ([Wu et al.,](#)
 425 [2009a](#)). Calculated by Eq. (8), silicate weathering contributes 4-12 % of the
 426 riverine Ca; including an uncertainty of 50% ([Wu et al., 2009a](#)), this propagates
 427 to a 2-24% silicate contribution.

428 Assuming $(Ca/SO_4)_{eva}$ (the Ca/SO₄ ratio of evaporites in source area) is
 429 0.95, which is equal to Ca/SO₄ ratios of source rivers (Tuotuo River and
 430 Chumaer River) ([Wu et al., 2009a](#)), evaporite dissolution contributes 45-81% of
 431 dissolved Ca to the Jinsha mainstream and 1-41% to the tributaries. Because
 432 mirabilites are abundant in saline lakes near the source of the Jinsha River ([Yu](#)
 433 [and Tang, 1980](#)), pyrite oxidation and sulphuric acid weathering ([Chetelat et al.,](#)
 434 [2008](#)) also can affect the concentration of dissolved SO₄ in the Jinsha River.
 435 The calculated $(Ca)_{eva}$ is the upper limit of evaporite Ca that can be obtained.
 436 Through the budget equation (3) of Ca, the contribution of Ca from carbonate
 437 weathering ranges from 6 to 43% in the mainstream and 47 to 88% in the
 438 tributaries.

439 In addition, the initial Ca isotopic composition ($\delta^{44/40}Ca_0$) of the Jinsha River
 440 water resulting from mixing of different rock sources could be calculated based
 441 on a simple mixing equation as follows:

$$442 \quad \delta^{44/40}Ca_0 = \sum_i \delta^{44/40}Ca_i \times \gamma_i^{Ca} \quad (9)$$

443 Where $\delta^{44/40}\text{Ca}_i$ represents the Calcium isotopic composition of source i , and
444 γ_i^{Ca} is the mixing proportion of Ca of each source i (evaporite, silicate 1, silicate
445 2 and carbonate) contributing to the dissolved load. Fantle and Tipper (2014)
446 compiled over 70 published Ca isotope studies, and obtained that the average
447 values of silicates and carbonates are 0.94‰ and 0.60‰, respectively. Thus,
448 0.94‰ was chosen as the $\delta^{44/40}\text{Ca}$ of the silicate endmember in this study.
449 Previous study (Tipper et al., 2006) suggested that the stable Ca isotope
450 composition of limestone in the Tibetan Plateau is 0.61‰, which is close to the
451 average value of worldwide carbonate (0.60‰), and also consistent with the
452 average value of sedimentary rocks of $0.64 \pm 0.09\%$ ($2\sigma_{\text{mean}}$; $N=78$) (Ewing
453 et al., 2008; Holmden, 2009; Jacobson and Holmden, 2008; Ludwik Halicz,
454 1999; Moore et al., 2013; Tipper et al., 2006; Tipper et al., 2008). Therefore,
455 0.61‰ was chosen as the carbonate endmember in this study. Moreover, we
456 suggest the average value of our gypsum samples (0.61‰) as the $\delta^{44/40}\text{Ca}$
457 value of the evaporite endmember, which is not only within the range of gypsum
458 data reported by Hensley (2006) (-0.52‰ to 1.68‰), but also similar to the
459 average $\delta^{44/40}\text{Ca}$ of anhydrites (0.65‰) suggested by other studies (Amini et
460 al., 2008; Holmden, 2009; Jacobson and Holmden, 2008).

461 Based on a conventional mixing model (Eq. (9)), the Jinsha River water
462 has a similar theoretical initial $\delta^{44/40}\text{Ca}$ value of 0.64‰, which is lower than
463 most of the measured values of the Jinsha River. In addition, a negative
464 correlation between $\delta^{44/40}\text{Ca}$ values and Si/Ca (Fig. 4a) also conflicts with the

465 conventional mixing model. Hence, Ca isotopes must be fractionated in the
466 Jinsha River.

467

468 **5.2 Potential calcium isotope fractionation processes**

469 **5.2.1 Vegetable growth**

470 Plants preferentially uptake lighter Ca isotopes, resulting in heavier Ca
471 isotope in the remaining soil solutions. These will therefore elevate riverine Ca
472 isotopes by mixing with river water ([Cenki-Tok et al., 2009](#); [Holmden and](#)
473 [Bélanger, 2010](#); [Schmitt et al., 2017](#)).

474 The topography of the middle and upper sections of the Jinsha River basin
475 is mainly dry and hot valleys with a slow growth rate of plants and low microbial
476 activity in the soil ([Liu, 2016](#)). The Normalized Difference Vegetation Index
477 (NDVI) was used to quantify the density of plant growth in the Jinsha River
478 watershed ([Table 1](#)). Results show that there is no significant relationship
479 between NDVI and the $\delta^{44/40}\text{Ca}$ values of tributaries, implying that the Ca
480 isotopic signal caused by plant growth may be overprinted by other signals, or
481 its signal is too dilute to elevate the $\delta^{44/40}\text{Ca}$ values of regional or global scale
482 rivers significantly. Therefore, the effect of plant growth on riverine isotopes may
483 need to be further constrained through tracing the Ca isotopic composition of
484 the Jinsha River in space and time.

485 **5.2.2 Mineral dissolution**

486 Mg stable isotope fractionation has been shown to occur not only during

487 precipitation, but also during the congruent dissolution of magnesite ([Pearce et](#)
488 [al., 2012](#)). There is also recent evidence that Ca isotopes can behave in the
489 same way, i.e. exhibiting isotope fractionation during dissolution of calcite, and
490 also at equilibrium (or dynamic equilibrium) ([Oelkers et al., 2019](#)). However,
491 studies on Ca isotope fractionation between silicate minerals and
492 corresponding fluids during water-rock interaction suggested that congruent
493 dissolution of granite minerals at low temperature does not fractionate Ca
494 isotopes ([Cobert et al., 2011](#); [Hindshaw et al., 2011](#); [Ryu et al., 2011](#)). From the
495 above, dissolution of silicate rocks along the Jinsha River are not expected to
496 cause significant Ca isotope fractionation.

497 **5.2.3 Clay formation and adsorption**

498 In the Jinsha River basin, similar clay mineral types exist between
499 tributaries and the main stream ([Zhao et al., 2019](#)), illite and chlorite constitute
500 the main part of the clay minerals in the suspended matter and sediments,
501 followed by montmorillonite and kaolinite ([Ding et al., 2013](#); [Wu et al., 2011](#);
502 [Zhao et al., 2019](#)). And the relative content of illite is 10 times higher than that
503 of montmorillonite ([Wu et al., 2011](#)). This is also consistent with results of
504 previous analyses of clay minerals in surface sediments of the whole
505 Changjiang River basin ([He et al., 2011](#)).

506 It is hard to constrain the type and amount of the neoformed clay mineral
507 directly. Fortunately, regional climate is linked to clay formation. For instance,
508 illite and chlorite are always formed in dry-cold areas, such as the Changjiang

509 source area. In contrast, dry and hot environments, like the upper reaches of
510 the Jinsha River, are conducive to the formation of montmorillonite ([He et al.,](#)
511 [2011](#)). From upstream to downstream, the climate of the Jinsha river catchment
512 changes from dry-cold to dry-hot climate ([Fig. 7](#)). However, illite and chlorite are
513 also primary components of clay minerals in sediment and suspended matters
514 of rivers under dry-hot condition ([from JS-3 to JS-16 in Fig.7](#)). Combined with
515 the topographical conditions, one of the possible reasons is that pre-weathered
516 material in the dry-cold plateau is being eroded and transported, which is also
517 consistent with the unsaturated state of illite and chlorite in the Jinsha river
518 water ([Table 2](#)). Although the precise location of the formation of clay minerals
519 in rivers is still debated (i.e., soil solutions and/or river particulate material), the
520 saturation indices of clay minerals in river water can reflect the soil water to a
521 degree because of the connectivity between the river and soil solution. Kaolinite
522 and montmorillonite are supersaturated in the Jinsha river water, combined with
523 dry and hot climate condition, part of them are neoformed in the upper reaches
524 of the Jinsha River ([from JS-3 to JS-16 in Fig. 7](#)). However, riverine $\delta^{44/40}\text{Ca}$
525 show no systemic change with climate along the riverside. Therefore, the
526 influence of neoformed clay minerals on riverine Ca isotopic composition is
527 minor, assuming that environmental conditions are key in clay mineral formation
528 ([Gislason et al., 1996](#); [Stefánsson and Gíslason, 2001](#)).

529 Previous studies suggested light Ca isotopes are preferentially adsorbed
530 to clays, and the degree of isotopic fractionation depends on types of clay

531 minerals and their grain sizes ([Brazier et al., 2019](#); [Ockert et al., 2013](#)). Recent
532 Ca isotope adsorption experiments show that no significant isotopic
533 fractionation occurs when Ca isotopes are adsorbed by kaolinite ([Brazier et al.,](#)
534 [2019](#)). This is inconsistent with results from Gussone and Dietzel ([2016](#)), who
535 suggested that Ca isotope could be adsorbed strongly onto kaolinite
536 accompanied with $\Delta^{44/40}\text{Ca}_{\text{ads-fluid}}$ ranging from -1.2~-3.0‰. Due to its fine grain
537 size (<10 μm), newly formed K-mica may also preferentially adsorb light Ca
538 isotopes, resulting in a positive apparent isotopic fractionation between 0.1‰
539 and 0.28‰ in the residual solution ([Brazier et al., 2019](#)). Moreover, Ca isotopes
540 adsorbed onto illite cause $\Delta^{44/40}\text{Ca}_{\text{ads-fluid}}$ ranging from -0.5 to -1.2‰ ([Gussone](#)
541 [and Dietzel, 2016](#)), and Ca adsorption and the related isotopic fractionation are
542 thought to be fully reversible ([Brazier et al., 2019](#)). In the Jinsha River waters,
543 k-mica, kaolinite and montmorillonite are supersaturated, and negative
544 correlations were obtained between their saturation index and $\delta^{44/40}\text{Ca}$ values
545 in tributaries. This conflicts with results from laboratory experiments, which
546 suggest that adsorption by clay minerals leads to heavier $\delta^{44/40}\text{Ca}$ in residual
547 solutions and there should be a positive correlation between the saturation
548 index of clay minerals and riverine $\delta^{44/40}\text{Ca}$ values. Therefore, the influence of
549 clay mineral adsorption on Ca isotopic compositions of Jinsha tributaries is
550 minor. In addition, although quantitative evaluation of the impact of Ca
551 adsorption on riverine $\delta^{44/40}\text{Ca}$ is difficult, Ca flux sorption to the exchangeable
552 fraction may be restrained by excess Na resulting from evaporite dissolution in

553 the mainstream of the Jinsha River, since it also could impact the $\delta^{44/40}\text{Ca}$
554 values if Na is replaced by lighter Ca isotopes preferentially ([Jacobson and](#)
555 [Holmden, 2008](#); [Ockert et al., 2013](#)).

556 **5.2.4 Carbonate precipitation**

557 Calcium isotopes are fractionated during authigenic carbonate
558 precipitation from aqueous solutions ([Gussone and Dietzel, 2016](#)), which
559 preferentially takes light Ca isotopes into the solid ([Blättler et al., 2015](#); [Böhm](#)
560 [et al., 2012](#); [Gussone et al., 2003](#); [Gussone et al., 2011](#); [Henderson et al., 2006](#);
561 [Holmden, 2009](#); [Jacobson and Holmden, 2008](#); [Nielsen and DePaolo, 2013](#);
562 [Oehlerich et al., 2015](#); [Steuber and Buhl, 2006](#); [Teichert et al., 2005](#); [Tipper et](#)
563 [al., 2006](#); [Wang et al., 2012](#); [Wang et al., 2013](#)), consistent with the fractionation
564 displayed by laboratory precipitation experiments of calcite ([Gussone et al.,](#)
565 [2003](#); [Gussone et al., 2011](#); [Lemarchand et al., 2004](#); [Tang et al., 2008](#); [Tang](#)
566 [et al., 2012](#)). If secondary Ca-bearing minerals are causing the observed
567 fractionation of Ca isotopes in the Jinsha River, the fractionation factor in this
568 process can be calculated ([Hindshaw et al., 2013](#)).

569 The correlation between metal isotopic compositions ($\delta^{44/40}\text{Ca}$, $\delta^{26}\text{Mg}$)
570 and saturation indices of carbonates could indicate carbonates precipitation
571 ([Fan et al., 2016](#); [Hindshaw et al., 2013](#); [Moore et al., 2013](#); [Pogge von](#)
572 [Strandmann et al., 2019a](#); [Pogge von Strandmann et al., 2019b](#); [Pogge von](#)
573 [Strandmann et al., 2019c](#); [Tipper et al., 2008](#)). The positive relationship between
574 riverine $\delta^{44/40}\text{Ca}$ values with CSI and Sr/Ca ratios ([Fig. 8a and b](#)), implies that

575 carbonates precipitation may elevate the Ca isotopic compositions of the Jinsha
576 River waters. f_{Ca} represents the fraction of Ca still in solution. If f_{Ca} equals to 1,
577 there will be no Ca incorporated into secondary minerals after its initial
578 dissolution. In contrast, all Ca from primary mineral dissolution will precipitate
579 as secondary minerals when f_{Ca} has a value of 0. Assuming that the release of
580 Ca and Na from bed rocks is congruent, f_{Ca} can be calculated as below:

$$581 \quad f_{Ca} = \left(\frac{Ca}{Na} \right)_{river} / \left(\frac{Ca}{Na} \right)_0 \quad (10)$$

582 Previous research suggested that Ca/Na (molar) values of sediment of the
583 Jinsha mainstream change slightly from Benzilan (3.46) to Panzhihua (2.85)
584 with an average value of 3.20 ([Wu et al., 2011](#)). Assuming the $(Ca/Na)_0$ of
585 Jinsha mainstream equals 3.20, then f_{Ca} has a range from 0.16 to 0.34. Similarly,
586 $(Ca/Na)_0$ of Tongtianhe (JS-1) equals 5.6 and its f_{Ca} equals 0.07. Additionally,
587 f_{Ca} values of the Jinsha mainstream show significant correlation with CSI ($R^2 =$
588 0.82) and pH values ($R^2 = 0.93$), implying the amount of carbonate precipitation
589 in the Jinsha mainstream ranges from 66% to 93% with an average of 75%.

590 [Fig. 9a](#) shows a relationship between measured riverine $\delta^{44/40}Ca$ values
591 and Ca/Na ratios of river samples. Both Rayleigh distillation model and
592 equilibrium fractionation processes are examined in the Jinsha mainstream
593 samples, and corresponding fractionation factor values are calculated.
594 According to the equilibrium fractionation model, the Ca isotope composition
595 can be modelled as:

596
$$\delta^{44/40}Ca_{river} = \delta^{44/40}Ca_0 - 1000(\alpha - 1) \times (1 - f_{Ca}) \quad (11)$$

597 In addition, to evaluate fractionation factors of the Rayleigh distillation
 598 model, a standard approach is conducted as follows ([Dellinger et al., 2015](#);
 599 [Hindshaw et al., 2013](#); [Pogge von Strandmann et al., 2017](#); [Pogge von](#)
 600 [Strandmann et al., 2012](#); [Zhao et al., 2019](#)):

601
$$\delta^{44/40}Ca_{river} = \delta^{44/40}Ca_0 + 1000(\alpha - 1) \times \ln(f_{Ca}) \quad (12)$$

602 where $\delta^{44/40}Ca_{river}$ corresponds to the Ca isotope composition of river water,
 603 and mainstream and tributaries of the Jinsha River have similar initial isotopic
 604 compositions ($\delta^{44/40}Ca_0 = 0.64\text{‰}$).

605 Different fractionation models lead to variable fractionation factors (α). For
 606 the Jinsha mainstream, the range of Ca isotope Rayleigh fractionation factor is
 607 0.99961-0.99983, with a median of 0.99976, which is consistent with basaltic
 608 river data that follow a Rayleigh relationship in Iceland (0.9998) ([Hindshaw et](#)
 609 [al., 2013](#)). Whereas, equilibrium fractionation results in a range of 0.99935-
 610 0.99963, with a best fit fractionation factor value of 0.99953, which is a little bit
 611 higher than the fractionation factor into inorganic calcite ($\alpha = 0.9990-0.9995$)
 612 ([Gussone et al., 2005](#)); the difference may come from diverse precipitation rate,
 613 difference temperature and solution chemistry.

614 Selecting 0.99953 as the α value of the equilibrium fractionation, f_{Ca} values
 615 of the Jinsha tributaries range from 0.47 to 0.90 based on Eq. (11), which
 616 corresponds to the amount of Ca precipitation, which ranges from 10% to 53%,
 617 with an average value of 35%. Similarly, choosing 0.99973 as the α value of the

618 Rayleigh fractionation model, according to equation (12), the range of f_{Ca} of the
619 Jinsha tributaries is 0.12-0.66, and the corresponding precipitation range is
620 34%-88%, with an average of 72%. Moreover, using the batch fractionation
621 model and the optimal fractionation factor, the f_{Ca} of the main stream of the
622 Jinsha River is 0.49-0.66, which is closer to the f_{Ca} calculated based on the
623 sediment composition of the riverbed. However, using the Rayleigh
624 fractionation model and its best fit α value could obtain the f_{Ca} of the Jinsha
625 River mainstream with a range of 0.02-0.13, which overestimates the Ca
626 precipitation amount in the main stream of the Jinsha River. In addition,
627 Rayleigh fractionation requires a closed system, while the river is an open
628 system, so the equilibrium fractionation model is more appropriate. Therefore,
629 the amount of carbonate precipitation in the tributary has a dissolved Ca uptake
630 range of 10%-53%. Considering the range of fractionation factor is from
631 0.99935 to 0.99963, the uncertainty of the evaluation of the amount of
632 carbonate precipitation is ~10%.

633 From the above, we suggest that carbonate precipitation has taken place
634 in the Jinsha River, which is congruous with the results obtained by Zhao et al.
635 (2019) through the study of Mg isotopes in the same river.

636

637 **5.3 Effect of evaporite weathering on Ca isotopes**

638 In Section 5.2.2, f_{Ca} values of the Jinsha River mainstream are lower than
639 those of the tributaries, which may indicate more carbonate has precipitated in

640 the mainstream. One of the reasons is that weathering of Ca-bearing evaporites,
641 mainly gypsum, which are widely distributed in the source area of the Jinsha
642 River, releases more Ca^{2+} into the river water, resulting in a higher saturation
643 index of carbonate (above zero), which gives rise to precipitation of carbonate
644 and elevated Ca isotopic compositions of the mainstream river water, since
645 secondary carbonates incorporate lighter Ca isotopes preferentially ([Gussone
646 et al., 2003](#); [Gussone et al., 2011](#); [Lemarchand et al., 2004](#); [Tang et al., 2008](#);
647 [Tang et al., 2012](#); [Tipper et al., 2006](#)).

648 In this study, we evaluated the amount of calcium carbonate precipitation,
649 and then assessed the effect of evaporite dissolution on calcium carbonate
650 precipitation and river Ca isotopes. The f_{Ca} values of the tributaries are variable,
651 ranging from 0.47 to 0.90 with an uncertainty of ~ 0.1 , which indicates that the
652 proportion of precipitated Ca ranges from 0% to 63% with the average of 35%.
653 However, f_{Ca} in the mainstream ranges from 0.07 to 0.34 with an average of
654 0.25, which suggests at least 66% of dissolved Ca has precipitated. This result
655 is lower than that of the tributaries, but in good agreement with previous studies
656 which indicated up to 70% of Ca in Himalayan rivers was removed through
657 carbonate precipitation ([Bickle et al., 2005](#); [Jacobson et al., 2002](#)).

658 Widespread limestone in the Jinsha River Basin releases plenty of
659 dissolved Ca into the river, and, combined with an arid climate, provides the
660 necessary conditions for the precipitation of carbonate. Weathering of evaporite
661 releases more dissolved Ca into river water and increases the precipitation of

662 carbonate by ~30%. Note that plants growth and clay mineral adsorption and/or
663 incorporation also uptake more Ca than Na, which will reduce riverine Ca/Na
664 ratios and f_{Ca} values. Therefore, what we have obtained is the upper limit of the
665 amount of precipitation.

666 Further, the influence of evaporite weathering still needs to be evaluated.
667 Ca isotope ratios at the source of the Changjiang river, published by Tipper et
668 al. ([2010](#)), are 1.04‰ in summer and by Zhu and MacDougall ([1988](#)) as
669 1.25‰, which is consistent with our results (1.11‰, JS-1). However, Ca
670 isotope ratios at the river mouth have an average of 0.77‰, which is similar to
671 the average value (0.80‰) of the tributaries of the Jinsha River. This suggests
672 that evaporite weathering in the upper reaches of the Changjiang river do not
673 affect its Ca isotopic composition entering into the ocean. Therefore, evaporite
674 weathering could fractionate Ca isotope significantly, but this signal appears to
675 be overprinted by other processes further downstream. In most cases, the
676 influence of evaporite dissolution is limited and only could affect the $\delta^{44/40}Ca$ of
677 small and regional rivers. However, some large rivers may also be affected by
678 evaporite weathering and have higher $\delta^{44/40}Ca$ values than others, such as the
679 Yellow River, which has high Ca isotope ratios in both summer and winter at its
680 estuary ([Tipper et al., 2010](#)). Additionally, while investigating the evolution of
681 paleoclimate using stable Ca isotopes, it may necessary to consider the effect
682 of evaporites weathering. For example, when the paleo-temperature is high, the
683 enhanced evaporation leads to the extensive distribution of evaporites, which

684 elevates $\delta^{44/40}\text{Ca}$ value of the continental weathering flux, and then affect the
685 global Ca mass balance.

686

687 **Conclusion**

688 This study investigated chemical weathering and solute sources
689 constrained by calcium and strontium isotopes in the upper reaches of the
690 Changjiang River. Hydrochemistry of the mainstream is different from that of
691 tributaries, and the contribution order of solute sources is evaporites >
692 carbonates > silicates for the mainstream, while carbonates > silicates >
693 evaporites for tributaries.

694 The $\delta^{44/40}\text{Ca}$ of the dissolved load in the upper reaches of the Jinsha River
695 ranges from 0.68‰ to 1.11‰ with an average of 0.87‰. The effects of
696 atmospheric input and biological input on the Ca isotope ratio of rivers are minor.
697 The conventional mixing of different rock sources cannot fully explain the Ca
698 isotope ratio of the Jinsha River and secondary processes must be invoked.
699 Owing to a weak negative correlation between the Ca isotope ratios and the
700 saturation indices of silicate clay minerals, adsorption or incorporation is not the
701 main factor that raises the Ca isotope ratio of the river. Combined with the
702 positive correlation between calcite saturation indices and $\delta^{44/40}\text{Ca}$ values, we
703 believe that calcium carbonate precipitation is the cause of elevated Ca isotope
704 ratios. Moreover, the Equilibrium fractionation model can be used to explaining
705 Ca isotopic compositions of the Jinsha River, and the calculated fractionation

706 factors are between 0.99935 and 0.99965, which are similar to fractionation
707 known to be caused by calcite precipitation.

708 Evaporite (mainly gypsum) weathering controls the amount of carbonate
709 precipitation indirectly through the release of Ca^{2+} into the river water which
710 elevates the CSI value. In the dry and cold plateau climate, at least 66% Ca
711 was removed from the mainstream of the Jinsha River while the average value
712 is ~35% in the tributaries, resulting in a heavier Ca isotope ratio in the main
713 stream than in the tributaries. However, the impact of evaporite weathering on
714 carbon budgets of rivers still needs more related research to test.

715

716 **Acknowledgments**

717 This work was funded by the 2nd Tibetan Plateau Scientific Expedition and
718 Research (2019QZKK0707), the Tianjin Science Fund for Distinguished Young
719 Scholars (18JCJQJC46200), the National Key R&D Program of China
720 (2016YFA0601002), National Natural Science Foundation of China
721 (41571130072), UK-China Joint Research and Innovation Partnership Fund
722 PhD Placement Programme (CSC NO. 201806250237) and Tianjin University's
723 Top Doctoral Thesis International Cultivation Programme. PPvS is funded by
724 ERC Consolidator grant 682760 CONTROLPASTCO2. We thank Prof. Wang
725 Zheng , Dr. Liang Zhang , Dr. Liang Qiu and Dr. Fujun Yue for their insightful
726 discussions during the manuscript preparation. We also thank Prof. Yucai Song
727 for providing gypsum samples. We appreciate the insightful comments and

728 constructive suggestions from the editor and the anonymous reviewers.

729

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Table 1. Chemical composition, Ca and Sr isotopic composition of the Jinsha River water.

Labels	Sample ID	T	pH	NDVI ^(a)	Ca ^(b)	Mg ^(b)	Na ^(b)	K ^(b)	Si ^(b)	Alk ^(b)	SO ₄ ^(b)	Cl ^(b)	NO ₃ ^(b)	Sr	$\delta^{44/40}\text{Ca}$	2sd	$^{87}\text{Sr}/^{86}\text{Sr}$	2sd
		°C		%	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	μmol/L	‰		
Mainstream																		
JS-1	Mainstream	15.3	8.66	0.23	1341	878	5555	127	91	2973	1152	5183	30	9.35	1.11	0.14	0.7098	2.81E-05
JS-4	Mainstream	14.3	8.56	0.42	1213	759	4115	97	86	2847	923	3590	26	6.92	0.94	0.14	0.7101	2.73E-05
JS-7	Mainstream	16.8	8.47	0.46	920	463	1853	53	89	2162	520	1792	16	3.93	0.89	0.14	0.7107	2.61E-05
JS-10	Mainstream	17.9	8.46	0.47	861	418	1771	59	87	1273	481	1604	17	3.60	0.99	0.14	0.7106	2.34E-05
JS-12	Mainstream	18.2	8.43	--	803	372	1372	51	90	1772	398	1253	12	2.99	1.02	0.10	0.7108	3.50E-05
JS-15	Mainstream	16.6	8.42	--	770	347	1235	37	92	1064	358	1106	16	2.70	0.87	0.10	0.7108	2.31E-05
JS-20	Mainstream	21.4	8.35	0.53	920	447	1546	36	101	1956	443	1370	22	3.17	1.07	0.14	0.7105	2.80E-05
Tributaries																		
JS-2	Tongtian Rive	16.1	8.48	0.53	1134	580	252	20	72	2442	492	46	28	2.96	0.84	0.14	--	--
JS-3	Se Qu	16.5	8.28	0.51	957	585	165	26	83	2681	266	28	21	1.77	0.88	0.14	0.7142	2.51E-05
JS-5	Zhen Qu	14.8	8.32	0.73	530	219	98	15	95	1287	99	28	10	0.78	0.75	0.10	0.7144	2.72E-05
JS-6	Ba Qu	12.7	8.25	0.42	755	288	112	30	88	2002	339	6	6	1.48	0.78	0.14	0.7157	2.32E-05
JS-8	Zong Qu	16.9	8.17	0.49	600	175	109	24	97	1412	54	12	15	0.76	0.83	0.14	0.7130	2.11E-05
JS-9	Ding Qu	14.4	8.23	0.46	538	158	81	32	93	1902	72	10	5	0.81	0.68	0.14	0.7126	2.31E-05
JS-11	Gang Qu	15.7	8.44	0.61	827	257	96	16	82	1751	172	12	5	2.27	0.75	0.10	0.7090	2.31E-05
JS-13	Zhubaluo Rive	15.1	8.41	0.63	469	72	41	7	71	940	48	7	3	0.64	0.81	0.14	0.7118	2.48E-05
JS-14	Chongjiang Ri	15.5	8.23	0.60	453	117	47	21	107	1695	15	12	14	0.81	0.74	0.14	0.7102	2.75E-05
JS-16	Shuoduoqang	12.8	8.14	0.56	712	230	80	10	84	1719	42	9	4	1.11	0.87	0.14	0.7091	2.31E-05
JS-18	Renli River	22.4	8.06	0.56	920	400	195	39	113	2304	101	75	43	1.19	0.83	0.14	0.7108	2.98E-05
Gypsum																		
G1-1	near Dang Qu														0.27	0.10		
G1-2	near Dang Qu														0.24	0.10		
G2	near Tuotuohe														0.80	0.10		
G3-1	near Tuotuohe														0.80	0.10		
G3-2	near Tuotuohe														0.95	0.10		

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1076 (a) NDVI: The Normalized Difference Vegetation Index calculated by GIS. (b) Major element data from Zhong (2017).

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1080 **Table 2.** Saturation Index of carbonates and clay minerals in the Jinsha River.

River labels	Mineral types						
	Calcite	Dolomite	Illite	Chlorite	Montmorillonite	Kalinite	Kmica
Saturation index of minerals (SI)							
Mainstream							
JS-1	0.93	1.67	-0.39	3.60	2.96	1.32	4.98
JS-4	0.79	1.35	-0.29	2.34	2.86	1.60	5.18
JS-7	0.56	0.84	-0.28	1.58	2.69	1.83	5.21
JS-10	0.32	0.36	-0.34	1.59	2.67	1.77	5.19
JS-12	0.42	0.54	-0.04	1.48	2.89	2.09	5.88
JS-15	0.16	-0.01	0.10	1.02	2.89	2.29	5.71
JS-20	0.47	0.72	-0.83	1.40	2.71	1.47	4.47
Tributaries							
JS-2	0.71	1.14	-1.94	0.76	1.49	0.68	3.07
JS-3	0.51	0.82	-0.62	0.24	2.29	1.88	4.80
JS-5	0.01	-0.38	-0.24	-1.27	2.38	2.33	5.24
JS-6	0.22	-0.03	0.93	-1.26	2.94	3.28	6.86
JS-8	-0.01	-0.54	0.20	-2.20	2.70	2.73	5.95
JS-9	0.08	-0.38	1.74	-1.36	3.56	4.00	7.98
JS-11	0.44	0.37	-0.40	0.16	2.35	2.11	5.08
JS-13	0.07	-0.96	-0.73	-2.84	1.80	2.21	4.84
JS-14	-0.01	-0.60	0.60	-2.51	2.88	3.05	6.40
JS-16	0.05	-0.44	0.52	-2.68	2.64	3.30	6.33
JS-18	0.32	0.37	-0.01	-0.31	3.13	2.38	5.60

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1090 **Table 3.** The fractionation factor and the amount of Ca precipitation in the
 1091 Jinsha River water.

River labels	Equilibrium fractionation model					
	$\alpha = 0.99935$		$\alpha = 0.99953$		$\alpha = 0.99963$	
	f_{Ca}	Removed Ca(%)	f_{Ca}	Removed Ca(%)	f_{Ca}	Removed Ca(%)
Mainstream						
JS-1	0.07	93	0.07	93	0.07	93
JS-4	0.16	84	0.16	84	0.16	84
JS-7	0.27	73	0.27	73	0.27	73
JS-10	0.26	74	0.26	74	0.26	74
JS-12	0.32	68	0.32	68	0.32	68
JS-15	0.34	66	0.34	66	0.34	66
JS-20	0.32	68	0.32	68	0.32	68
Tributaries						
JS-2	0.68	32	0.55	45	0.43	57
JS-3	0.62	38	0.47	53	0.32	68
JS-5	0.82	18	0.75	25	0.69	31
JS-6	0.77	23	0.68	32	0.59	41
JS-8	0.70	30	0.58	42	0.47	53
JS-9	0.92	8	0.90	10	0.87	13
JS-11	0.82	18	0.75	25	0.68	32
JS-13	0.72	28	0.62	38	0.51	49
JS-14	0.83	17	0.76	24	0.70	30
JS-16	0.63	37	0.49	51	0.35	65
JS-18	0.69	31	0.57	43	0.46	54

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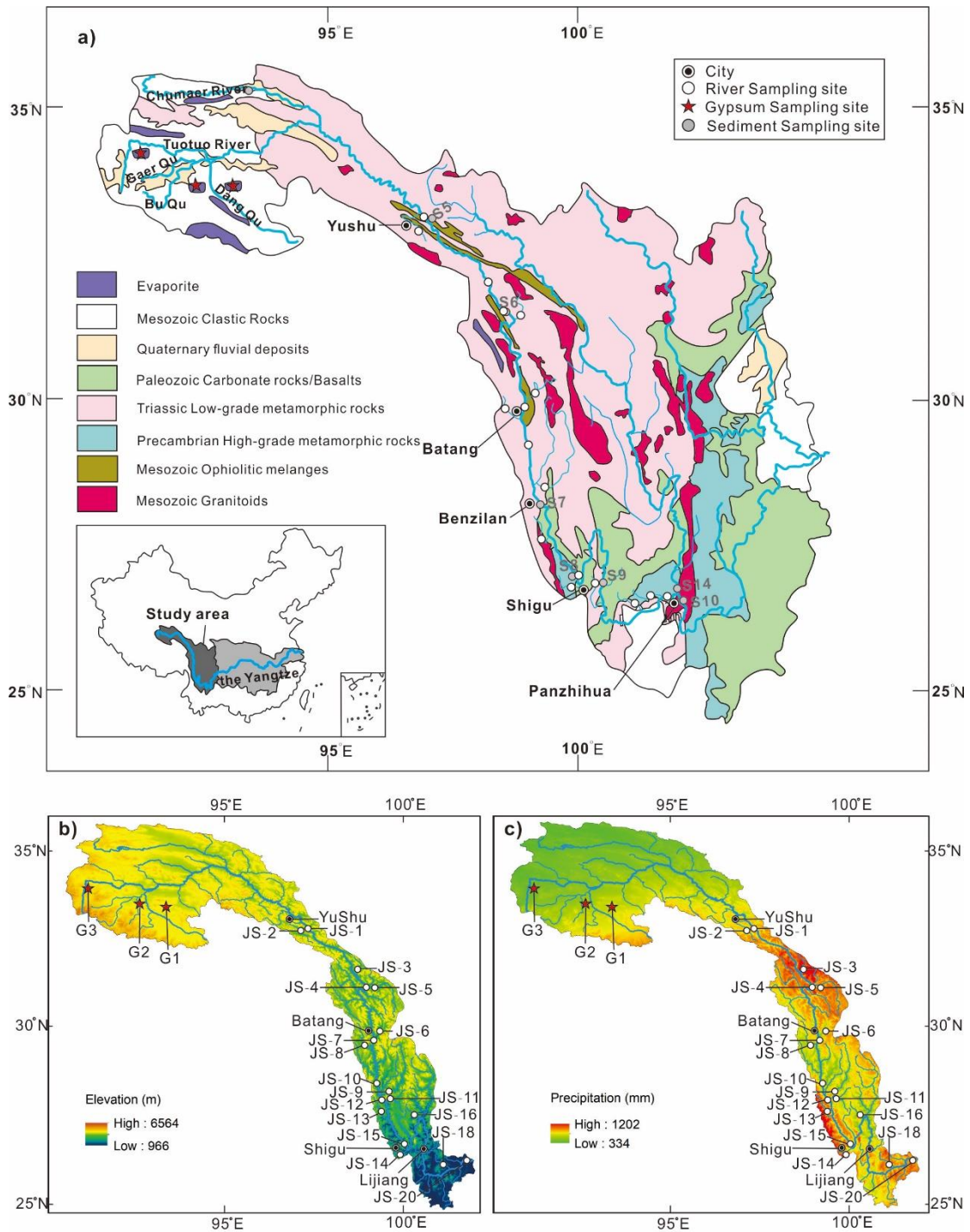
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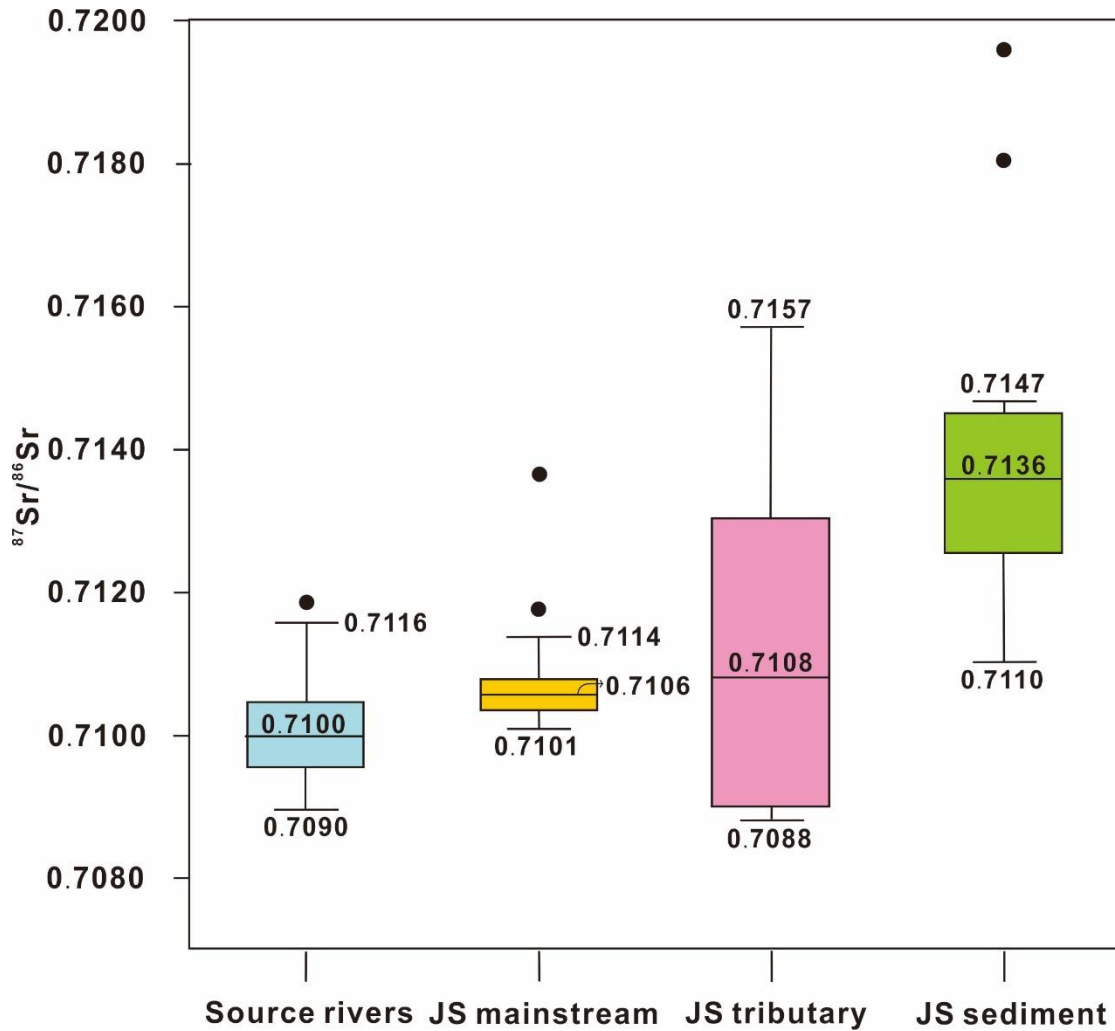


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1101 **Fig. 1.** (a) Geological map of the headwaters of the Changjiang River and the
 1102 Jinsha River basin, modified from (Wu et al., 2011); (b) and (c) show elevation
 1103 and precipitation of the Jinsha River basin separately. White solid circles
 1104 represent the river sampling site of this study, grey solid circles (S5-S14) are

1105 sediment sampling locations in previous research (Wu et al., 2011), red stars
1106 represent gypsum sampling sites and the concentric circles are cities.

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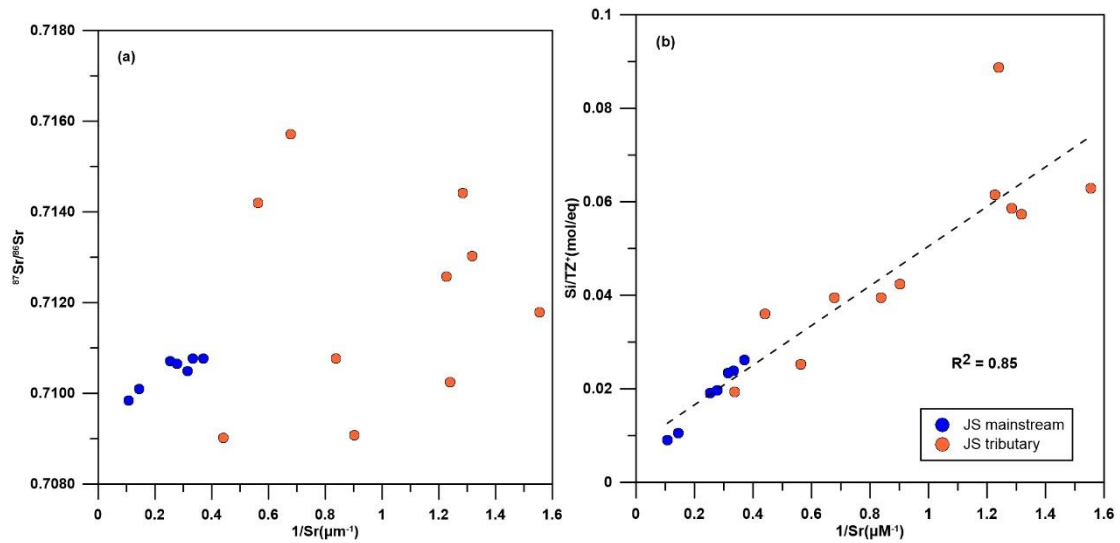


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1109 **Fig. 2.** Sr isotopic compositions in the Jinsha River basin. Each box consists
1110 of a rectangle and three horizontal lines. Those horizontal lines represent the
1111 min value, median value and max value of the data separately from bottom to
1112 upper. The bottom horizontal line of the rectangle represents the first quartile
1113 (25%), which is the median of the data points lower than the median. And
1114 median is the second quartile. On the contrary, the top horizontal line
1115 represents the third quartile (75%), which is the median of the data points

1116 higher than the median. The black dots mean abnormal values.

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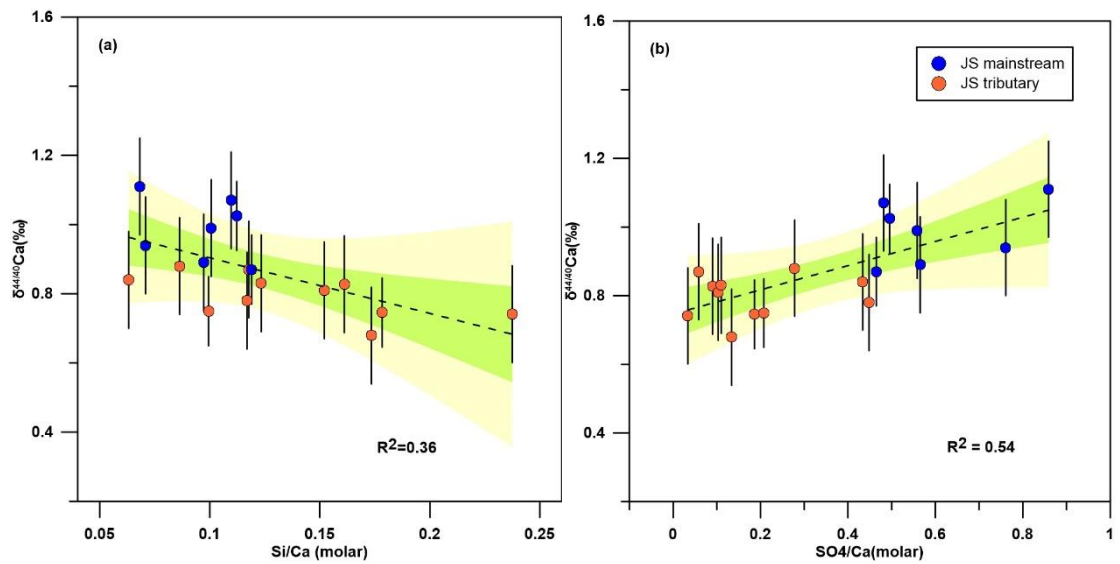


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1119 **Fig. 3.** (a) A plot of $1/Sr$ and $^{87}Sr/^{86}Sr$ in the Jinsha River; (b) A plot of $1/Sr$ and

1120 Si/TZ^+ in the Jinsha River.

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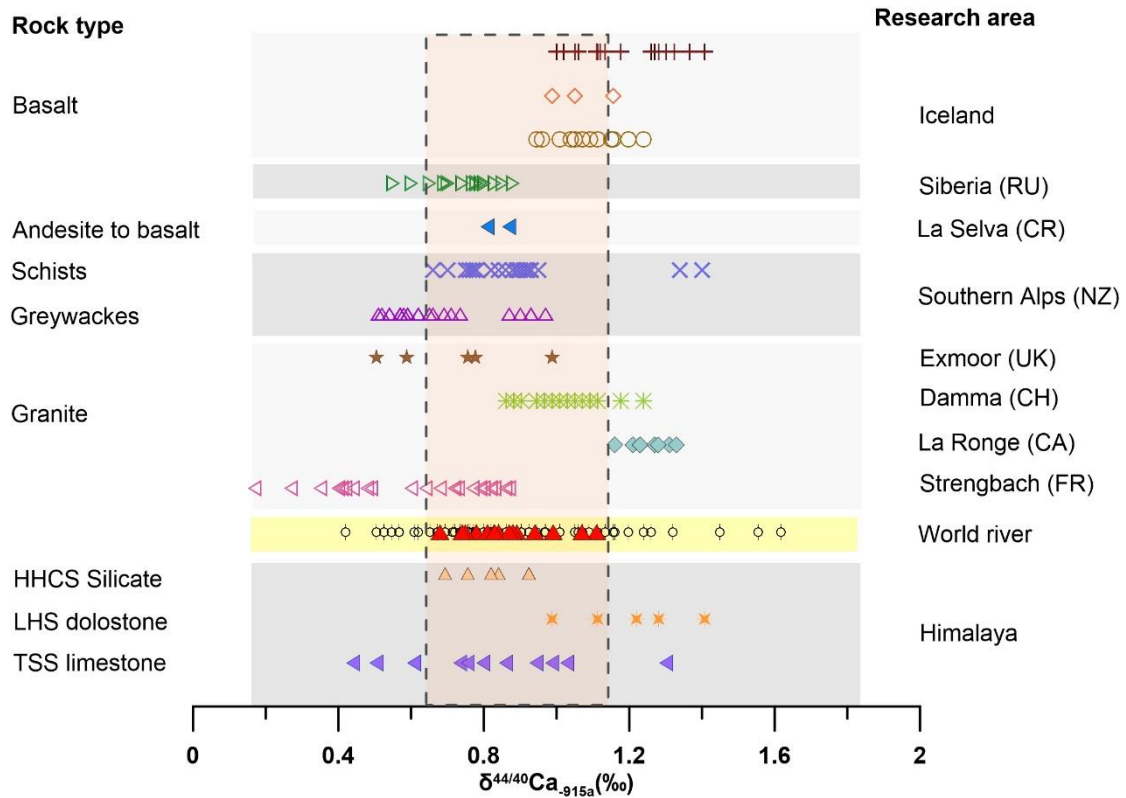
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1123 **Fig. 4.** (a) Plot of Si/Ca and $\delta^{44/40}Ca$ in the Jinsha River; (b) Plot of SO_4/Ca and

1124 $\delta^{44/40}Ca$ in the Jinsha River. The green and yellow areas represent 95% and

1125 99.99% confidence interval, respectively.

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1128 **Fig. 5.** Ca isotopic variation in river waters (modified from (Schmitt, 2016)). The

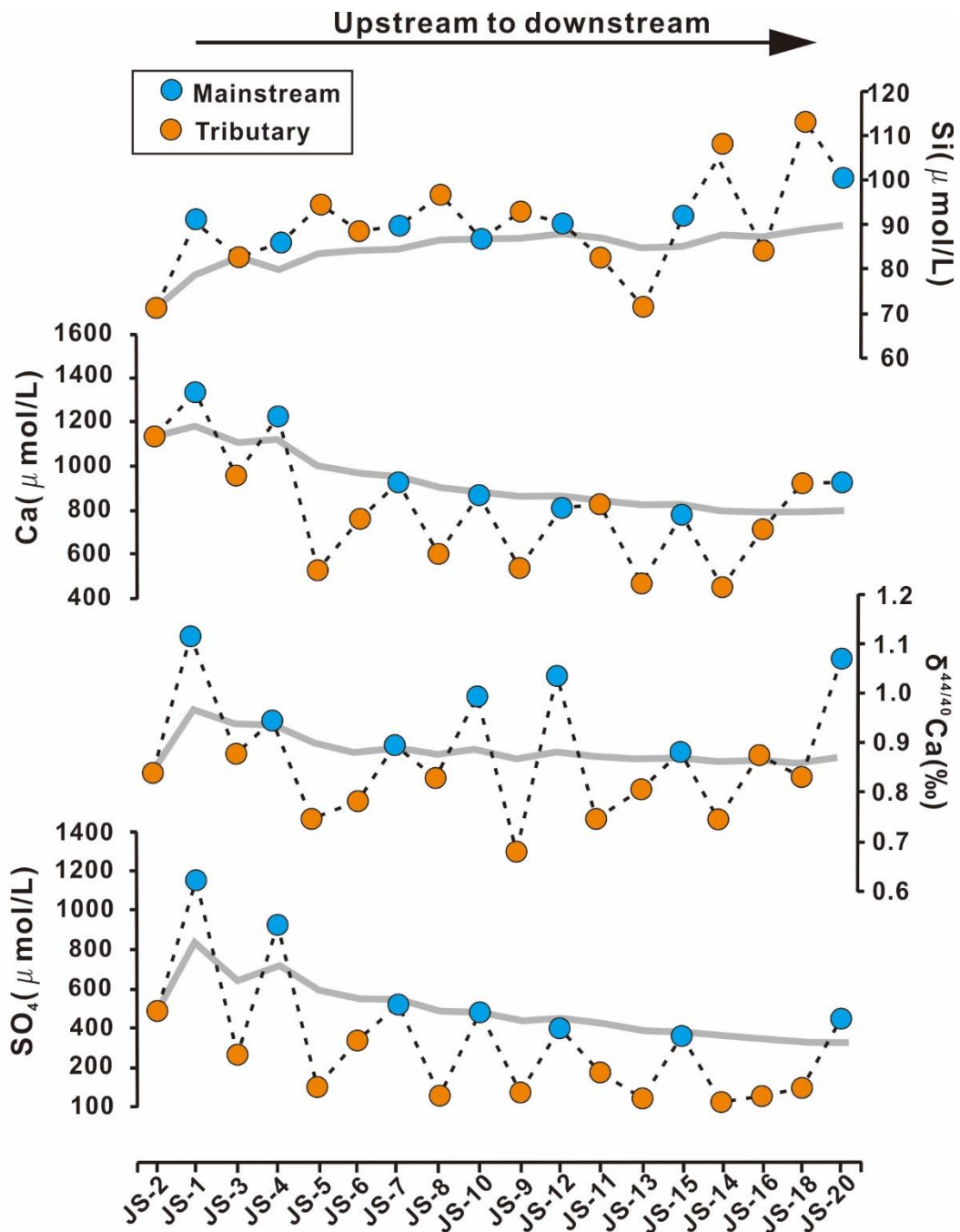
1129 red solid triangles represent our data in this study; world river data are from

1130 (Schmitt et al., 2003; Tipper et al., 2006; Tipper et al., 2010; Zhu and

1131 Macdougall, 1988) and other data sources can be seen in text. All values are

1132 normalized to the NIST SMR 915a standard.

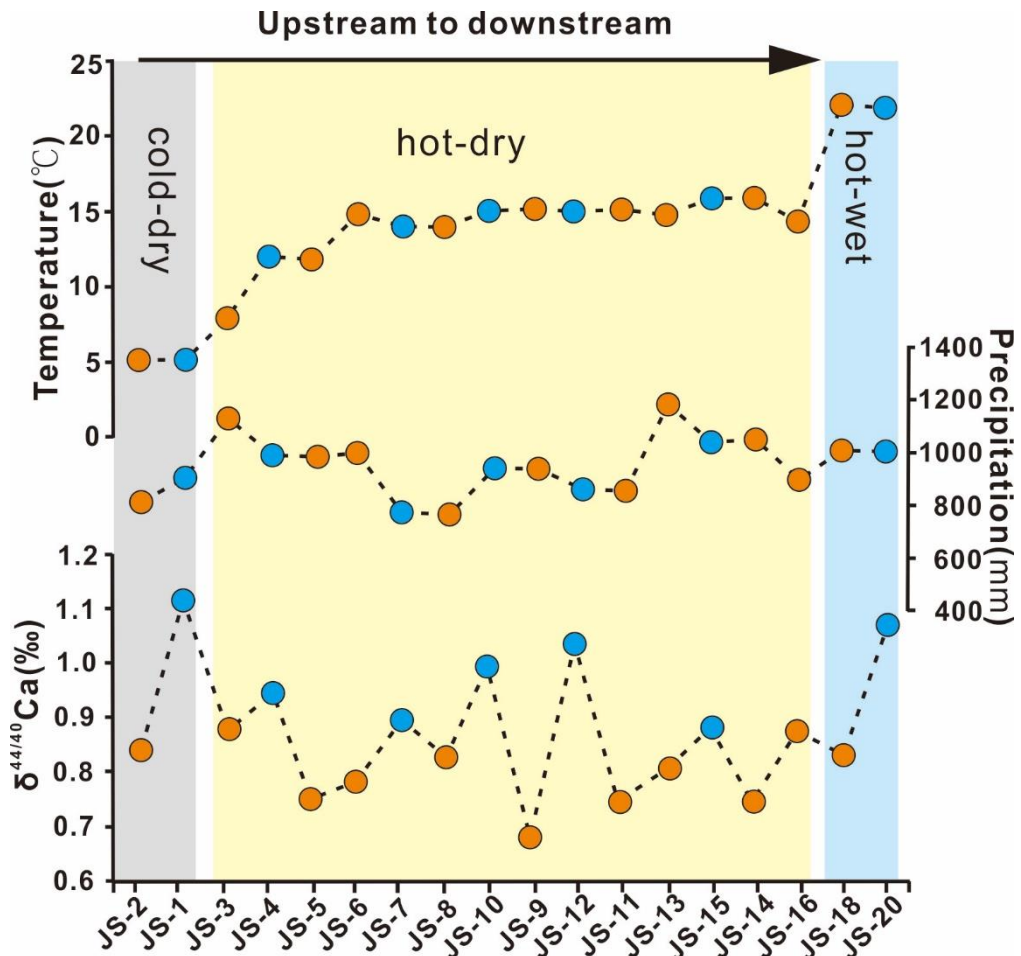
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1135 **Fig. 6.** Si, Ca and SO₄ concentrations and Ca isotope compositions of the
 1136 Jinsha River water samples from upstream to downstream. Grey lines
 1137 represent moving averages of all of the corresponding data.

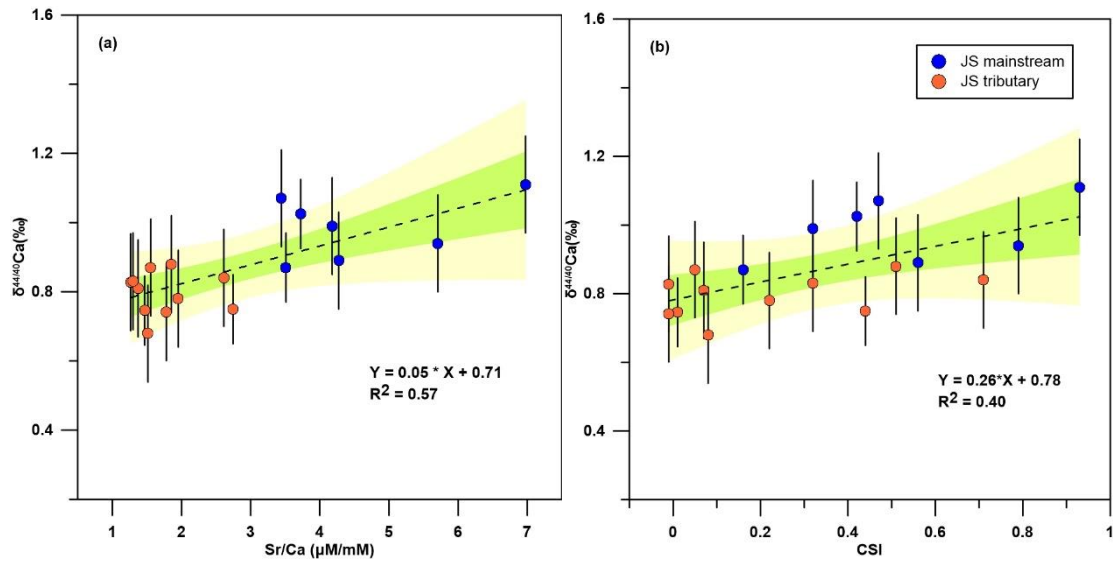
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1140 **Fig. 7.** The change of climate factors (air temperature and precipitation) and Ca
 1141 isotope compositions of the Jinsha River water samples from upstream to
 1142 downstream. The Grey rectangle area represents the dry-cold climate, the
 1143 yellow area represents the dry and hot environments and the blue area
 1144 represents the hot-wet climate.

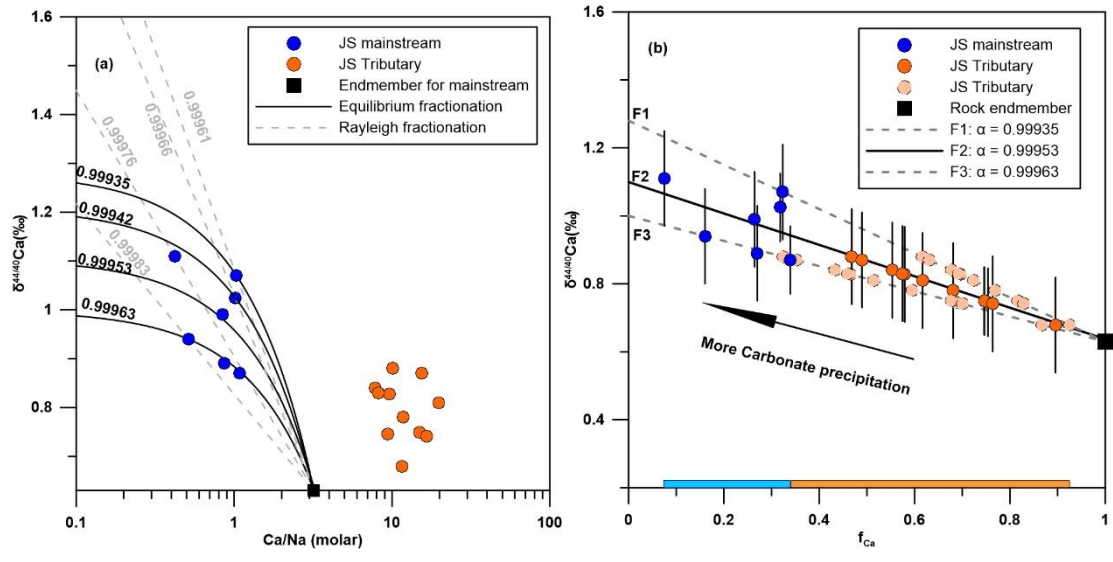
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1147 **Fig. 8.** (a) A plot of Sr/Ca and $\delta^{44/40}\text{Ca}$ in the Jinsha River; (b) A plot of CSI and
 1148 $\delta^{44/40}\text{Ca}$ in the Jinsha River. The green and yellow area represents the 95% and
 1149 99.99% confidence interval respectively.

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1152 **Fig. 9.** The relationships between Ca isotope composition of river waters and
 1153 (a) dissolved Ca/Na ratios and (b) the fraction of Ca remaining in solution (f_{Ca})
 1154 under the Equilibrium model.