1	Seismically enhanced solute fluxes in the Yangtze River
2	headwaters following the 2008 Wenchuan earthquake
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13	ABSTRACT
14	Large earthquakes alter physical and chemical processes at the Earth's surface,
15	triggering landslides, fracturing rock, changing large-scale permeability, and influencing
16	hydrologic pathways. The resulting effects on global chemical cycles are not fully
17	known. Here we show changes in the dissolved chemistry of the Min Jiang, in the
18	Yangtze River headwaters, following the 2008 $M_{\rm w}$ 7.9 Wenchuan earthquake. Total
19	solute fluxes transported by the Min Jiang increased after the earthquake, accompanied
20	by a ~4x increase in Na*/Ca ratios (where Na* is Na ⁺ corrected for atmospheric and
21	evaporite contributions) and a 0.000644 \pm 0.000146 increase in ⁸⁷ Sr/ ⁸⁶ Sr isotopic ratios.
22	These changes are consistent with enhanced contribution from silicate sources. We infer

23	DOI:10.1130/G37246.1 that the CO ₂ consumption rate via silicate-derived alkalinity increased 4.3 ± 0.4 times. If
24	similar changes are associated with other large earthquakes, enhanced solute export could
25	directly link tectonic activity with weathering and alkalinity fluxes that supply nutrients
26	to ecosystems, influence seawater chemistry evolution, and steer Earth's long-term
27	carbon cycle and climate.
28	INTRODUCTION
29	Rivers collect and transport material from across Earth's surface, so their
30	chemistry integrates geological and environmental processes over space and time (e.g.,
31	Berner and Berner, 1996; Gaillardet et al., 1999). Variability in river chemistry over
32	timescales from days to seasons to decades is increasingly well understood (e.g.,
33	Raymond and Cole, 2003; Tipper et al., 2006; Godsey et al., 2009; Torres et al., 2015), as
34	are the global implications (Maher and Chamberlain, 2014). The effects of infrequent
35	events such as large earthquakes on river chemistry are less well known, since these
36	events are not typically represented in observational records even though their cumulative
37	effects may be significant over the centennial or longer timescales of their recurrence.
38	Large earthquakes on continental faults perturb hydrologic pathways (Rojstaczer
39	et al., 1995; Montgomery and Manga, 2003; Claesson et al., 2004; Skelton et al., 2014),
40	and changes in solute chemistry of groundwaters and streams have been proposed as
41	possible earthquake warning indicators (e.g. Rojstaczer et al., 1995; Skelton et al., 2014).
42	Earthquake-driven changes in river solute fluxes could be important for quantifying
43	(bio)geochemical fluxes and for understanding terrestrial geochemical and hydrological
44	processes.

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a seismic event affects river chemical signatures. The Wenchuan opportunity arises in
part because of data on Min Jiang river chemistry prior to 2008 (Qin et al., 2006; Yoon et
al., 2008; Huh, 2010), providing the basis for direct comparison with samples collected
after the earthquake.

51 The 2008 Wenchuan earthquake occurred along the Longmen Shan mountain 52 range that forms the eastern margin of the Tibetan Plateau (Robert et al., 2010). The 53 Longmen Shan is characterized by steep slopes and high relief, increasing in mean 54 elevation by ~3500 m over less than 100 km distance (Fig. 1a). The geology of the region 55 is dominated by bedrock with alumino-silicate minerals, including metamorphic 56 argillaceous sandstone and flysch, granite and monzonitic granite, and detrital sediments, 57 as well as limestones (Fig. DR1). The Wenchuan earthquake was generated along the 58 Yingxiu–Beichuan and Pengguan faults that run S40–50°NE along the Longmen Shan 59 (Xu et al., 2009). The earthquake and associated aftershocks caused more than 56,000 60 landslides over ~ 200 km length of the mountain range, whereas the extent of landslides in 61 the region was limited prior to the earthquake (Li et al., 2014). The climate of the region 62 is dominated by the Asian and Indian summer monsoons, with 75% of annual precipitation (600-1100 mm/yr) during May to October. The annual water discharge of 63 the Min Jiang, the major river draining the Longmen Shan, was 1.06×10^{10} m³ in 2000– 64 65 2011, and the difference of annual water discharge before and after the earthquake was <66 20% (Fig. 2a), smaller than inter-annual variability (Wang et al., 2015). 67

68 MATERIALS AND METHODS

69	River water samples for this study were collected weekly between December
70	2009 and the end of 2011 from two hydrological stations, at Weizhou and
71	Zhenjiangguan, both on the main course of the Min Jiang (Fig. 1). Hydrologic parameters
72	at both stations are monitored regularly by the Chinese Hydrology Bureau (CHB). The
73	Weizhou station in the town of Wenchuan lies in the zone of high peak ground
74	acceleration (PGA) during the 2008 earthquake, and consequently in a region
75	significantly affected by co-seismic landslides and other visible damage (Fig. 1). The
76	Zhenjiangguan station is farther upstream, still within the zone of measurable earthquake-
77	associated ground acceleration, but where PGA was much lower than at Weizhou and
78	where there were few earthquake-triggered landslides (Fig. 1). In addition, single samples
79	were collected in 2011 from nine revisited sites distributed throughout the river basin
80	(Fig. 1), matching sites that had been sampled at least once before the earthquake (Qin et
81	al., 2006; Yoon et al., 2008; Huh, 2010). Filtered water samples were analyzed for
82	dissolved major ions and Sr^{2+} concentrations, and ${}^{87}Sr/{}^{86}Sr$ isotopic ratios (Table DR1,
83	Figs. DR2-4; see Methods in the GSA Data Repository). The chemistry of the samples
84	collected in this study was compared to dissolved chemistry data from prior to the
85	earthquake at equivalent sites. The data set from the Weizhou station enables comparison
86	of pre- and post-earthquake annual time-series (Table DR2). For the other samples,
87	collection season was matched as closely as possible to previous studies (Table DR3).
88	RESULTS

89 **Pre- and Post-Earthquake Times-Series from Weizhou Station**

90	When comparing data at Weizhou from 2010–2011 versus data from 2001–2002,
91	prior to the earthquake, a systematic increase is observed in Na*/Ca molar ratios (Fig. 2b,
92	where $Na^* = Na^+$ derived from silicate weathering; see Methods in the GSA Data
93	Repository) and K/Ca ratios (Fig. DR5). These differences are significantly greater than
94	the variability observed in the long-term record of dissolved chemistry for the Min Jiang
95	acquired by the CHB between the 1970s and 2000 (Qin et al., 2006), suggesting that the
96	higher ratios observed in the 2010–2011 data reflect a distinct post-earthquake change in
97	solute composition. Unlike concentrations, elemental and isotopic ratios are not directly
98	influenced by dilution, so the observed changes cannot be explained by changes in
99	precipitation or discharge amounts. The changes in elemental ratios are also accompanied
100	by an increase in the average dissolved 87 Sr/ 86 Sr isotope ratios from 0.712663 ± 0.000200
101	to 0.713307 \pm 0.000207. Coincident increases in dissolved Na [*] , K ⁺ , and ⁸⁷ Sr/ ⁸⁶ Sr are
102	consistent with silicate mineral sources. Ratios of Mg/Ca and Sr/Ca do not show similar
103	changes (Fig. DR3), most likely because river waters are at carbonate saturation both
104	before and after the earthquake (Yoon et al., 2008).
105	Paired Data from Other Sites

106 Pre-earthquake time series data are not available at Zhenjiangguan (cf. Fig. DR6), 107 but we can compare individual paired data from before and after the earthquake at this 108 site and several others. Increases in both Na*/Ca and Sr isotope ratios (Figs. 1b, c and 3a, 109 b) are observed at all of the sites within the zone of significant PGA, and the direction of 110 change is consistent with that observed at Weizhou (Fig. 2). The magnitude of post-111 earthquake Na*/Ca increase (0.02–0.22, mean 0.07 \pm 0.07) at these paired sites is 112 significantly larger than the annual variability at Weizhou (0.02, 1 σ pre-earthquake; 0.04,

1σ post-earthquake) and Zhenjiangguan (0.03, 1σ post-earthquake), suggesting that the
observed changes are not artifacts of the times of sample collection. Sites 1 and 2,
farthest from the Wenchuan earthquake epicenter and activated faults, show relatively
little change in Na*/Ca after the earthquake (less than 0.02), reflecting their greater
distance from the region of strongest PGA (Fig. 3).
The relationship between the magnitude of observed change (Δ , difference
between post- and pre-earthquake ratios) in solute chemistry and mean PGA during the
Wenchuan earthquake in the catchment area upstream of each sampling site is not
straightforward (Fig. 3c, d). Nonetheless, for the main stem, sites showing highest Δ
values for both Na $*$ /Ca and 87 Sr/ 86 Sr are ones where mean PGA was relatively high (e.g.,
sites 7 and 8, and at Weizhou), while sites with lower PGA are associated with least
chemical change (e.g., site 2). For the tributary sites, the relationship is less clear, with
sites 3, 4 and 5 all showing large changes in Na*/Ca despite a range in catchment-
averaged PGA (Figs. 1b, 3c). The larger magnitude of $\Delta Na^*/Ca$ at tributary sites
compared to the main stem and the lack of relationship to PGA might be explained by
smaller tributary catchment areas, such that smaller perturbations have a greater effect
than on the main stem. Overall, the first-order relationship with PGA for the main stem
(i.e., significant change within the earthquake-affected zone, but less change farther from
the center of this zone at sites 1 and 2) is consistent with a link between the earthquake
and observed changes in river chemistry.

133 **DISCUSSION**

134 Causes of Changing River Chemistry Following the Wenchuan Earthquake

135	The dissolved Na [*] /Ca, K/Ca, and 87 Sr/ 86 Sr of the Min Jiang systematically shifted
136	towards more silicate compositions across multiple sites and over multiple years
137	following the Wenchuan earthquake. Observed changes persisted at least for 3 years
138	(through December of 2011, when the last samples in this study were collected), so any
139	perturbation must have responded rapidly and been sustained for several years. Release
140	of deep basinal brines or greater contribution from human activities are unlikely causes
141	since we do not observe coincident changes in Cl^2 or SO_4^2 concentrations, as would be
142	expected for such sources (e.g., Gaillardet et al., 1999). Herein we propose that the
143	observed changes are related to the effects of earthquake shaking on fluid pathways and
144	the minerals exposed to fluids by bedrock fracturing and/or by seismic landslides.
145	In more detail, at shallow depths (centimeters to several meters depth),
146	earthquakes trigger extensive co- and post-seismic landslides (e.g., Li et al., 2014), which
147	can act as solute generators by producing reactive fine-grained sediment (Wang et al.,
148	2015) and by focusing flow through this material (e.g., Watanabe et al., 2005; Emberson
149	et al., in press). Leaching of exchangeable cations from finely ground landslide debris
150	could also contribute to the solute load. Co-seismic landslides are prevalent throughout
151	the lower reaches of the Min Jiang study region (Li et al., 2014; Fig. 1), but the spatial
152	extent of observed changes in solute chemistry extends beyond the zone of most
153	concentrated mapped landslide activity, suggesting that other processes play a major role.
154	At greater depths of tens to hundreds of meters, earthquakes can fracture rock
155	(Molnar et al., 2007), alter permeability (Rojstaczer et al., 1995), and perturb hydrologic
156	systems over regional to continental scales, extending beyond regions of visible co-
157	seismic damage (Montgomery and Manga, 2003; Skelton et al., 2014; Shi et al., 2015).

158	Direct measurements of permeability along the Pengguan and Beichuan fault zones
159	showed initial increase followed by healing over exponential decay times of 0.6–2.5
160	years (Xue et al., 2013), but larger spatial scale changes in the hydrologic system
161	following shaking and seismic disturbance may persist for longer (Rojstaczer et al., 1995;
162	Claesson et al., 2004; Skelton et al., 2014). Groundwaters are typically concentrated in
163	silicate-derived cations as a result of prolonged water-rock contact (e.g., Tipper et al.,
164	2006). Post-seismic discharge of such groundwater could shift river chemistry toward
165	higher solute fluxes and more silicate composition. Evacuation of waters close to
166	equilibrium and replacement with more dilute waters could also stimulate higher mineral
167	dissolution rates (Maher and Chamberlain, 2014; Rempe and Dietrich, 2014), as could
168	the exposure of new mineral surfaces (White and Brantley, 2003), for example in bedrock
169	micro-fractures.
170	With the current data, we are not able to distinguish definitively the contribution

171 from seismically altered flowpaths versus enhanced dissolution in landslide debris, nor 172 can we distinguish whether additional solutes have their immediate source from primary 173 minerals, exchangeable sites, or concentrated groundwaters. Greater mechanistic insight 174 might be gained by future studies tracking spatial patterns of hydrochemical change and 175 longer-term evolution, including the return to pre-earthquake river composition.

176 **In**

Implications for Geochemical Fluxes

Independent of mechanism, the results from the Min Jiang offer empirical
evidence that a high-magnitude, low-frequency earthquake can have a significant,
previously-unrecognized effect on river chemistry. The increased flux of alkalinity
following the Wenchuan earthquake enhanced CO₂ drawdown and contributed more

181	radiogenic ⁸⁷ Sr to the oceans. The post-earthquake dissolved ⁸⁷ Sr/ ⁸⁶ Sr ratios of Min Jiang
182	main stem river waters increased by a mean of 0.000644 ± 0.000146 relative to those
183	prior to the earthquake (excluding site 2). Sr concentrations did not significantly change
184	at the same time (Figs. DR3 and 4), implying a net increase in the delivery of ⁸⁷ Sr to the
185	oceans, with potential implications for interpreting the geologic record of seawater
186	87 Sr/ 86 Sr composition (Raymo et al., 1988; Edmond, 1992). The rates of net CO ₂
187	consumption associated with silicate alkalinity (\emptyset CO ₂) after the earthquake (2010–2011)
188	are 4.3 ± 0.4 times higher than prior to the earthquake, based on average monthly solute
189	concentrations, drainage area, and water discharge (see Methods in the GSA Data
190	Repository). Assumptions about the composition of the silicate mineral end-member do
191	not affect the relative magnitude of $\emptyset CO_2$ before and after the earthquake, as long as the
192	composition of silicate minerals did not change significantly.
193	The Wenchuan case suggests that changes in tectonic activity have the potential to
194	increase riverine alkalinity fluxes to the oceans by changing the frequency of
195	earthquakes. The extent to which such seismic changes in solute flux affect seawater
196	composition and the global carbon cycle (e.g., Raymo et al., 1988; Berner, 2004) remains
197	to be assessed. The magnitude of long-term change will depend on the duration that
198	earthquake-triggered changes persist and how the extent of chemical change varies for
199	different earthquakes. Whether other earthquakes cause similar effects may relate to a
200	number of factors including event magnitude, regional seismicity and earthquake return
201	times, the extent of induced landslides, the nature of fracture development and changes in
202	hydrological pathways, and regional lithology. These questions will only be answered by
203	further investigation to explore how the magnitude and duration of change vary for

- 204 different earthquakes, and to understand the underlying mechanisms causing observed
- changes.
- 206

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298	
299	FIGURE CAPTIONS
300	
301	Figure 1. (a) Map of the 2008 $M_{\rm w}$ 7.9 Wenchuan earthquake region, showing sampling
302	sites, epicenter, co-seismic landslides (yellow polygons, from Li et al., 2014), and
303	contours for peak ground accelerations (PGA, from USGS earthquake hazard program,
304	http://earthquake.usgs.gov/earthquakes). Dots with stars inside are river water sample
305	sites at Weizhou and Zhenjiangguan hydrological stations; dots (main stem) and
306	diamonds (tributaries) are revisited sites along the Min Jiang (1, Source of the Min Jiang;

307 2, Songpan; 3, Riwu Qu; 4, Heishui; 5, Zagunao; 6, Wenchuan; 7, Yingxiu; 8, Guan

308 Xian; 9, Dujiangyan). The magnitudes of observed change (Δ) in (b) Na*/Ca and (c)

- $309 \quad {}^{87}\text{Sr}/{}^{86}\text{Sr}$ are shown by color shading.
- 310

311	Figure 2. (a) Seasonal patterns of Min Jiang river water discharge before and after the
312	2008 Wenchuan earthquake. Water discharge totaled 11.5×10^9 m ³ (2005) and 11.9×10^9
313	m^3 (2010) at the Weizhou station. (b) Annual time series of Na*/Ca ratios, with means
314	and standard deviations (1 σ) on the right of the panel; pre-earthquake (EQ) data are from
315	samples collected near the Weizhou station in 2001 and 2002 (Qin et al., 2006).
316	
317	Figure 3. Comparison of Min Jiang river dissolved (a) Na^*/Ca and (b) ${}^{87}Sr/{}^{86}Sr$ before
318	and after the 2008 Wenchuan earthquake. Data are for water samples collected from the
319	same sites and during the same seasons. Pre-EQ data are from Qin et al. (2006), Yoon et
320	al. (2008) and Huh (2010); post-EQ data are from the samples collected in 2011 in this
321	study. Pre-EQ ⁸⁷ Sr/ ⁸⁶ Sr data are not available for tributary sites. Analytical uncertainties
322	are smaller than symbol sizes. Gray shading in (a) shows the pre-EQ Na*/Ca variability
323	of 0.02 (1 σ). The site numbers correspond to Figure 1; ZJG and WZ are Zhenjiangguan
324	and Weizhou stations, respectively. Magnitude of changes (Δ) between pre-EQ and post-
325	EQ can be compared to the mean PGA in each catchment (c and d). Bars for WZ in (c)
326	show standard deviations (1σ) of the data in Figure 2b.
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- ¹GSA Data Repository item 2015xxx, xxxxxxxx, is available online at
- 329 www.geosociety.org/pubs/ft2015.htm, or on request from editing@geosociety.org or
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