

# Strontium isotopes in Chilean rivers: the flux of unradiogenic continental Sr to seawater.

Katherina Fiege<sup>a,b</sup>, Christian A. Miller<sup>a,c</sup>, Laura F. Robinson<sup>a</sup>, Ricardo Figueroa<sup>d</sup>,  
Bernhard Peucker-Ehrenbrink<sup>a,e\*</sup>

<sup>a</sup> *Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA;* <sup>b</sup> *Institute of Geology and Paleontology, University of Heidelberg, 69120 Heidelberg, Germany;* <sup>c</sup> *MIT/WHOI Joint Program in Oceanography, USA;* <sup>d</sup> *Aquatic Systems Research Unit, Environmental Science Center EULA-Chile, University of Concepcion, PO Box 160-C, Concepcion, Chile;* <sup>e</sup> *Laboratoire d'Etudes en Géophysique et Océanographie Spatiale (LEGOS), CNES/ENRS/UPS/IRD, Observatoire Midi-Pyrénées, 14 av. E. Belin, 31400 Toulouse, France.*

\* Corresponding author: [behrenbrink@whoi.edu](mailto:behrenbrink@whoi.edu), phone: 01 508 289 2518, fax: 01 508 457 2193.

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## Abstract

Analyses of Chilean river waters indicate that the average yield of unradiogenic Sr ( $\sim 517$  moles Sr km<sup>-2</sup> yr<sup>-1</sup>, <sup>87</sup>Sr/<sup>86</sup>Sr  $\sim 0.7057$ ) from western South America (1,220,853 km<sup>2</sup>) into the southeastern Pacific Ocean is  $\sim 2$ -4 times higher than that from Iceland ( $\sim 110$  moles Sr km<sup>-2</sup> yr<sup>-1</sup>,

21  $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7025$ ) and the Deccan traps, but lower than fluxes of unradiogenic Sr from ocean  
22 islands in the Lesser Antilles and Réunion. The Sr flux from western South America accounts  
23 for about 1.8% of the annual dissolved Sr delivered to the ocean via rivers. If Chilean rivers  
24 analyzed in this study accurately characterize runoff from western South America, active  
25 convergent continental margins release about as much unradiogenic Sr to seawater as a 0-1 Myr  
26 old mid-ocean ridge segment of equivalent length. Modulations of the flux of unradiogenic Sr  
27 from active margins over geologic time scales have to be considered as an additional driving  
28 force of change in the marine Sr isotope record, supplementing temporal variations in the  
29 submarine hydrothermal flux as a source of unradiogenic Sr to seawater. Such modulations can  
30 be driven by changes in the surface exposure of volcanic arc terrains, changes in climate, ocean  
31 currents and geographic latitude due to plate tectonics, as well as topographic changes that can  
32 affect local rainfall, runoff and erosion.

33

## 34 **1. Introduction**

35 Of the radiogenic isotope systems, the  $^{87}\text{Sr}/^{86}\text{Sr}$  of continental runoff has been studied most  
36 comprehensively (e.g., Faure et al., 1967; Fisher and Stueber, 1976; Wadleigh et al., 1985;  
37 Åberg and Wickman, 1987; Goldstein and Jacobsen, 1987; Palmer and Edmond, 1989, 1992;  
38 Cameron and Hattori, 1997). Prior to the discovery of submarine hydrothermal vents in 1977 the  
39 marine Sr isotope record was viewed as reflecting the changing balance between two contrasting  
40 continental sources; unradiogenic runoff from unradiogenic basaltic terrains and radiogenic Sr  
41 derived from granitic terrains (Brass, 1976). Since the discovery of submarine hydrothermal  
42 vents the marine strontium isotope record has generally been interpreted and modeled as a

43 mixture of unradiogenic hydrothermal Sr and radiogenic continental Sr with minor contributions  
44 from the diagenesis of marine sediments (e.g., Albarede et al., 1981; Palmer and Edmond, 1989).

45 To date, ~193 exorheic rivers representing ~47% of the total continental runoff have been  
46 characterized at least once for  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr concentration (Peucker-Ehrenbrink, in prep., and  
47 references therein). Despite this significant body of work, runoff from several large-scale  
48 drainage regions remains poorly defined and, thus far, has had to be approximated through  
49 comparison of similarities in bedrock characteristics with better-characterized drainage areas  
50 (Palmer and Edmond, 1989).

51 Of all large continental drainage regions (Graham et al., 1999, 2000; Peucker-Ehrenbrink,  
52 2009), the region of South America (1,220,853 km<sup>2</sup>) that drains into the southeastern Pacific is  
53 characterized by the youngest bedrock (~96 Myr) and the highest percentage (37.3%) of exposed  
54 extrusive bedrock (Peucker-Ehrenbrink and Miller, 2007). On average, this region also receives  
55 abundant rainfall (e.g., New et al., 2002; Muñoz et al., 2007) and generates about 4% of the  
56 annual global runoff from the equivalent of 1% of the total continental land area. Surprisingly,  
57 we could not find any published Sr isotope analysis of waters draining this region, only a  
58  $^{87}\text{Sr}/^{86}\text{Sr}$  value of 0.7075 for hydrous precipitates in Atacama Desert soils (Rech et al., 2003).  
59 Even the comprehensive review of Palmer and Edmond (1989) did not attempt to include this  
60 drainage region into the assessment of the continental flux of Sr into the oceans, although they  
61 did predict that inclusion of runoff from “relatively young volcanic island arc terrains of the  
62 western Pacific, Cenozoic platform carbonates and plateau basalts” (Palmer and Edmond, 1989,  
63 p. 22) would shift the empirically-determined average  $^{87}\text{Sr}/^{86}\text{Sr}$  of continental runoff from 0.7119  
64 to 0.7114. This study was conducted to estimate the isotope composition and flux of continental  
65 Sr to the southeastern Pacific Ocean.

66

## 67 **2. Regional Geology**

68 Rivers investigated in this study were sampled in central and southern Chile and are part of a  
69 larger number of mid-size river basins that drain the western side of South America into the  
70 southwestern Pacific. As the regional geology and tectonic setting of the western Andes as well  
71 as the geological makeup of Chilean drainage basins have recently been summarized (Stern,  
72 2004; Muñoz et al., 2007) we restrict the discussion of these features to a brief summary. The  
73 basins investigated by us are dominated by Pleistocene and Holocene sedimentary sequences,  
74 which commonly consist of fluvial, alluvial or deltaic deposits. Volcanic sequences are often  
75 intercalated with sedimentary units and are mainly composed of volcanic ash, pyroclastics and  
76 basaltic to dacitic lavas. These units vary in age from Jurassic to Quaternary. Intrusive and  
77 metamorphic rocks are more abundant in the southern river basins. The intrusive rocks include  
78 diorites, granites, tonalites, and gabbros, whereas amphibolites, phengites, metapelites,  
79 metacherts and rare ultramafic rocks dominate metamorphic sequences of Paleozoic to Triassic  
80 age. The locations of the river water samples collected in this area are shown in Figure 1 and are  
81 listed in Table 1.

82 The lithologic composition and age structure of large-scale continental drainage regions  
83 (Graham et al., 1999, 2000) has been analyzed by Peucker-Ehrenbrink and Miller (2007).  
84 Among all drainage regions, the drainage area of western South America stands out as the region  
85 with the youngest average bedrock age (96 Myr) and also as the area most dominated by  
86 extrusive bedrock (37.3%). The  $^{87}\text{Sr}/^{86}\text{Sr}$  of the basaltic arc rocks from the southern volcanic  
87 zone of the Andes ranges from 0.70384 to 0.70451 (Hickey et al., 1986). These values are

88 similar to those of the northern Andean volcanic zone, but less radiogenic than the central  
89 Andean volcanic zone.

90       Runoff from Chile into the eastern Pacific Ocean varies strongly with latitude. North of  
91 latitude 32.5°S runoff is almost negligible as evaporation dominates the water balance. Muñoz  
92 et al. (2007) show that annual runoff increases from less than 100 mm north of 32.5°S to >800  
93 mm south of 35°S, and reaches >2000 mm for the BioBio River and other rivers south of 38°S.  
94 Rivers analyzed by us were sampled between latitudes 33.5°S and 42.5°S and thus capture the  
95 region that generates the majority of the runoff in Chile. Regions in northern Chile and Peru (36  
96 km<sup>3</sup> runoff per year from a Peruvian drainage area of 279,689 km<sup>2</sup>) generate little runoff into the  
97 western Pacific. In contrast, runoff into the eastern Pacific from Colombia (260 km<sup>3</sup> yr<sup>-1</sup>) and  
98 Ecuador (116 km<sup>3</sup> yr<sup>-1</sup>, with 48% of the total coming from the Esmeralda River system) is  
99 volumetrically significant with respect to the total runoff into the Pacific Ocean from the western  
100 side of South America (~1266 km<sup>3</sup> yr<sup>-1</sup>; Peucker-Ehrenbrink, 2009).

101

### 102 **3. Sampling and analytical methods**

103       All samples were filtered in the field through 0.45 μm Sterivex HV cartridge filters using 60  
104 ml all-plastic syringes (Henke-Sass-Wolf GmbH) and stored in precleaned 125 ml PE bottles (EP  
105 Scientific). Samples were not acidified, but most were kept refrigerated after they had arrived at  
106 WHOI. Some basic sample properties such as temperature, pH, and conductivity were  
107 determined in the field on some samples (see Table 1).

108       Samples were analyzed for major anions (Cl and SO<sub>4</sub>) by ion chromatography (Dionex).  
109 Major and some trace cations (Na, Mg, K, Ca, Rb, Sr, Ba) were determined by single-collector

110 ICPMS (ThermoFinnigan ELEMENT2). Concentrations of Mg, Ca, Sr and Ba were determined  
111 by isotope dilution, whereas Na, K and Rb were quantified using standard calibration curves,  
112 prepared from single element standard solutions (NIST 3100 series).

113 Strontium was quantitatively separated and purified from the samples using Sr-Spec  
114 (Eichrom) resin in 300  $\mu$ l columns. Samples were loaded in 1 ml 3.5N HNO<sub>3</sub> and Sr was eluted  
115 with 5 ml deionized water. Recovery was quantitative and separation from potential isobaric  
116 interferences Ca and Rb was excellent, as demonstrated by average <sup>88</sup>Sr/<sup>44</sup>Ca and <sup>88</sup>Sr/<sup>85</sup>Rb  
117 values in the eluant of  $1 \times 10^4$  and  $8 \times 10^4$ , respectively. Strontium isotope compositions were  
118 determined with a ThermoElectron NEPTUNE multicollector ICPMS. Whenever possible we  
119 optimized the <sup>88</sup>Sr ion beam intensity to  $\sim 45$  V ( $10^{11}$   $\Omega$  resistor). Under these conditions  $\sim 200$   
120 ng Sr was consumed per analysis. Krypton and Rb interferences were monitored and corrected  
121 off-line. The importance of off-line Kr corrections increases depending on the Kr levels detected  
122 at the time of analyses. For reasons we do not fully understand, ion beam intensities on masses  
123 82 and 83 vary over weeks and months between less than 1 mV to  $>10$  mV, and were  $\sim 8$  mV on  
124 the day of analysis. Isobaric interferences from <sup>86</sup>Kr on <sup>86</sup>Sr are corrected by using <sup>84</sup>Kr to  
125 subtract Kr until the <sup>84</sup>Sr/<sup>88</sup>Sr equals the canonical value of 0.00675476 (Hart et al., 2004), while  
126 iteratively correcting for mass bias. The fact that the <sup>86</sup>Sr/<sup>84</sup>Sr is  $\sim 17.7$  whereas the <sup>86</sup>Kr/<sup>84</sup>Kr is  
127  $\sim 0.3$  results in large error demagnification when correcting <sup>86</sup>Sr for <sup>86</sup>Kr contributions with this  
128 scheme. Two analyses of the NBS 987 standard reference material that were measured with the  
129 river water samples and corrected for Kr and instrumental mass bias using the above scheme  
130 yielded <sup>87</sup>Sr/<sup>86</sup>Sr values of 0.710295 and 0.710298. Reported <sup>87</sup>Sr/<sup>86</sup>Sr values are normalized to a  
131 NBS 987 value of 0.710240 (see table 1) and are listed to the 5<sup>th</sup> decimal place owing to the  
132 uncertainties in the Kr correction ( $\leq \pm 100$  ppm,  $2\sigma$ ).

133

#### 134 **4. Results**

135 The analytical data are summarized in Table 1 and the best correlation between  
136 concentrations of Sr with any of the major ions, Ca, is shown in Fig 2A. We have also compiled  
137 available information on annual runoff (in km<sup>3</sup> yr<sup>-1</sup>) and drainage basin sizes (in km<sup>2</sup>) (Dirección  
138 General de Aguas, 1998; Muñoz et al., 2007) in order to extrapolate our findings to the large-  
139 scale drainage area of western South America (Graham et al., 1999, 2000). Not all rivers were  
140 sampled at their mouths, and some were sampled only along major tributaries (e.g., Calle Calle  
141 river in the Valdivia river basin; Tinguiririca river in the Rapel river basin). For instance, the  
142 Tinguiririca river (sample 22) was sampled upstream of the confluence with the Cachapoal river  
143 (6370 km<sup>2</sup>; Gobierno de Chile, 2004) that together form the Rapel river. The Tinguiririca  
144 drainage basin (4730 km<sup>2</sup>) is the smaller of the two major tributary basins that make up the Rapel  
145 drainage basin (13,695 km<sup>2</sup>) but we presume that sample 22 is representative of the Rapel river.  
146 Despite this deficiency, we presume that the data are representative of the major drainage basins  
147 they represent. Where we do have multiple samples from the same river system the <sup>87</sup>Sr/<sup>86</sup>Sr  
148 values are either rather homogeneous (Tolten river), decrease (Itata river) or increase (BioBio  
149 river) slightly towards the coast, and thus provide no evidence for systematic bias of the <sup>87</sup>Sr/<sup>86</sup>Sr  
150 values.

151 In the few cases where data on drainage basin size and/or annual water discharge were  
152 unavailable (Mapocho, Rio Llonco, Rio Pichicolo, Rio Huinay) we did not include those river  
153 basins in our analysis. This does not significantly bias our results because contributions from  
154 those rivers are small owing to their small size (e.g., Huinay, Pichicolo, Lonco), or because their  
155 isotope composition and Sr concentration are similar to the large rivers we do have data for (e.g.,

156 Mapocho). The radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr}=0.70986$ ) Andalien river is a small river draining the  
157 Coastal Mountain Range between the Itata river in the North and the BioBio river in the South.  
158 In contrast to the BioBio and Itata rivers that drain the Andes and are thus affected by both  
159 rainfall and snow melt, runoff in the Andalien river is only determined by rainfall in the Coastal  
160 Mountain Range that varies smoothly between 10-50 mm per month during the austral summer  
161 and 150-200 mm per month during the austral winter (Muñoz et al., 2007). We use an average  
162 runoff of  $0.48 \text{ km}^3 \text{ yr}^{-1}$  that is based on an average of low (austral summer,  $0.08 \text{ km}^3 \text{ yr}^{-1}$ ) and  
163 high (austral winter,  $0.9 \text{ km}^3 \text{ yr}^{-1}$ ) runoff estimates given in Quiñones and Montes (2001). Our  
164 estimate of the drainage basin area of  $\sim 850 \text{ km}^2$  is based on a map of the drainage basin outline  
165 in Habit et al. (2007). The overall contribution of this radiogenic river to the total flux of Sr is  
166 negligible.

167

## 168 **5. Discussion**

### 169 *5.1. Average $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentration of Chilean rivers*

170 The average  $^{87}\text{Sr}/^{86}\text{Sr}$ , weighted according to Sr concentration (average:  $0.496 \mu\text{M}$ ) and  
171 average discharge from nine rivers, is 0.7057 (Fig. 2B, star). The weighting procedure does not  
172 introduce significant bias because  $^{87}\text{Sr}/^{86}\text{Sr}$  does not correlate with Sr concentration and the non-  
173 weighted average (0.70537) and median (0.70458)  $^{87}\text{Sr}/^{86}\text{Sr}$  are similar to the flux-weighted  
174 isotope composition (0.7057). This weighted average value does not change significantly if  
175 corrections are made for atmospheric, i.e. recycled, Sr of marine origin. If all Cl in the rivers is  
176 ultimately derived from seawater with a molar Cl/Sr value of 6260, between 1% and 5% of the  
177 Sr in most rivers analyzed could be of seawater origin. Exceptions are the Rio Pichicolo  
178 (CH049, highest Sr concentration, Fig. 2B) that receives contributions from hydrothermal



179 springs and two rivers draining into the fjords of southern Chile - the Rio Llonco (CH058) and  
180 Rio Huinay (CH059). Based on the Cl concentrations, all of the Sr in the Rio Pichicolo could be  
181 of seawater origin, though the isotopic composition of 0.70442 that is similar to values of  
182 volcanic rocks in Chile (Hickey et al., 1986; Notsu et al., 1987) demonstrates that this cannot be  
183 the case. Based on measured Cl concentrations, as much as one third of the Sr in the Rio Llonco  
184 could be derived from seawater. The isotope composition of the Rio Llonco of 0.70908 and the  
185 low Sr concentration of 0.016  $\mu\text{M}$  indicates that a significant portion of the riverine Sr could  
186 indeed be of marine origin. Correcting for this contribution, however, will not significantly  
187 change the Sr isotope composition of the non-marine component. Only 0.25% of the Sr in the  
188 Rio Huinay (Fjord district, sample CH059) can be recycled seawater Sr. The isotope  
189 composition of 0.70565 indicates that most of the Sr is of non-marine origin, and corrections for  
190 marine inputs will not significantly affect this value. In summary, we consider the weighted  
191 average  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.7057 as representative of the continental runoff from Chile into the  
192 southeastern Pacific Ocean.

193

## 194 5.2. Average $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr flux to the southeastern Pacific Ocean.

195 The annual Sr flux from the entire large-scale drainage region of western South America is  
196 estimated by extrapolating the results from the Chilean rivers analyzed in this study to the entire  
197 large-scale drainage region. The geologic similarities between Peru, Ecuador and Colombia with  
198 Chile allow us to assume that the isotope composition of runoff of all the rivers draining into the  
199 eastern Pacific is similar to that measured in Chilean rivers. This approach is justified by  
200 considering the similarities in  $^{87}\text{Sr}/^{86}\text{Sr}$  between the Northern Volcanic Zone of the Andes  
201 (Colombia, Ecuador) and the Southern Volcanic Zone of central and southern Chile (Stern,

202 2004). The Central Volcanic Zone (southern Peru, northern Chile) is characterized by more  
203 radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$ , but low runoff limits its contribution to the dissolved Sr flux into the eastern  
204 Pacific Ocean (see review by Stern, 2004). The extrapolated Sr flux for the entire drainage  
205 region of western South America is  $\sim 6.3 \times 10^8$  moles per year, equivalent to  $\sim 1.8\%$  of the global  
206 riverine Sr flux ( $3.33 \times 10^{10}$  moles per year; Palmer and Edmond, 1989). This flux corresponds to  
207 an average Sr yield of  $517 \text{ moles Sr km}^{-2} \text{ yr}^{-1}$  that we compare in the following section with  
208 estimates from three other extensively studied drainage regions dominated by volcanic  
209 lithologies: Iceland (Gannoun et al., 2006), the Lesser Antilles and Réunion (Rad et al., 2007),  
210 and the Indian Deccan Traps (Dessert et al., 2001).

211

212 *5.3. Comparison of  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr flux from the Andean arc with Iceland, the Lesser Antilles*  
213 *and Reunion, and the Deccan Traps.*

214 Based on sampling of Icelandic rivers that account for  $\sim 35 \text{ km}^3$  runoff per year, the average  
215 Sr concentration in Icelandic rivers is  $0.068 \mu\text{M}$  ( $6 \text{ ng g}^{-1}$ ; Gannoun et al., 2006; see Fig. 3, open  
216 triangles). This is much less than the runoff-weighted average Sr concentration in Chilean rivers  
217 of  $\sim 0.5 \mu\text{M}$  ( $43 \text{ ng g}^{-1}$ ). If the dissolved Sr concentration estimated by Gannoun et al. (2006) is  
218 typical for Icelandic rivers ( $170\text{-}198 \text{ km}^3$  runoff per year; Baumgartner and Reichel, 1975;  
219 Dessert et al., 2003), about  $1.2 \times 10^7$  moles of dissolved Sr, or  $110 \text{ moles Sr km}^{-2} \text{ yr}^{-1}$ , are  
220 delivered annually to the ocean by Icelandic rivers. Similarly, if the  $^{87}\text{Sr}/^{86}\text{Sr}$  analysis of the  
221 Austari Jökulsa of 0.7025 (Gannoun et al., 2006) is characteristic of Icelandic rivers, runoff from  
222 Iceland is isotopically similar to the depleted upper mantle.

223 Weathering of the Deccan flood basalts delivers approximately  $3.8 \times 10^8 \text{ mol Sr yr}^{-1}$ , or 705  
224 moles  $\text{Sr km}^{-2} \text{ yr}^{-1}$ , equivalent to  $\sim 1\%$  of the global riverine flux of Sr to the ocean (Dessert et al.,

225 2001; Fig. 3, open squares). This flux is derived from an area that accounts for only about 0.5%  
226 of the continental land area, indicative of the disproportionate contribution of basalt weathering  
227 to continental Sr runoff. Compared to most other large igneous provinces, however, Deccan  
228 flood basalts are unusually radiogenic ( $^{87}\text{Sr}/^{86}\text{Sr}$  0.705-0.715) and thus generate runoff with  
229  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.7076 to 0.7149 (average: 0.7098, weighted according to Sr concentration; Dessert  
230 et al., 2001). While the isotope composition of runoff from this basalt province is atypical of  
231 large volcanic provinces, the Sr flux is likely more representative. However, owing to the  
232 radiogenic nature of river draining the Deccan traps, the flux of unradiogenic Sr ( $^{87}\text{Sr}/^{86}\text{Sr}$  of  
233 0.7035) from the Deccan traps is quite low, similar to that from Iceland.

234 These fluxes can be compared to Sr fluxes from small ocean islands (Rad et al., 2007), such  
235 as Martinique (1100 km<sup>2</sup>, ~1.76 km<sup>3</sup> yr<sup>-1</sup> surface runoff) and Guadeloupe (1179 km<sup>2</sup>, ~3.54 km<sup>3</sup>  
236 yr<sup>-1</sup> surface runoff) in the Lesser Antilles, and Réunion in the Indian Ocean (2512 km<sup>2</sup>, ~6.28  
237 km<sup>3</sup> yr<sup>-1</sup> surface runoff). We compare the surface (river) runoff from these islands with river  
238 data from western South America, Iceland and the Deccan traps, but emphasize that the total Sr  
239 flux from these areas may be significantly higher if subterranean Sr fluxes are significant. While  
240 the lack of data for subterranean fluxes prevents us from quantifying such contributions for the  
241 drainage areas of western South America, Iceland or the Deccan traps, Rad et al. (2007) have  
242 quantified subsurface fluxes from small islands of the Lesser Antilles and Réunion.  
243 Contributions from surface runoff to the total Sr flux range from 20% (Martinique) to 30%  
244 (Réunion) and 60% (Guadeloupe). The unradiogenic Sr yield for these islands (see Fig. 3) could  
245 thus easily be higher by factors of 2 (Lesser Antilles) and 3 (Réunion) if the subterranean  
246 contributions are taken into account.

247

248 5.4. Global significance of unradiogenic Sr runoff from volcanically-dominated continental  
249 margins.

250 Runoff from western South America combines two important characteristics of runoff from  
251 Iceland and the Deccan Traps: unradiogenic Sr and high Sr yields. This drainage region thus  
252 yields abundant dissolved Sr that is isotopically more similar to high-temperature (HT) mid  
253 ocean ridge (MOR) vent fluids ( $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.70285-0.70465; Bach and Humphris, 1999) and  
254 volcanic islands (Louvat, 1997; Rad et al., 2007) than to average continental runoff ( $^{87}\text{Sr}/^{86}\text{Sr}$  of  
255 0.7119; Palmer and Edmond, 1989). We estimate the flux of unradiogenic ( $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.7035)  
256 Sr from this region using a model of two-component isotope mixing between an average upper  
257 crustal component ( $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.7119; Palmer and Edmond, 1989) and a HT MOR-vent  
258 component ( $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.7035; Palmer and Edmond, 1989). With this, the yield of unradiogenic  
259 riverine ( $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.7035) Sr from western South America is 377 moles Sr km<sup>-2</sup> yr<sup>-1</sup>  
260 (equivalent to a total flux of 4.6x10<sup>8</sup> mole yr<sup>-1</sup>), a factor of 2-3 higher than the yield of  
261 unradiogenic Sr from Iceland or the Deccan traps, and a factor of up to two lower than  
262 unradiogenic Sr yields from the Lesser Antilles and Réunion (gray symbols in Fig. 3). These  
263 yields do not include subterranean contributions that can be significant (e.g. Lesser Antilles,  
264 Réunion; Rad et al., 2007), but are not quantified for western South America, Iceland and the  
265 Deccan traps.

266 Estimates of magmatic heat dissipation (6.3-12x10<sup>19</sup> J yr<sup>-1</sup>; Butterfield et al., 2001) for 0-1  
267 Myr old MOR crust, average fluid temperature (350°C; Palmer and Edmond, 1989; 1624 J g<sup>-1</sup>,  
268 Butterfield et al., 2001) and Sr concentration in such HT fluids (100 μM; Palmer and Edmond,  
269 1989) allow us to compare the global flux of Sr from HT-vents (3.9-7.4x10<sup>9</sup> M yr<sup>-1</sup>) with the flux  
270 of unradiogenic Sr from continental arcs. Per length of volcanically active arc (~5000 km for the

271 Andes), the yield of unradiogenic arc strontium ( $9.2 \times 10^4$  mole  $\text{km}^{-1}$   $\text{yr}^{-1}$ ) rivals the yield of Sr  
272 from HT fluids interacting with a young MOR segment of equivalent length ( $7.8$ - $14.8 \times 10^4$  mole  
273  $\text{km}^{-1}$   $\text{yr}^{-1}$ ; assuming a global MOR length of 50,000 km). Consequently, temporal variations in  
274 the flux of unradiogenic Sr from such unradiogenic continental arcs have the potential to  
275 contribute to the observed temporal variations in the seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  record.

276 Such temporal variations in runoff can be forced by the plate-tectonic movement of such  
277 areas into more humid climate zones. Increases in runoff can also be triggered by topographic  
278 uplift that leads to enhanced orographic rainfall and physical erosion (e.g. Ernst, 2004), and by  
279 higher temperatures that accelerate weathering reactions. Alternatively, a greater areal  
280 abundance of young active margins can lead to enhanced delivery of unradiogenic continental Sr  
281 to seawater. Such processes need to be considered as complementary mechanisms to variable  
282 submarine hydrothermal Sr emissions for modulating the flux of unradiogenic Sr to seawater (cf.  
283 Brass, 1976). However, models of the temporal evolution of unradiogenic Sr fluxes from  
284 volcanically-dominated active margins critically depend on reconstructing uplift histories of  
285 coastal mountain belts (e.g. Gregory-Wodzicki, 2000; Garzzone et al., 2008) that induce  
286 orographic rainfall. Such reconstructions need to be focused on the initial uplift, as the first  
287 1000-2000 meters uplift trigger most of the precipitation enhancement (Browning, 1980).  
288 Competing factors such as shifts in ocean currents that influence moisture transport to land also  
289 need to be taken into account. As the evolution of these factors has not been reconstructed with  
290 sufficient temporal resolution and spatial precision (i.e., typical uncertainties of paleoelevation  
291 estimates are on the order of 1000-1500 m; Gregory-Wodzicki, 2000; Carzzone et al., 2008) for  
292 the drainage area of western South America, modeling the effects variable contributions of

293 unradiogenic Sr have had on the evolution of seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  would be highly speculative at  
294 this point.

295

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305

## 306 **7. References**

307 Åberg, F., Wickman, F.E., 1987. Variations of  $^{87}\text{Sr}/^{86}\text{Sr}$  in water from streams discharging into  
308 the Bothnian Bay, Baltic Sea. *Nordic Hydrology* 18, 33-42.

309 Albarede, F., Michard, A., Minster, J.F., Michard, G., 1981.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in hydrothermal  
310 waters and deposits from the East Pacific Rise at 21°N. *Earth and Planetary Science Letters*  
311 55, 229-236.

312 Bach, W., Humphris, S.E., 1999. Relationship between the Sr and O isotope compositions of  
313 hydrothermal fluids and the spreading and magma-supply rates at oceanic spreading centers.  
314 *Geology* 27, 1067-1070.

315 Baumgartner A., Reichel, E., 1975. *The World Water Balance*. Elsevier, Amsterdam, 179 pp +  
316 31 maps.

317 Brass, G.W., 1976. The variation in the marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio during Phanerozoic time:  
318 interpretation using a flux model. *Geochimica et Cosmochimica Acta* 40, 721-730.

319 Browning, K.A., 1980. Structure, mechanism, and prediction of orographically enhanced rain in  
320 Britain. *Global Atmospheric Research Programme Publication Series* 23, 85-114.

321 Butterfield, D.A., Nelson, B.K., Wheat, C.G., Mottl, M.J., Roe, K.K., 2001. Evidence for basaltic  
322 Sr in midocean ridge-flank hydrothermal systems and implications for the global oceanic Sr  
323 isotope balance. *Geochimica et Cosmochimica Acta* 65, 4141-4153

324 Cameron, E.M., Hattori, K., 1997. Strontium and neodymium isotope ratios in the Fraser River,  
325 British Columbia: a riverine transect across the Cordilleran orogen. *Chemical Geology* 137,  
326 243-253.

327 Carziona, C.N., Hoke, G.E., Libarkin, J.C., Withers, S., MacFadden, B., Eiler, J., Gosh, P.,  
328 Mulch, A., 2008. Rise of the Andes. *Science* 320, 1304-1307.

329 Das, A., Krishnaswami, S., 2007. Elemental geochemistry of river sediments from the Deccan  
330 Traps, India: Implications to sources of elements and their mobility during basalt-water  
331 interaction. *Chemical Geology* 242, 232-254.

332 Dessert, C., Dupré, B., François, L.M., Schott, J., Gaillardet, J., Chakrapani, G.J., Bajpai, S.,  
333 2001. Erosion of Deccan Traps determined by river geochemistry: impact on the global  
334 climate and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of seawater. *Earth and Planetary Science Letters* 188, 459-474.

335 Dirección General de Aguas, 1998. Water balance of Chile. Santiago de Chile.

336 Ernst, W.G., 2004. Regional crustal thickness and precipitation in young mountain chains.  
337 Proceedings of the National Academy of Sciences of the United States of America 101 (42),  
338 14,998-15,001.

339 Faure, G., Crocket, J. H., Hueley, P.M., 1967. Some aspects of the geochemistry of strontium  
340 and calcium in the Hudson Bay and the Great Lakes. *Geochimica et Cosmochimica Acta* 31,  
341 451-461.

342 Fisher, R.S., Stueber, A.M., 1976. Strontium isotopes in selected streams within the  
343 Susquehanna river basin. *Water Resources Research* 12, 1061-1068.

344 Gannoun, A., Burton, K.W., Vigier, N., Gislason, S.R., Rogers, N., Mokadem, F., Sigfuson, B.,  
345 2006. The influence of weathering process on riverine osmium isotopes in a basaltic terrain.  
346 *Earth and Planetary Science Letters* 243, 732-748.

347 Gobierno de Chile, Ministerio de Obras Publicas, Dirección General de Aguas, Diciembre 2004.  
348 Cuenca del Rio Rappel, Cade-Idepe Consultores en Ingenieria, 190 pp.

349 Goldstein, S.J., Jacobsen, S.B., 1987. The Nd and Sr isotope systematics of river-water dissolved  
350 material: implications for the sources of Nd and Sr in seawater. *Chemical Geology*, 245-272.

351 Graham, S.T., Famiglietti, J.S., Maidment, D.R., 1999. Five-minute,  $\frac{1}{2}^\circ$ , and  $1^\circ$  data sets of  
352 continental watersheds and river networks for use in regional and global hydrologic and  
353 climate system modeling studies. *Water Resources Research*, 35(2), 583-587.

354 Graham, S.T., Famiglietti, J.S., Maidment, D.R., 2000. Five-minute,  $\frac{1}{2}^\circ$ , and  $1^\circ$  data sets of  
355 continental watersheds and river networks for use in regional and global hydrologic and  
356 climate system modeling studies: watershed and drainage network data evaluated at three  
357 spatial resolutions with supporting documentation. Digital data on 5 minute,  $\frac{1}{2}$  degree and 1



358 degree resolution, geographic (lat/long) global grids. Boulder, CO: NOAA National  
359 Geophysical Data Center. Nine spatial layers with multiple attributes.

360 Gregory-Wodzicki, K., 2000. Uplift history of the Central and Northern Andes: A review.  
361 Geological Society of America Bulletin 112 (7), 1091-1105.

362 Habit, E., Belk, M., Victoriano, P., Jaque, E., 2007. Spatio-temporal distribution patterns and  
363 conservation of fish assemblages in a Chilean coastal river. *Biodiversity Conservation* 16,  
364 3179-3191, doi: 10/1007/s10531-007-9171-9.

365 Hart, S.R., Ball, L., Jackson, M., 2004 (additions and revisions, Feb. 2005). Sr isotopes by laser  
366 ablation PIMMS: Application to cpx from Samoan peridotite xenoliths. WHOI Plasma  
367 Facility Open File Technical Report 11, ([http://www.whoi.edu/science/GG/people/shart/  
368 open\\_file.htm](http://www.whoi.edu/science/GG/people/shart/open_file.htm)).

369 Hickey, R.L., Frey, F.A., Gerlach, D.C., 1986. Multiple sources for basaltic arc rocks from the  
370 southern volcanic zone of the Andes (34°-41°S): Trace element and isotopic evidence for  
371 contributions from subducted oceanic crust, mantle, and continental crust. *Journal of*  
372 *Geophysical Research* 91 (B6), 5963-5983.

373 Louvat, P., 1997. Etude géochimique de l'érosion fluviale d'îles volcaniques à l'aide des bilans  
374 d'éléments majeurs et traces. Ph.D. thesis, Université Paris 7, 322 p.

375 McArthur, J.M., Howarth, R.J., 2004. Strontium isotope stratigraphy. In *A Geologic Time Scale*  
376 *2004* (F.M. Gradstein, J.G. Ogg and A.G. Smith). Cambridge Univ. Press, Cambridge, UK,  
377 96-105.

378 Muñoz, J.F., Fernandez, B., Vargas, E., Pastén, P., Gomez, D., Rengifo, P., Muñoz, J., Atenas,  
379 M., Jofré, J.C., 2007. Chilean water resources. In *The Geology of Chile* (T. Moreno and W.  
380 Gibbons, Eds.). Geological Society of London, Bath, 215-230.

381 New, M., Lister, D., Hulme, M., Makin, I., 2002. A high-resolution data set of surface climate  
382 over global land areas. *Climate Research* 21, 1-25.

383 Notsu, K., Lopez-Escobar, L., Onuma, N., 1987. Along-arc variation of Sr-isotope composition  
384 in volcanic rocks from the Southern Andes (33°S-55°S). *Geochemical Journal* 21, 307-313.

385 Palmer, M.R., Edmond, J.M., 1989. The strontium isotope budget of the modern ocean. *Earth*  
386 *and Planetary Science Letters* 92, 11-26.

387 Palmer, M.R., Edmond, J.M., 1992. Controls over the strontium isotope composition of river  
388 water. *Geochimica et Cosmochimica Acta* 56, 2099-2111.

389 Peucker-Ehrenbrink, B., Miller, M.W., 2007. Quantitative bedrock geology of the continents and  
390 large-scale drainage regions. *Geochemistry, Geophysics, Geosystems* 8 (5), Q06009, doi:  
391 10.1029/2006GC001544.

392 Peucker-Ehrenbrink, B., 2009. Land2Sea database of river drainage basin sizes, annual water  
393 discharges, and suspended sediment fluxes. *Geochemistry, Geophysics, Geosystems* 10 (6),  
394 Q06014, doi:10.1029/2008GC002356.

395 Quiñones, R.A., Montes, R.M., 2001. Relationship between freshwater input to the coastal zone  
396 and the historical landings of the benthic/demersal fish *Eleginops maclovinus* in central-south  
397 Chile. *Fisheries Oceanography* 10 (4), 311-328.

398 Rad, S.D., Allègre, C.J., Louvat, P., 2007. Hidden erosion on volcanic islands. *Earth and*  
399 *Planetary Science Letters* 262, 109-124.

400 Rech, J.A., Quade, J., Hart, W.S., 2003. Isotopic evidence for the source of Ca and S in soil  
401 gypsum, anhydrite, and calcite in the Atacama Desert, Chile. *Geochimica et Cosmochimica*  
402 *Acta* 67, 575-586.

403 Stern, C.R., 2004. Active Andean volcanism: its geologic and tectonic setting. *Revista*  
404 *Geologica de Chile*, 31 (2), 161-206.

405 Wadleigh, M.A., Veizer, J., Brooks, C., 1985. Strontium and its isotopes in Canadian rivers:  
406 fluxes and global implications. *Geochimica et Cosmochimica Acta* 49, 1727-1736.

407

408 **Figure 1:** Map of South America, Chile (in gray) and sampling area (box). Inset shows  
409 sampling locations (black circles) and outlines of Chilean river basins sampled in this study. The  
410 northern Coastal basin includes the Andalien river basin. The southern Coastal basin includes  
411 the Rio Cisne, the Rio Llonco and the Rio Huinay.

412

413 **Figure 2A:** Strontium ( $\mu\text{M}$ , logarithmic scale) versus calcium ( $\text{mM}$ , logarithmic scale)  
414 concentrations in rivers draining Chile (filled circles), Iceland (small gray triangles; Gannoun et  
415 al., 2006), the Indian Deccan Traps (open squares; Dessert et al., 2001), the Lesser Antilles (open  
416 circles; Rad et al., 2007), and Reunion (large open triangles; Rad et al., 2007). The Chilean  
417 sample CH049 (Rio Pichicolo) with very high Sr (see Fig. 2B) and Ca concentrations is not  
418 shown.

419 **Figure 2B:** Strontium concentrations ( $\mu\text{M}$ , logarithmic scale) versus  $^{87}\text{Sr}/^{86}\text{Sr}$  in Chilean (filled  
420 circles), Lesser Antilles (open circles) and Reunion rivers (large open triangles). The average Sr  
421 concentration ( $0.50 \mu\text{M}$ ,  $43 \mu\text{g l}^{-1}$ ) and isotope composition ( $^{87}\text{Sr}/^{86}\text{Sr}=0.7057$ ) of the Chilean  
422 rivers, weighted according to water flux, is shown as a star.

423

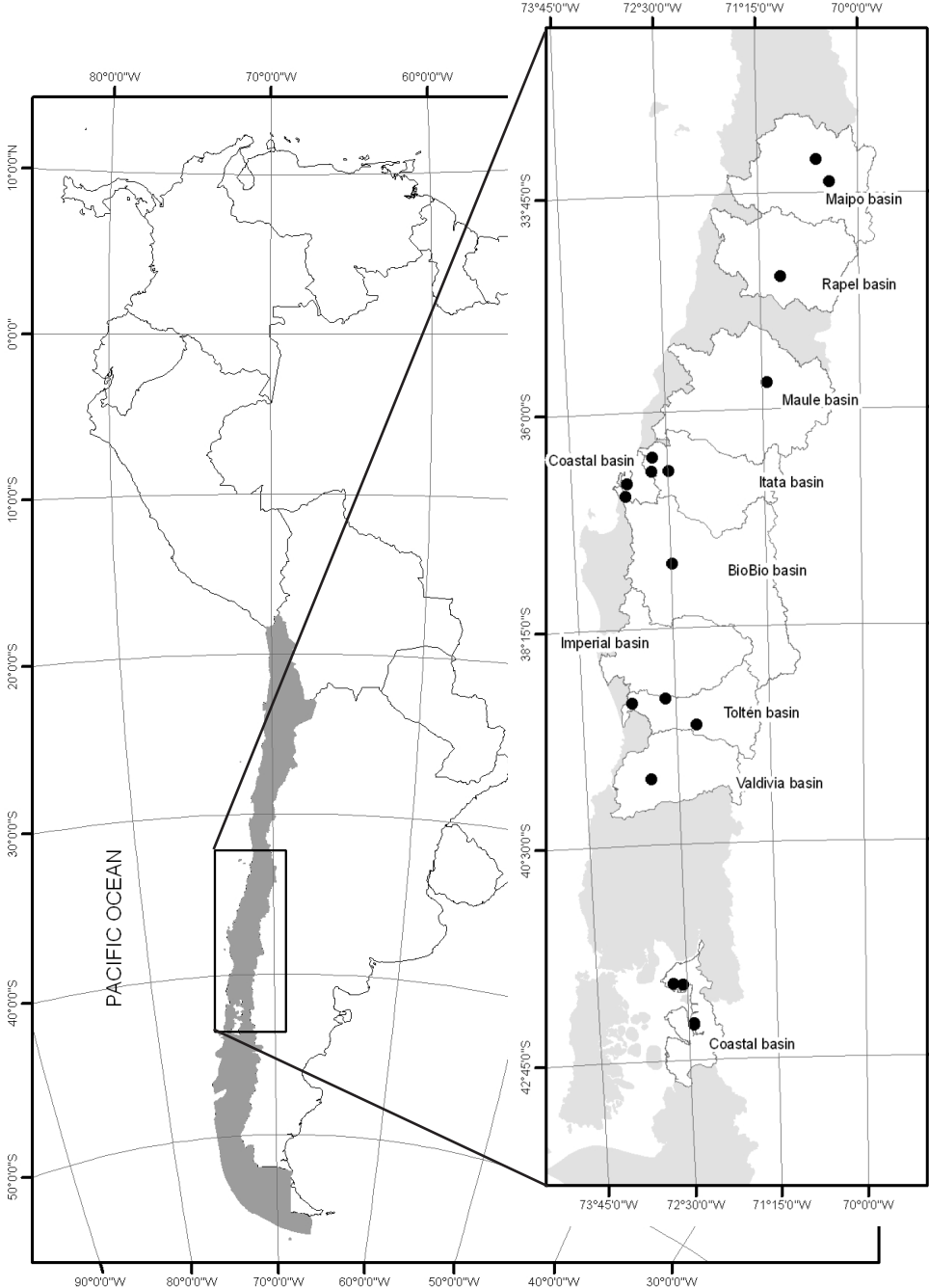
424 **Figure 3:** Strontium yield (area-normalized Sr flux) versus specific surface runoff (area-  
425 normalized water flux) from western South America (filled circle) the Deccan traps (squares),

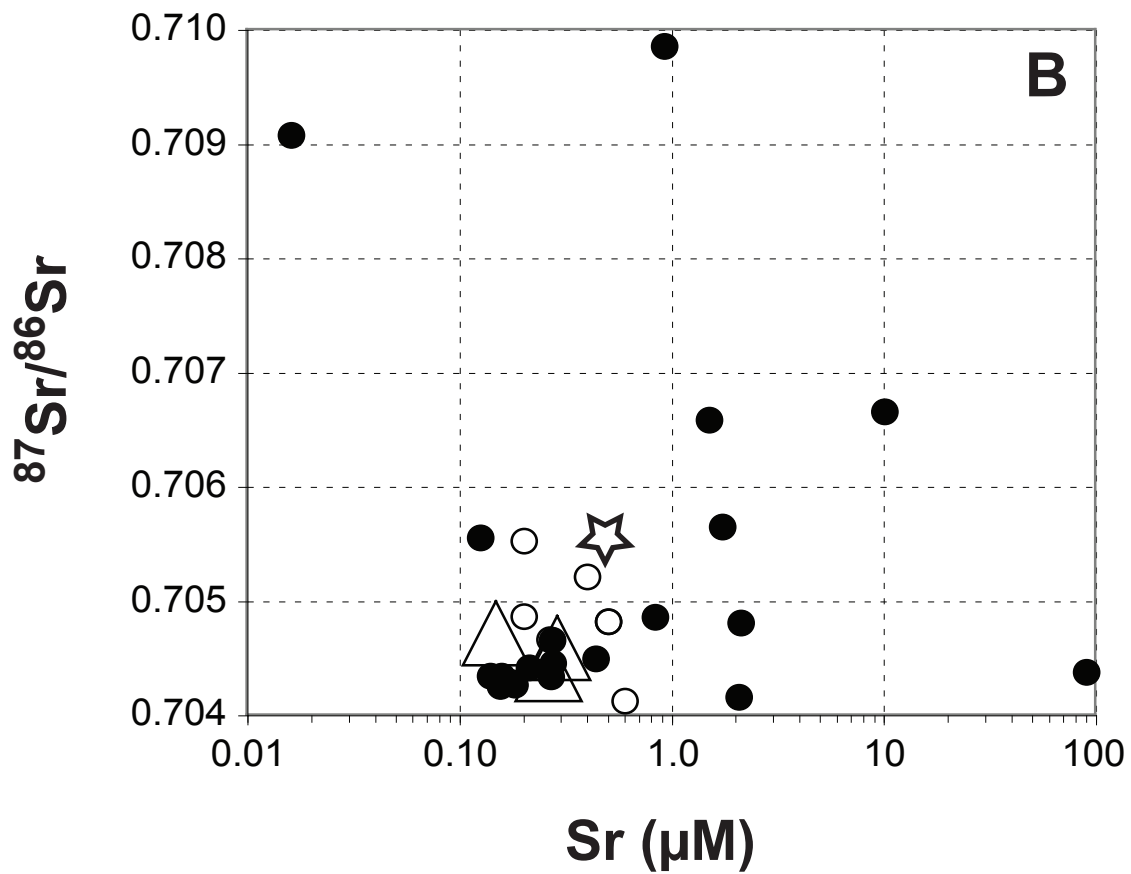
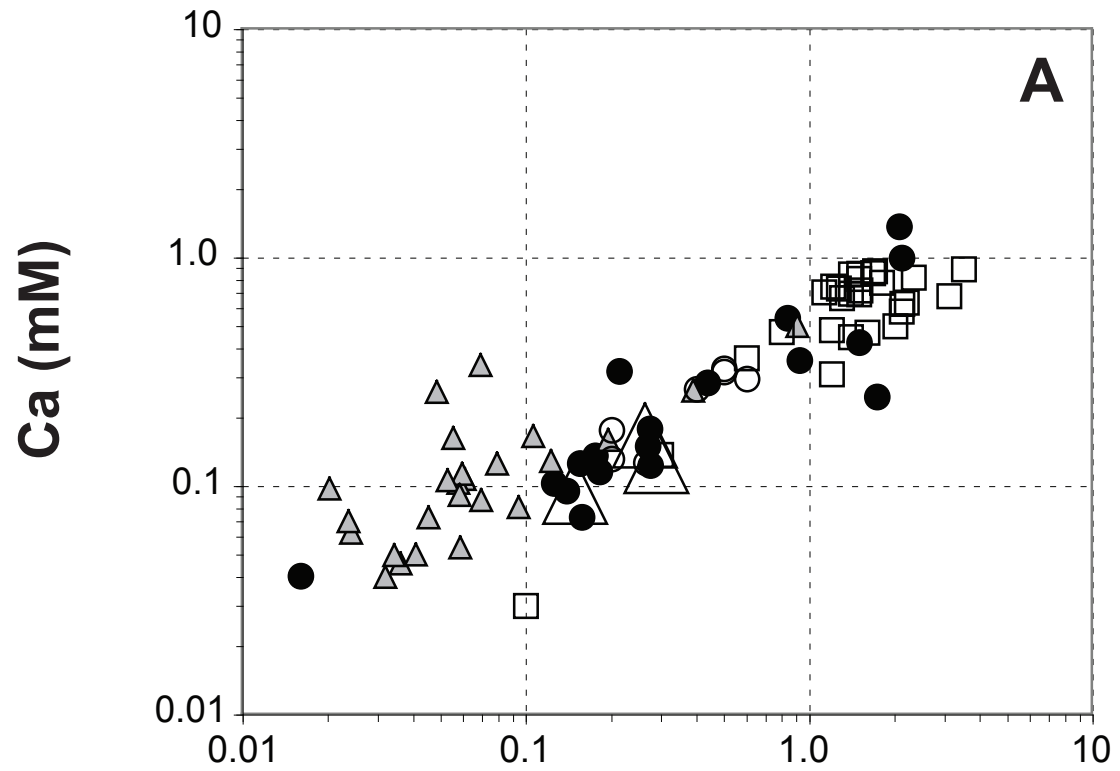
426 Iceland (small gray triangle), Martinique and Guadeloupe (lesser Antilles, open circle), and  
427 Reunion (large triangle). The gray symbols represent the yield of unradiogenic Sr ( $^{87}\text{Sr}/^{86}\text{Sr}$  of  
428 0.7035) from these areas. In the case of Iceland the flux of unradiogenic Sr is assumed to be  
429 identical to the total Sr flux, because of the presumed unradiogenic nature of riverine Sr in  
430 Iceland (see text for details).

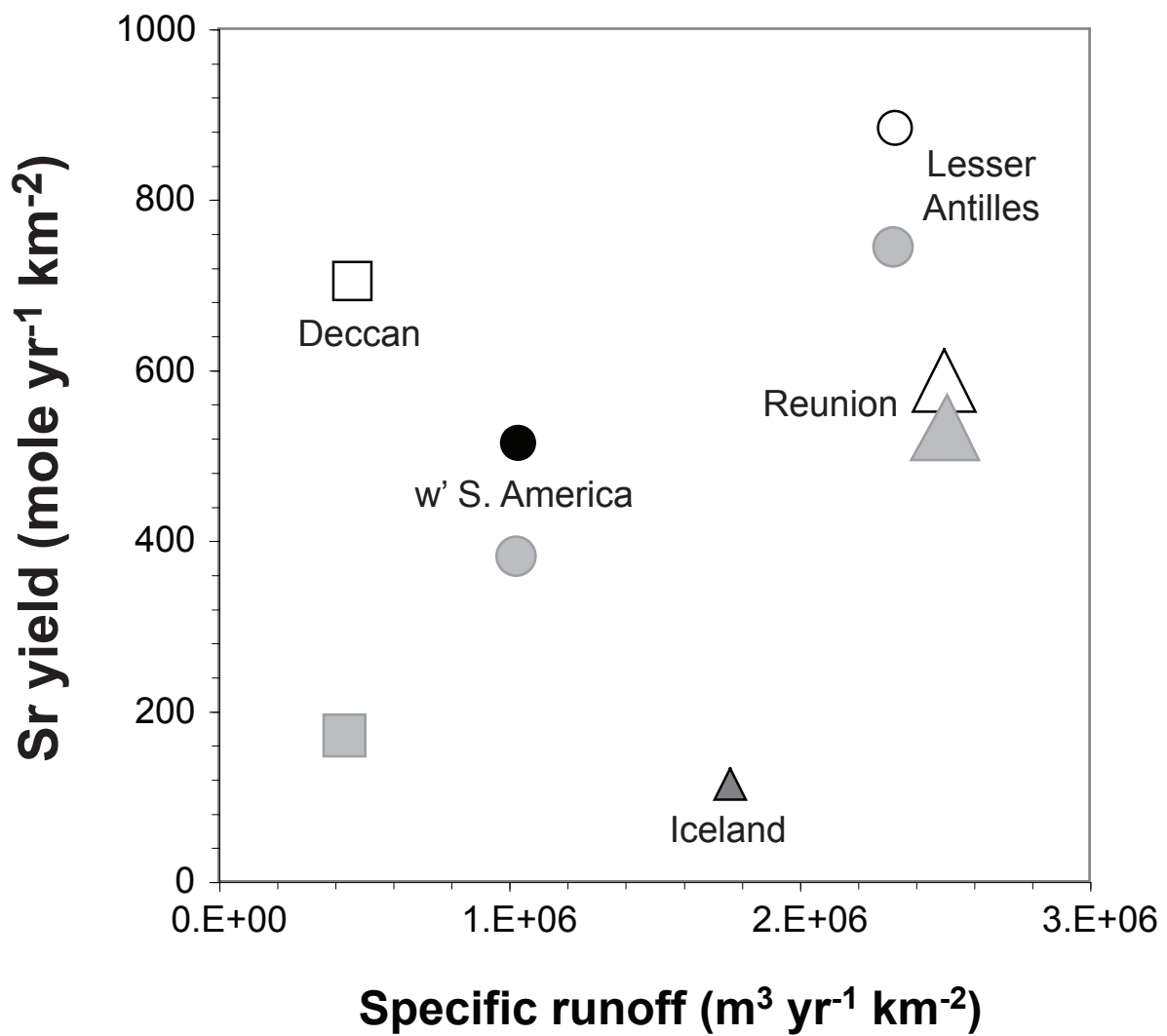
431

432 **Table 1: Physical and chemical data for rivers in central and southern Chile.**

Fiege et al. (CHEMGE4601, 2009) - Figure 1







**Table 1: Physical and chemical data for rivers in central and southern Chile**

ID	River	Large River Basin	Total Drainage Basin	Runoff	Latitude	Longitude	Altitude	Date	Time	Temp.	pH	Conduct.	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>	<sup>87</sup> Sr/ <sup>86</sup> Sr
			km <sup>2</sup>	km <sup>3</sup> yr <sup>-1</sup>	deg min S	deg min W	m	mm/dd/yr	24 h	°C		µS cm <sup>-1</sup>	mM	µM	mM	mM	mM	mM	nM	µM	nM	
1 (CH001)	Mapocho				33°23.687'	70°31.279'	1227	01/28/07					0.15	1894	0.276	0.281	1.37	0.030	37.2	2.07	68.0	0.70416
3 (CH003)	Maipo	Maipo	<b>15,157</b>	<b>3.14</b>	33°37.729'	70°21.288'	940	01/29/07					2.49	3.30		0.387	3.69	0.070	73.9	<b>10.06</b>	85.6	<b>0.70666</b>
22 (Tg 1 Tinguiririca)	Tinguiririca	Rapel	<b>13,695</b>	<b>5.38</b>	34°36.750'	70°58.908'		09/16/06	10:30	9.5	8.6	128.6	0.16	366	0.328	0.110	0.545	0.026	38.6	<b>0.835</b>	25.3	<b>0.70486</b>
6 (CH013)	Maule	Maule	<b>20,865</b>	<b>17.96</b>	35°43.415'	71°10.578'	423	01/31/07					0.19	174	0.365	0.129	0.285	0.033	45.8	<b>0.436</b>	22.3	<b>0.70450</b>
7 (CH026)	Itata	Itata	11,385	11.39	36°27.997'	72°41.498'	17	02/02/07					0.33	3.5	0.905	0.472	0.428	0.046	3.03	1.50	0.13	0.70659
8 (IT 1 Itata 1)	Itata	Itata	11,385	11.39	36°37.453'	72°28.893'		06/28/06	15:20	11.2	7.3	73.2	0.053	29	0.189	0.094	0.124	0.022	24.3	0.275	19.7	0.70446
9 (IT 2 Itata 2)	Itata	Itata	<b>11,385</b>	<b>11.39</b>	36°37.453'	72°41.742'		06/29/06	17:00	10	6.8	79	0.055	34.2	0.177	0.080	0.150	0.026	21.7	<b>0.269</b>	22.5	<b>0.70434</b>
2 (CH02)	Andalien	Andalien	<b>~850</b>	<b>~0.48</b>	36°48.115'	73°58.004'		12/02/04	10:40				0.16	10.2	0.58	0.177	0.356	0.043	17	<b>0.921</b>	70.2	<b>0.70986</b>
4 (CH05)	BioBio	BioBio	<b>24,782</b>	<b>31.69</b>	36°52.128'	73°02.671'		12/02/04	9:00				0.088	50.7	0.238	0.099	0.179	0.025	22.7	<b>0.273</b>	18.2	<b>0.70466</b>
21 (BU 2 Bueno 2)	Bueno	BioBio	24,782	31.69	37°35.200'	72°28.508'		08/22/06					0.036	6.7	0.085	0.043	0.073	0.007	7.52	0.157	16.6	0.70435
11 (CH029)	Tolten	Tolten	8,040	18.4	38°58.633'	72°38.183'	226	02/03/07					0.049	28.1	0.202	0.075	0.126	0.025	22.5	0.155	24.5	0.70426
13 (TL 1 Tolten 1)	Tolten	Tolten	<b>8,040</b>	<b>18.4</b>	39°00.653'	73°04.907'		06/25/06	16:00	11	7.5	28.1	0.040	15.6	0.136	0.056	0.096	0.019	17.3	<b>0.139</b>	13.7	<b>0.70435</b>
12 (CH034)	Tolten	Tolten	8,040	18.4	39°16.46'	72°13.804'	223	02/04/07					0.035	19.3	0.159	0.066	0.116	0.023	22.4	0.182	12.5	0.70427
14 (CH038)	Calle Calle	Valdivia	<b>9,902</b>	<b>29.27</b>	39°48.595'	72°51.89'	14	02/04/07					0.038	16.2	0.118	0.046	0.103	0.016	16.4	<b>0.125</b>	21.0	<b>0.70556</b>
15 (CH048)	Cisne		<b>5,302</b>	<b>12.21</b>	41°57.492'	72°40.682'	34	02/06/07					0.045	12	0.125	0.083	0.136	0.016	11.3	<b>0.175</b>	22.7	<b>0.70429</b>
16 (CH049)	Pichicolo				41°58.495'	72°33.178'	73	02/06/07					2.78	606		0.034	0.320	0.021	39.7	0.213	8.7	0.70442
19 (CH058)	Llonco				42°22.434'	72°24.649'	0.3	02/06/07					0.033	12.2	0.042	0.008	0.041	0.006	4.6	0.016	18.9	0.70908
20 (CH059)	<i>Fundacion Huinay</i>				42°22.863'	72°24.929'	33	02/06/07					0.028	24.5	0.047	0.045	0.246	0.165	19.9	1.73	4.35	0.70565
W' South America			1,220,853	1,273																	0.496	0.7057

Notes: Bold-faced numbers have been used for calculating regional averages.