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E. T. Tipper, J. Gaillardet, A. Galy, P. Louvat, M. J. Bickle, et al.. Calcium isotope ratios in the world's largest rivers: A constraint on the maximum imbalance of oceanic calcium fluxes. *Global Biogeochemical Cycles*, American Geophysical Union, 2010, 24, 10.1029/2009GB003574 . insu-03605292

HAL Id: insu-03605292

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Submitted on 11 Mar 2022

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Calcium isotope ratios in the world's largest rivers: A constraint on the maximum imbalance of oceanic calcium fluxes

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Received 20 May 2009; revised 5 January 2010; accepted 16 April 2010; published 30 September 2010.

[1] The oceanic mass balance of calcium (Ca) is defined by a balance between the inputs (rivers and hydrothermal) and outputs (bulk carbonate) of Ca. Large rivers were analyzed for Ca isotope ratios ($^{44}\text{Ca}/^{42}\text{Ca}$, expressed as $\delta^{44}\text{Ca}$) to investigate the source and cycling of riverine Ca, and to add an isotopic mass balance constraint to the oceanic budget of Ca. The new data account for approximately one-third of the total Ca supplied to the oceans by rivers. Inter-sample and seasonal variability was assessed by analyzing more than one sample for many rivers. The range in the $\delta^{44}\text{Ca}$ of large rivers at high water stand is extremely narrow at 0.27‰. Variations in $\delta^{44}\text{Ca}$ do not correlate with proxies for carbonate, silicate or evaporite derived Ca, and are more likely related either to inherent variability in the lithological sources of Ca or to process related fractionation. The spread in riverine $\delta^{44}\text{Ca}$ overlaps with the spread in marine limestone $\delta^{44}\text{Ca}$ consistent with most riverine Ca coming from the recycling of limestones. The Ca isotope composition of continental runoff has an average $\delta^{44}\text{Ca}$ value of $0.38 \pm 0.04\text{‰}$, identical to recent (5 M.yr) bulk carbonate ooze ($0.33 \pm 0.13\text{‰}$, 2S.D.). Isotopic mass balance constrains that the input and output fluxes of Ca to and from the oceans, are balanced to within 15% over time-scales similar to the residence time of Ca in the oceans (1 M.yr). A greater imbalance between the fluxes would result in a detectable difference between the $\delta^{44}\text{Ca}$ value of bulk carbonate and the riverine input at the current level of uncertainty. The input and output fluxes could be imbalanced over much shorter time-scales (such as glacial-interglacial cycles), in which case the ocean-carbonate system will not yet have responded, because of the long residence time of Ca. The maximum current flux imbalance of 15% would be sufficient to account for the total variations in Ca concentration over the Tertiary. Such an interpretation is not unique, but is the simplest interpretation given the similarity between the input and output isotopic compositions, and rules out hypotheses of extreme imbalance in the recent global biogeochemical cycle of Ca.

Citation: Tipper, E. T., J. Gaillardet, A. Galy, P. Louvat, M. J. Bickle, and F. Capmas (2010), Calcium isotope ratios in the world's largest rivers: A constraint on the maximum imbalance of oceanic calcium fluxes, *Global Biogeochem. Cycles*, 24, GB3019, doi:10.1029/2009GB003574.

1. Introduction

[2] The global biogeochemical cycle of carbon is intimately coupled to that of the base metal calcium (Ca) [e.g., *Walker*

et al., 1981; *Berner et al.*, 1983; *Holland*, 1984]. Calcium carbonate skeletons provide the foundation of much marine life. These accumulate from the oceans to form the carbonate reservoir of Ca and carbon, five orders of magnitude larger than the ocean-atmosphere reservoir [*Ridgwell and Edwards*, 2007]. The dominant size of the carbonate reservoir makes it of critical importance for the balance of carbon between the solid Earth and ocean-atmosphere. In the continental crust Ca is the fifth most abundant element [*Taylor and McLennan*, 1985]. It is an essential nutrient for the continental biosphere [*Perakis et al.*, 2006] and its solubility in water as Ca^{2+} makes it commonly the most concentrated cation species in river waters [*Drever*, 1997]. Over geological time-scales, Ca is released from silicate minerals

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during weathering of both the continental and oceanic crust, and transferred to the carbonate reservoir [Holland, 2003]. The net result of the chemical reaction controlling this transfer of Ca, sequesters one mole of atmospheric carbon dioxide for each mole of silicate Ca transferred [Urey, 1952; Walker et al., 1981]. It is widely accepted that the weathering of Ca-bearing silicate minerals in this way has mediated atmospheric carbon dioxide levels over Earth's history [Bernier and Kothavala, 2001; Walker et al., 1981], maintaining an equable climate. Over shorter time-scales, in a surface ocean saturated with respect to carbonate minerals, the Ca isotopic composition of Ca^{2+} should vary directly with $p\text{CO}_2$ [De La Rocha and DePaolo, 2000].

[3] Despite the critical role of Ca for both the biosphere and the carbon cycle there is widespread disagreement concerning the oceanic balance of Ca [e.g., Milliman, 1993; Milliman and Droxler, 1996; De La Rocha and DePaolo, 2000]. Ca is supplied to the oceans mainly by rivers, but also by hydrothermal circulation, with Ca derived from the alteration of the continental and oceanic crust [Holland, 1984]. Ca is removed from seawater mainly by carbonate precipitation and accumulation of this carbonate on the ocean shelves [Milliman, 1993]. It is not presently known with any degree of accuracy whether these inputs or outputs are balanced in the modern system, let alone in the geological past. Milliman [1993] estimated in a detailed review, that either the modern carbonate accumulation exceeded the inputs by a factor of two, or that groundwater supply of Ca must be significantly larger than currently acknowledged. Holland [2005], on the other hand, proposed modern Ca fluxes implying that the Ca budget was close to steady state, but that overall in the Tertiary, the output fluxes must have outweighed the input fluxes. Modeling approaches have produced contrasting results of oceanic Ca evolution [Bernier and Kothavala, 2001; Bernier, 2004; Demicco et al., 2005; Hardie, 1996; Wilkinson and Algeo, 1989]. Data to constrain these assertions are insufficient. Although Ca concentrations have been reconstructed from fluid inclusions provide a valuable constraint [e.g., Horita et al., 2002; Lowenstein et al., 2001], they have low temporal resolution and relatively large uncertainty.

[4] The source of riverine Ca, and the absolute magnitude of the continental flux of Ca are also subjects for debate. The source of Ca is important because although the weathering of silicate minerals consumes CO_2 over geological time-scales, the weathering of carbonate minerals has no net influence on atmospheric CO_2 over million year time-scales [Bernier and Kothavala, 2001; Urey, 1952], though destruction of the carbonate reservoir by weathering can have consequences for the global carbon cycle over shorter time-scales [Calmels et al., 2007; Li et al., 2008; Edmond and Huh, 2003]. Partitioning riverine Ca^{2+} ions between lithological sources (carbonate, silicate and evaporite) is non-trivial [e.g., Gaillardet et al., 1999]. At a global scale it is estimated that two thirds of riverine Ca is derived from the weathering of carbonate rocks [Bernier and Bernier, 1996; Gaillardet et al., 1999; Meybeck, 1987] implying that the recycling of ancient carbonates dominates weathering sources of Ca.

[5] Tracing Ca in ocean and weathering systems via geochemical methods has relied on indirect proxy elements such as strontium with similar chemical characteristics to Ca [e.g., Lear et al., 2003]. Recently, a significant body of research has focused on attempting to use the stable isotope ratios of Ca to infer details of the potential changes in seawater Ca over geological time [e.g. De La Rocha and DePaolo, 2000; Fantle and DePaolo, 2005; Farkaš et al., 2007, 2006; Heuser et al., 2005; Kasemann et al., 2005; Schmitt et al., 2003a, 2003b; Sime et al., 2007; Soudry et al., 2004; Zhu and Macdougall, 1998]. Ca has six isotopes and the analysis of the $^{44}\text{Ca}/^{40}\text{Ca}$ ratio by thermal ionization mass spectrometry (TIMS) or the $^{44}\text{Ca}/^{42}\text{Ca}$ ratio by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has been a rapidly expanding field of research in recent years [DePaolo, 2004]. The approach is attractive because Ca isotope ratios potentially provide a direct tracer of the pathways followed by the Ca ion in its global biogeochemical cycle. However, the interpretations between marine Ca isotope records are discordant with some workers interpreting the data as evidence for a dynamic system over the last 20 M.yr [e.g., Fantle and DePaolo, 2007; Griffith et al., 2008], whilst other studies propose that the modern Ca isotope budget is at steady state [e.g., Schmitt et al., 2003a].

[6] One major disadvantage, with all previous reconstructions of oceanic Ca concentrations based on marine records of Ca isotope ratios, is that an a priori knowledge of both the Ca isotope composition of the inputs of Ca to the oceans (mainly rivers), and the bulk isotopic fractionation factor between carbonate and seawater is required. Models of oceanic Ca have a high degree of sensitivity to these parameters [Fantle and DePaolo, 2005; Sime et al., 2007]. However, current understanding of Ca isotope behavior in weathering systems at a continental scale is extremely limited. There are only nine published Ca isotope measurements of the world's largest rivers [Schmitt et al., 2003a; Tipper et al., 2008a; Zhu and Macdougall, 1998]. Only a handful of studies have addressed Ca isotope systematics in the weathering environment at small spatial scales [Bullen et al., 2007; Cenki-Tok et al., 2009; Ewing et al., 2008; Jacobson and Holmden, 2008; Page et al., 2008; Schmitt et al., 2003a; Tipper et al., 2006a, 2008a; Wiegand et al., 2005]. These studies have revealed some systematic, but relatively unconstrained variations in Ca isotope ratios. Plants preferentially incorporate the light isotopes of Ca [Schmitt et al., 2003a; Wiegand et al., 2005; Page et al., 2008], leading to an enrichment in the heavy isotopes of Ca in pore waters. Similarly, the precipitation of secondary mineral phases such as soil carbonates or travertines leads to an enrichment in the heavy isotope ratios in the associated waters [Tipper et al., 2006a, 2008a].

[7] Although these small-scale studies demonstrated a fractionation control of Ca isotope ratios during weathering, it is currently not known whether this fractionation at small spatial scales is maintained when considering rivers that drain continental-scale basins. In this contribution, a new comprehensive data set of riverine Ca isotope measurements determined by high resolution MC-ICP-MS is presented. The potential controls on riverine Ca isotopes are reviewed and the data are used to estimate the average Ca isotope

composition of continental runoff, the predominant source of Ca to the oceans. The riverine Ca isotope data are compared to bulk carbonate Ca isotope data from the last 5 M.yr. It is found that both the inputs and outputs from the oceans have Ca isotope compositions that are within error, and the data bring a direct new constraint on the oceanic balance of Ca. Isotopic mass balance is used to show that the data imply that the input and output fluxes are likely to balance within 10–15%.

2. Materials and Methods

[8] Most of the samples analyzed were from archive collections of river waters, but some were collected specifically for the purposes of this study. All samples were filtered on collection through $<0.45 \mu\text{m}$ filters and acidified, ready for cool storage ($<7^\circ\text{C}$). Most of the samples are from large rivers, integrating continental scale outputs to the oceans, though a handful of first order tributaries draining monolithological catchments (granite, basalt and limestone) were also analyzed. Many of the samples presented in this study have had major and/or trace element data and other isotope ratios published elsewhere (see the caption to Table 1). The rivers span a diverse range of tectonic, climatic and lithological settings, from the Amazon in the tropics, to the Mackenzie from the Arctic. The rivers draining the Himalaya Tibetan Plateau region are weathering-limited rivers and the Congo is transport-limited [e.g., *Stallard*, 1995].

[9] Most samples are from the mouth, at the high water stage providing the most representative samples of global runoff, as most of the Ca flux occurs at maximum discharge. For some large rivers (Irrawaddy, Salween, Chiang Jiang (Yangtze), and Huanghe (Yellow River)) more than one water stage was analyzed. For the Mekong and Salween, samples ace158 and ace156 are from the Tibetan headwaters. The Nile was sampled at Luxor (Egypt) 830 km upstream of the mouth, and the Columbia was sampled at Trojan, Oregon, 120 km upstream of the mouth, otherwise samples are from the mouth.

[10] Ca isotope ratios ($^{44}\text{Ca}/^{42}\text{Ca}$) were analyzed by MC-ICP-MS in Cambridge and the Institut du Physique du Globe de Paris (IPGP) and the procedures have been previously described [*Tipper et al.*, 2006a, 2008a, 2008b]. Data are presented as $\delta^{44}\text{Ca}$ relative to the NIST SRM915a standard with an overall analytical uncertainty of 0.07‰. An overview of the methods is given in Text S1.¹

3. Riverine Ca Isotope Ratios

[11] Ca concentrations, discharge, Ca flux, Ca and Sr isotope ratios and $\text{Si}(\text{OH})_4/\text{Ca}$ ratios from the present study are presented in Table 1. A compilation of the literature data on large rivers is available in Text S1. The Ca concentrations in the large rivers analyzed in the present study show very large variations. Out of the largest rivers, the Huanghe has the highest Ca concentration at $1430 \mu\text{mol/L}$ (dry season sample). However, the Seine River (known to be polluted [*Roy et al.*,

1999]) has a Ca concentration that is significantly higher at $2384 \mu\text{mol/L}$. Despite the fact that the Huanghe is the most concentrated large river, it contributes less than 1% of the total Ca supplied to the oceans out of the 60 largest rivers in the world. Many rivers are much more dilute such as the Amazon, with a Ca concentration between $135\text{--}550 \mu\text{mol/L}$. Although an order of magnitude more dilute than the Huanghe, the very high discharge of the Amazon ensures that it delivers ca. 11% of the total Ca flux to the oceans out of the 60 largest rivers in the world. First order tributaries show considerably more variability in Ca concentrations than the large rivers, ranging from $2514 \mu\text{mol/L}$ (Provence, L'Huveane, a limestone river) to $20\text{--}30 \mu\text{mol/L}$ (Arran, granitic rivers). Despite the fact that riverine Ca concentrations vary by over 2 orders of magnitude, the $^{44}\text{Ca}/^{42}\text{Ca}$ ratio only varies by 0.74‰ in all the rivers analyzed. The large rivers at high water stand have a very narrow range of $\delta^{44}\text{Ca}$ values (0.27‰). To assess inter-sample variability, more than one sample was analyzed from each river where possible. Two samples of the Amazon are in agreement within 0.01‰, and the two large tributaries (the Madeira and Solimoes) only differ from the main river by up to 0.07‰, within analytical uncertainty. The Mackenzie River at the mouth, and its major tributary, the Red Arctic, have indistinguishable $\delta^{44}\text{Ca}$ values to within 0.02‰. Small seasonal variations in some rivers may be however resolvable, and are discussed further below.

[12] The Ca isotope composition of river waters is inherited from both heterogeneity of the lithological sources of Ca, and from any mass-dependent fractionation that occurs during weathering. There are three principal lithological sources of Ca: carbonate, evaporite and silicate rocks. At a global scale, it is estimated that approximately two thirds of riverine Ca is derived from the weathering of carbonate rocks [*Berner and Berner*, 1996; *Gaillardet et al.*, 1999; *Meybeck*, 1987]. Additional smaller sources of Ca could come from industrial effluents or rain inputs. The fractionation of Ca isotope ratios is known to occur by two mechanisms during weathering related processes: (1) the precipitation of soil (secondary) carbonates [*Tipper et al.*, 2006a, 2008a] and (2) the uptake of Ca by biomass [*Page et al.*, 2008; *Schmitt et al.*, 2003a; *Wiegand et al.*, 2005].

[13] Lithological sources of Ca are not well constrained and show considerable spread (Figure 1) based on literature compilations of data. Ca isotope ratios in bulk carbonates (limestones) are relatively well constrained [*Fantle and DePaolo*, 2005, 2007], and are potentially offset from the average $\delta^{44}\text{Ca}$ Ca value of silicate rocks [*Skulan et al.*, 1997; *DePaolo*, 2004; *Tipper et al.*, 2006a; *Zhu and Macdougall*, 1998] (Figure 1). There are only a handful of published dolostone data [*Komiya et al.*, 2008; *Tipper et al.*, 2008a], which are also, on average, offset from silicate rocks. Evaporites (gypsum and anhydrite) on the other hand, encompass the complete range of Ca isotope values from limestone to dolostone rocks [*Hensley*, 2006; *Jacobson and Holmden*, 2008; *Russell et al.*, 1978] (Figure 1). When the Ca isotope data from small rivers draining mono-lithological catchments are compared to the Ca isotope data of the various rock types, they generally overlap, although no rivers draining explicitly evaporites have been analyzed.

¹Auxiliary materials are available with the HTML. doi:10.1029/2009GB003574.

Table 1. Ca Isotope Data, Ca Concentrations, and Fluxes From the Largest Rivers in the World^a

River	Sample	Date	Stage	Discharge (km ³ /yr)	Ca Conc (μ mol/L)	Ca Flux (10 ¹⁰ mol/yr)	$\delta^{44}\text{Ca} \pm 2\text{S.D.}$	$\delta^{43}\text{Ca} \pm 2\text{S.D.}$	$\Delta^{43}\text{Ca}^c$	N	$^{87}\text{Sr}/^{86}\text{Sr}$	Si(OH) ₄ /Ca Molar Ratio	SO ₄ /Ca	SI
Limestone rivers														
Seine ^{b,c}	BP8	Jan-94	H	12.9	2384	3	0.34 ± 0.07	0.15 ± 0.15	-0.02	3	0.7082	0.03	0.15	1.15
Jura Doub ^{b,d}	Ju02-24	Nov-02	H	-	1275	-	0.41 ± 0.06	0.18 ± 0.26	-0.03	3	0.7074	0.02	0.01	0.37
Jura Planches ^{b,d}	Ju02-34	Nov-02	H	-	2279	-	0.27 ± 0.05	0.17 ± 0.16	0.03	3	0.7076	0.02	0.01	0.41
Jura Tacon ^{d,e}	Ju01-11	Nov-01	M	-	1762	-	0.46 ± 0.06	0.18 ± 0.07	-0.05	2	0.7074	0.02	0.02	0.70
Jura Tacon replicate ^{d,e}	Ju01-11	Nov-01	M	-	1762	-	0.43 ± 0.04	0.29 ± 0.24	0.07	2	0.7074	0.02	0.02	0.70
Jura Tacon ^{d,e}	Ju02-10	Apr-02	L	-	1334	-	0.59 ± 0.08	0.31 ± 0.16	0.01	2	0.7073	na	0.05	0.72
Jura Tacon ^{d,e}	Ju02-28	Nov-02	H	-	1663	-	0.53 ± 0.07	0.17 ± 0.28	-0.09	2	0.7074	0.02	0.01	0.80
Jura Ain ^{d,e}	Ju01-14	Nov-01	M	-	2320	-	0.44 ± 0.07	0.07 ± 0.21	-0.16	2	0.7073	0.02	0.02	0.48
Jura Ain ^{d,e}	Ju02-04	Apr-02	L	-	1727	-	0.50 ± 0.09	0.19 ± 0.27	-0.07	4	0.7073	0.01	0.06	0.47
Provence-Choranches ^b	Pr07-1	Feb-07	L	-	1344	-	0.60 ± 0.10	0.34 ± 0.13	0.03	5	na	na	0.02	0.08
Provence-l'Huveaune ^b	Pr07-42	Feb-07	L	-	2514	-	0.32 ± 0.07	0.15 ± 0.16	-0.01	3	na	na	0.05	-0.34
Soaso ^{b,f}		Aug-04	L	-	584	-	0.35 ± 0.04	0.12 ± 0.05	-0.06	2	na	0.02	0.05	Na
Asian rivers														
Yangtze He (headwaters) ^e	ace160	Sept-03	H	-	1013	-	0.51 ± 0.07	0.17 ± 0.36	-0.08	3	0.7105	0.10	0.37	1.51
Yangtze He ^{b,f}	CH94-1	Aug-94	H	928	719	67	0.36 ± 0.08	0.05 ± 0.28	-0.13	4	0.7107	0.11	0.24	0.06
Yangtze He replicate ^{b,f}	CH94-1	Aug-94	H	928	719	67	0.38 ± 0.01	0.21 ± 0.33	0.01	3	0.7107	0.11	0.24	0.06
Yangtze He replicate ^{c,f}	CH94-1	Aug-94	H	928	719	67	0.39 ± 0.03	0.27 ± 0.09	0.07	4	0.7107	0.11	0.24	0.06
Yangtze He ^b	CH93-1	Nov-93	L	-		-	0.45 ± 0.08	0.33 ± 0.09	0.10	5	0.7107	na	0.27	0.01
Huang He ^{b,g}	CH94-6	Aug-94	H	41	1220	5	0.57 ± 0.03	0.34 ± 0.06	0.05	3	0.7111	0.10	0.87	0.70
Huang He replicate ^{b,g}	CH94-6	Aug-94	H	41	1220	5	0.48 ± 0.04	0.20 ± 0.10	-0.04	3	0.7111	0.10	0.87	0.70
Huang He ^b	CH93-6	Nov-93	L	-	1430	-	0.69 ± 0.05	0.49 ± 0.09	0.13	3	0.7112	na	0.81	0.91
Salween (headwaters) ^b	ace152	Sep-03	H	-	851	-	0.27 ± 0.10	0.09 ± 0.16	-0.04	4	0.7127	0.09	0.50	1.44
Salween (headwaters) ^c	ace152	Sep-03	H	-	851	-	0.24 ± 0.02	0.03 ± 0.04	-0.10	2	0.7127	0.09	0.50	1.44
Salween (Mouth) ^b	THN1	May-05	H	211	804	17	0.39 ± 0.04	0.19 ± 0.09	-0.01	3	0.7140	0.19	0.27	na
Salween (Mouth) ^b	THN3	May-05	H	211	760	16	0.44 ± 0.02	0.34 ± 0.06	0.11	3	0.7140	0.18	0.28	na
Salween (Mouth) ^b	THN4	May-05	H	211	741	16	0.44 ± 0.02	0.28 ± 0.21	0.05	3	0.7140	0.17	0.28	na
Salween (Mouth) ^b	THN5	Jun-05	H	211	795	17	0.43 ± 0.09	0.25 ± 0.10	0.03	3	0.7146	0.17	0.27	na
Irawaddy (mouth) ^b	HTD11	May-05	M	486	285	14	0.42 ± 0.03	0.27 ± 0.16	0.05	4	0.7108	0.69	0.20	na
Irawaddy (mouth) ^b	HTD16	Jun-05	H	486	273	13	0.43 ± 0.04	0.19 ± 0.23	-0.03	3	0.7108	0.68	0.20	na
Irawaddy (mouth) ^b	HTD5	Nov-04	L	486	369	18	0.43 ± 0.05	0.30 ± 0.10	0.08	3	0.7104	0.78	0.12	na
Irawaddy (mouth) ^b	HTD9	Jan-05	L	486	485	24	0.39 ± 0.03	0.34 ± 0.28	0.14	3	0.7105	0.67	0.13	na
Irawaddy (mouth) ^b	HTD1	Sep-04	H	486	269	13	0.41 ± 0.08	0.24 ± 0.12	0.03	4	0.7105	0.78	0.17	na
Irawaddy (mouth) replicate ^b	HTD1	Sep-04	H	486	269	13	0.33 ± 0.07	0.21 ± 0.03	0.04	3	0.7105	0.78	0.18	na
Mekong (Mouth) ^{b,g}	92-1	Aug-92	H	467	1001	47	0.44 ± 0.01	0.34 ± 0.07	0.11	3	0.7102	0.17	0.34	na
Mekong (Mouth) replicate ^{b,g}	92-1	Aug-92	H	467	1001	47	0.38 ± 0.01	0.22 ± 0.18	0.03	3	0.7102	0.17	0.34	na
Red (Hongha Mouth) ^{b,g}	Sutlej ^{c,f}	May-01	H	123	639	8	0.33 ± 0.04	0.26 ± 0.02	0.09	3	0.7114	0.26	0.34	na
Narmada ^{b,g}	IN98-2	Jun-98	H	39	790	3	0.32 ± 0.12	0.32 ± 0.17	0.15	1	0.7114	0.07	0.83	na
Narmada replicate ^{b,g}	IN98-2	Jun-98	H	39	790	3	0.38 ± 0.07	0.13 ± 0.18	-0.07	3	0.7114	na	3.63	na
Narmada replicate ^{b,g}	IN98-2	Jun-98	H	39	790	3	0.41 ± 0.04	0.19 ± 0.29	-0.01	3	0.7114	na	3.63	na
Ganges-Brahmaputra														
Meghna ^{b,f}	BR221	Aug-02	H	-	411	-	0.38 ± 0.01	0.25 ± 0.23	0.05	3	0.7232	0.32	0.16	na
Brahmaputra ^{b,f}	BR200	Aug-02	H	510	396	20	0.31 ± 0.03	0.12 ± 0.04	-0.04	3	0.7179	0.32	0.20	-0.73
Yarlung Tsangpo ^{b,f}	ace127	Sep-03	H	-	509	-	0.29 ± 0.06	0.06 ± 0.13	-0.08	3	0.7130	0.20	0.31	0.98
Yarlung Tsangpo ^{c,f}	ace127	Sep-03	H	-	509	-	0.26 ± 0.00	0.12 ± 0.20	-0.01	2	0.7130	0.20	0.31	0.98
North and South America														
Amazon at Obidos ^{b,h}	AM6/1.14	May-01	H	6590	150	99	0.31 ± 0.02	0.18 ± 0.12	0.02	3	0.7115	0.85	0.17	-1.87
Amazon ab. Xingu ^{b,i}	s336	na	na	-	137	-	0.32 ± 0.02	0.21 ± 0.01	0.05	3	0.7109	0.96	0.16	na
Solimoes ^{b,h}	AM6/1-01	May-01	H	-	237	-	0.25 ± 0.00	0.06 ± 0.14	-0.07	3	na	na	0.12	-1.36

Table 1. (continued)

River	Sample	Date	Stage	Discharge (km ³ /yr)	Ca Conc (μmol/L)	Ca Flux (10 ¹⁰ mol/yr)	$\delta^{44}\text{Ca} \pm 2\text{S.D.}$	$\delta^{43}\text{Ca} \pm 2\text{S.D.}$	$\Delta^{43}\text{Ca}^a$	N	$^{87}\text{Sr}/^{86}\text{Sr}$	Si(OH) ₄ /Ca Molar Ratio	SO ₄ /Ca	SI
Madeira ^{b,j}	AM6/1-03	May-01	H	-	106	-	0.34 ± 0.02	0.18 ± 0.14	0.00	3	na	na	0.52	-2.09
Orinoco ^{b,k}	or451	Mar-83	L	1135	133	15	0.31 ± 0.07	0.23 ± 0.26	0.07	3	0.7182	0.96	0.32	na
Mackenzie (mouth) ^{b,k}	Can96-6	Aug-96	H	308	890	27	0.37 ± 0.03	0.12 ± 0.10	-0.07	3	0.7110	0.06	0.49	0.13
Mackenzie (mouth) replicate ^{b,k}	Can96-6	Aug-96	H	308	890	27	0.32 ± 0.02	0.23 ± 0.04	0.07	3	0.7110	0.06	0.49	0.13
Mackenzie (mouth) replicate ^{b,k}	Can96-6	Aug-96	H	308	890	27	0.34 ± 0.04	0.06 ± 0.30	-0.11	3	0.7110	0.06	0.49	0.13
Red Arctic ^{b,k}	Can96-7	Aug-96	H	-	1418	-	0.32 ± 0.03	0.13 ± 0.14	-0.03	3	0.7130	0.03	0.94	0.06
Red Arctic replicate ^{b,k}	Can96-7	Aug-96	H	-	1418	-	0.32 ± 0.02	0.11 ± 0.20	-0.05	3	0.7130	0.03	0.94	0.06
Yukon ^{b,k}	Can96-4	Aug-96	H	200	773	15	0.39 ± 0.02	0.29 ± 0.18	0.09	3	0.7170	0.12	0.57	-0.19
Columbia ^{b,f}		Jun-05	M	236	164	4	0.34 ± 0.04	0.29 ± 0.20	0.12	3	0.7121	1.57	0.21	na
Columbia ^{b,f}		Jun-05	M	236	164	4	0.40 ± 0.03	0.13 ± 0.09	-0.08	3	0.7121	1.57	0.21	na
African														
Nile ^{b,f}		Apr-04	L	83	701	6	0.48 ± 0.05	0.25 ± 0.15	0.00	5	0.7070	0.16	0.31	na
Nile ^{c,f}		Apr-04	L	83	701	6	0.55 ± 0.17	0.32 ± 0.20	0.04	3	0.7070	0.16	0.31	na
Congo ^{b,g}		Nov-89	H	1200	810	97	0.27 ± 0.10	0.08 ± 0.22	-0.06	4	0.7192	0.19	0.43	na
Silicate														
Nass ^{b,l}	Can99-30	Jun-99	H	-	230	-	0.35 ± 0.06	0.21 ± 0.01	0.03	3	0.7053	0.12	0.30	-1.41
Stikine ^{b,l}	Can99-39	Jun-99	H	-	249	-	0.46 ± 0.02	0.16 ± 0.16	-0.07	3	0.7055	0.15	0.37	-0.86
Reunion Riviere de l'est ^{b,m}	95-DR3	Feb-95	H	-	107	-	0.20 ± 0.11	0.02 ± 0.15	-0.08	4	0.7044	2.58	0.10	-1.13
Antilles Bras David ^{b,l}	AN03-17	3-Feb	H	-	139	-	0.40 ± 0.06	0.25 ± 0.04	0.04	4	-	8.02	na	na
Arran, UK ^{c,f}	NGS D	Apr-04	H	-	32	-	0.74 ± 0.06	0.30 ± 0.18	-0.08	3	0.7254	1.26	1.11	na
Arran, UK ^{c,f}	NGS G	Apr-04	H	-	21	-	0.54 ± 0.09	0.27 ± 0.19	0.00	3	0.7133	3.35	1.40	na

^aOn a three isotope plot of $\delta^{44}\text{Ca}$ vs $\delta^{43}\text{Ca}$ the data define an array with a gradient of 0.55, within uncertainty of the theoretical gradient of 0.51. All data are within uncertainty of the equilibrium mass fractionation line, with the $\Delta^{43}\text{Ca}^a$ (following the same definition as given by Young and Gaby [2004, Tables 2 and 3]). Discharge data are from Gaillardet et al. [1999].

^bCa isotope data from the present study analyzed at IPGP.

^cMajor element and Sr isotope data from Roy et al. [1999].

^dMajor element and Sr isotope data from Calmels [2007].

^eCa isotope data from the present study analyzed in Cambridge.

^fSr isotope data from Tipper et al. [2006b].

^gChemical data or $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from Gaillardet et al. [1999].

^hMajor element data from Dosseto et al. [2006].

ⁱMajor element and Sr isotope data from Siallard and Edmond [1983].

^jMajor element and Sr isotope data from Edmond et al. [1996].

^kMajor element and Sr isotope data from Millot et al. [2003].

^lMajor element and Sr isotope data from Gaillardet et al. [2003].

^mMajor element and Sr isotope data from Louvat and Allegre [1997].

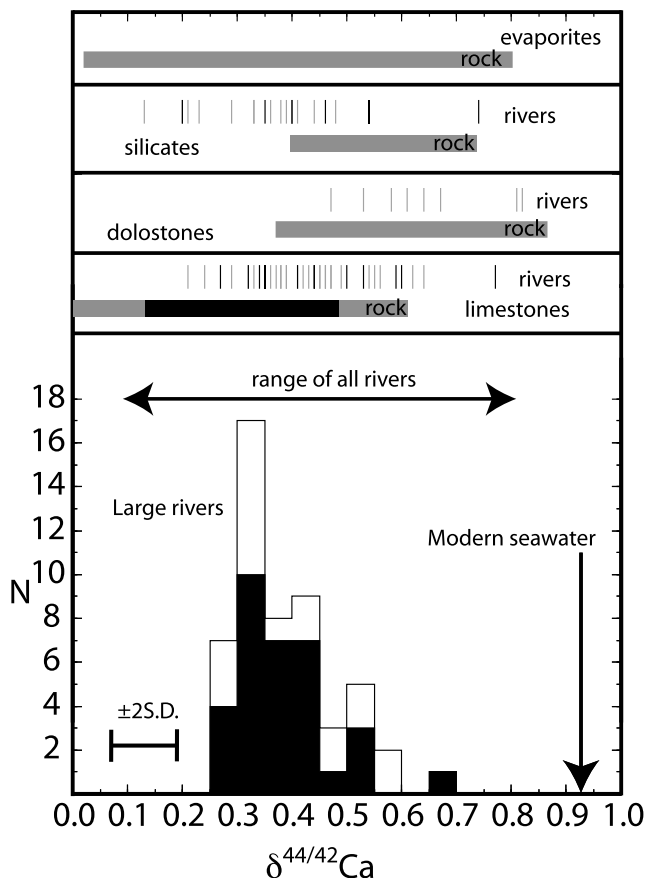


Figure 1. Summary of Ca isotope data in the main lithological sources (grey bars with limestone data from *Fantle and DePaolo* [2005, 2007], *Farkaš et al.* [2007], and *Steuber and Buhl* [2006]; dolostone data from *Komiya et al.* [2008] and *Tipper et al.* [2008a]; silicate rock data from *Skulan et al.* [1997], [*Zhu and Macdougall*, 1998], *DePaolo* [2004], and *Tipper et al.* [2006a]; evaporite data from *Hensley* [2006], *Jacobson and Holmden* [2008], and *Russell et al.* [1978]) and rivers (vertical bars, black is from this study and grey is from previous work). The black bar for limestone rock is the bulk carbonate ooze of *De La Rocha and DePaolo* [2000], *Fantle and DePaolo* [2005], *Fantle and DePaolo* [2007], and [*Sime et al.*, 2007], most representative of limestone, rather than individual tests or cements (grey bar). The histogram shows the data for the largest rivers in the world (black is from this study, and white is from *Schmitt et al.* [2003a], *Zhu and Macdougall* [1998], and [*Tipper et al.*, 2008a]).

3.1. Rivers Draining Silicate Rocks

[14] The Ca isotope variations in first order tributaries draining silicate lithologies from the present study show quite large variations (0.54‰). The two very dilute rivers draining granite from the Isle of Arran show δ^{44}_{42} Ca values that are unusually high (mean is 0.64‰) compared to most other rivers draining silicate rocks. Although it is tempting to speculate that the Ca in these rivers has been influenced by rain or sea-salt (seawater has δ^{44}_{42} Ca of 0.93‰, [*Hippler*

et al., 2003; *Wieser et al.*, 2004; *Tipper et al.*, 2008b]), the Sr isotope ratios of the same samples argue strongly against this. The Sr isotope ratios of these rivers are elevated (typical of crustal rocks) and significantly different from seawater (Table 1). It is therefore more plausible that these rivers are significantly influenced by fractionation processes such as precipitation of secondary phases or uptake by plants during weathering. When all Ca isotope data for rivers draining silicate rocks are compiled, there is a hint that the dissolved load is marginally offset to lower Ca isotope ratios than the rock itself (Figure 1), though Ca isotope data from rivers draining silicate rocks are dominated by analysis from the Strengbach catchment in France [*Schmitt et al.*, 2003a; *Cenki-Tok et al.*, 2009]. This may be of significance for understanding the apparent difference between silicate rock and marine limestone Ca isotope compositions, where limestones, on average have a lower δ^{44}_{42} Ca than silicate rocks.

3.2. Rivers Draining Carbonate Rocks

[15] When small rivers draining limestone are compared to limestone rock, there is equally a hint that the rivers have δ^{44}_{42} Ca values that are offset from limestone rocks, a conclusion reached by *Tipper et al.* [2006a] and *Tipper et al.* [2008a] based on data from small Himalayan rivers draining Tethyan limestones. In these rivers, *Tipper et al.* [2006a] proposed that the isotopically heavy values of the rivers could be reconciled by ubiquitous secondary carbonate precipitation (with lower Ca isotope ratios than the waters), a phenomenon known to occur in Himalayan rivers [*Galy et al.*, 1999; *Jacobson et al.*, 2002; *Bickle et al.*, 2005]. The Ca isotope data on rivers draining limestones from the present study, show a slightly more complex behavior. The small rivers draining the Jura mountains from Eastern France show variable δ^{44}_{42} Ca (range is 0.3‰). The stream, Choranche, sampled as it exited a karstic network of the Vercors in the South of France, was observed to be precipitating secondary calcite very close to the sampling site, and indeed has an elevated δ^{44}_{42} Ca of 0.6‰. In contrast, the Huveane River in Provence, was also sampled close to abundant travertine precipitation, but has a low δ^{44}_{42} Ca value of 0.32‰. One difficulty with interpreting these variable spot samples results is that the bedrock δ^{44}_{42} Ca values are not known for the specific localities, which are potentially variable. Although there is no simple relationship between δ^{44}_{42} Ca values and the calcite saturation index, for any of the rivers (Figure 2c), there is a greater spread in the riverine δ^{44}_{42} Ca values for rivers with a calcite saturation index >0, indicative of carbonate precipitation being of importance for the variability of δ^{44}_{42} Ca. More systematic work on Ca isotopes on rivers draining limestone is required. No new data of rivers draining dolostone are presented, but *Tipper et al.* [2008a] showed that the Ca isotope compositions of these rivers was consistent with the Ca isotope data of the rock (Figure 1).

3.3. Large Rivers

[16] Given that there are limited systematic trends for Ca isotope ratios in rivers draining mono-lithological catchments, it is not surprising that there is no relationship between δ^{44}_{42} Ca values and proxies of lithological sources such as

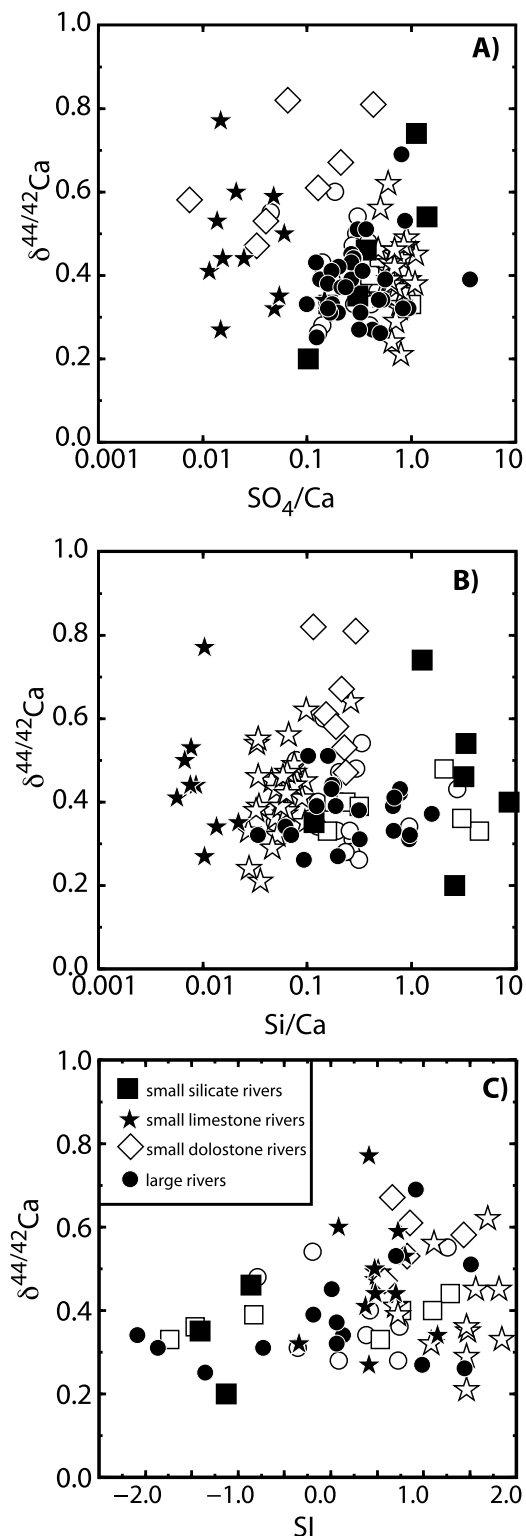


Figure 2. The lack of relationship between Ca isotope ratios in rivers with lithological proxies such as Si/Ca (silicate to carbonate), $\text{SO}_4^{2-}/\text{Ca}$ (evaporite), or potential tracers of carbonate precipitation such as the calcite saturation index. Open symbols are literature data.

Si/Ca (approximate tracer of the proportion of carbonate to silicate contributions to the dissolved load; see Figure 2b) or $\text{SO}_4^{2-}/\text{Ca}$ (evaporite tracer; see Figure 2a) or potential indices of calcite precipitation such as the calcite saturation index (Figure 2). The only notable Ca isotope composition is the Huanghe, which has a higher Ca isotope composition than most rivers. Evaporite weathering is responsible for 45% of the total dissolved solids in the Huanghe [Gaillardet *et al.*, 1999], a significantly higher proportion than in most rivers, and perhaps the evaporites of the Huanghe basin have high $\delta^{44}\text{Ca}$ values. Generally, variations in $\delta^{44}\text{Ca}$ values in large rivers are strongly attenuated, because they integrate over continental spatial scales, homogenizing many small, more variable reservoirs of Ca, as indicated by the narrower range of Ca isotope ratios in large rivers (0.4‰), as compared to all rivers (0.7‰; see Figure 1).

[17] The major advantage of integrating over continental scales is that the predominant control on riverine Ca isotope ratios can be identified. The striking similarity between the Ca isotope ratios of limestones and the largest rivers on Earth may be strongly suggestive of the overall continental signature of $\delta^{44}\text{Ca}$ values being dominated by the recycling of limestones. Given that two-thirds of global riverine Ca is thought to be derived from the weathering of carbonates [Berner and Berner, 1996; Gaillardet *et al.*, 1999; Meybeck, 1987], the small variability in riverine $\delta^{44}\text{Ca}$ values is likely to be dominated by variability in the $\delta^{44}\text{Ca}$ of limestones (and to a lesser extent dolostones) exposed on the continents. This raises the possibility that if limestones have secular variations in $\delta^{44}\text{Ca}$ values over geological time [Farkaš *et al.*, 2007], the major variability in riverine $\delta^{44}\text{Ca}$ values is due to past variation in limestone and seawater $\delta^{44}\text{Ca}$. Additional variations could be induced by the inherent variability in evaporite rocks (Figure 1) or process related fractionation [Page *et al.*, 2008; Schmitt *et al.*, 2003a; Tipper *et al.*, 2006a, 2008a; Wiegand *et al.*, 2005] such as uptake by plants or secondary carbonate precipitation as discussed above. However, the data suggest that the Ca isotope composition of rivers at a continental scale is dominated by the composition of limestones, and that at a global scale, processes fractionating Ca isotope ratios exert a second order control.

[18] Despite the very small range in riverine $\delta^{44}\text{Ca}$ values, several rivers show the same systematic trend between high and low water stand for both Ca concentrations Mg/Ca ratios and $\delta^{44}\text{Ca}$ values (Figure 3). At high water stand, the Chiang-Jiang, Huanghe and Ganges Rivers show lower Ca concentrations (between a factor of 0.3 and 0.8 lower). $\delta^{44}\text{Ca}$ values are also lower in the wet season in each of these rivers, implying that the Ca has a different source between the wet and dry season, and is not merely diluted by high runoff. The Irrawaddy shows limited seasonal variation in $\delta^{44}\text{Ca}$ (Figure 3a). The time-series from the Salween falls within the same trend as these rivers, but all the samples analyzed were from the high water stand. When seasonal changes in $\delta^{44}\text{Ca}$ are compared to Mg/Ca ratios (which normalizes out any dilution effects due to higher runoff in the wet season), a striking relation is observed for several rivers (Figure 3b). Both Mg/Ca ratios and $\delta^{44}\text{Ca}$

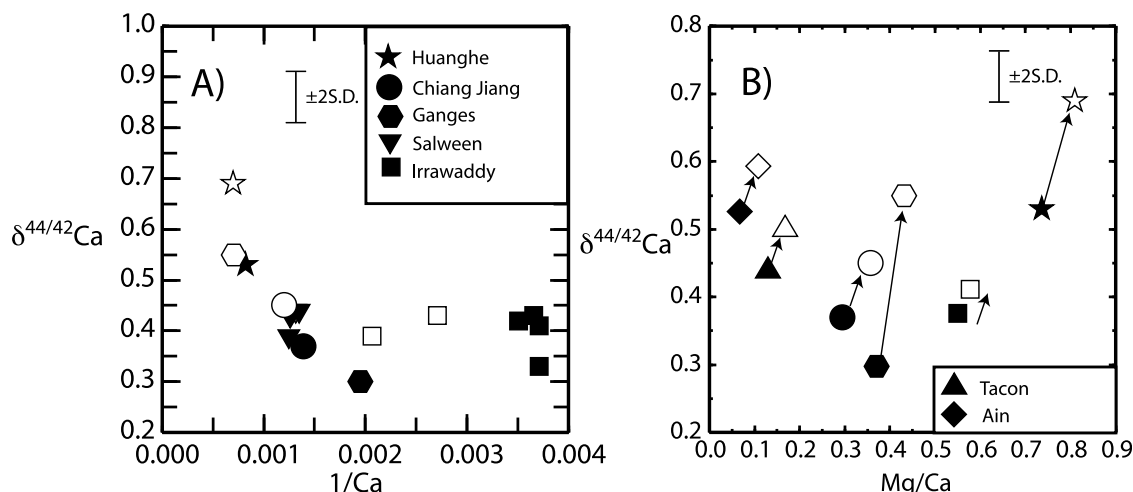


Figure 3. (a) Small systematic seasonal variations between $\delta^{44}\text{Ca}$ and Ca concentrations for several large rivers. For each river, the black points are the wet season samples, and the white points are the dry season samples. The Ganges data are from *Schmitt et al.* [2003a] and *Tipper et al.* [2008a]. (b) Mg/Ca ratios and $\delta^{44}\text{Ca}$ values vary systematically in several rivers between the wet and dry season. The variations are consistent with carbonate precipitation.

values are higher in the dry season. Such trends would be consistent with secondary calcite precipitation in soils or calcretes as has been observed in Himalayan rivers [*Jacobson et al.*, 2002; *Tipper et al.*, 2006b, 2008a], where up to 70% of Ca removal fractionates both Mg/Ca ratios and Ca isotope ratios. Alternatively, at low water stand, much of the base flow is likely derived from groundwater sources, potentially with a different Ca isotope composition to shallow soil runoff, at high water stand. Such an explanation is consistent with *Tipper et al.* [2006a, 2008a] although more recently, *Jacobson and Holmden* [2008] have observed that groundwaters with a very long residence time have a Ca isotope composition similar to rock.

[19] These seasonal variations in $\Delta^{43}\text{Ca}'$ are at the extreme limit of what is currently observable, and any interpretation is preliminary, but finding the same systematic seasonal trend in several rivers is a strong indication that some rivers show a seasonal response for Ca isotope ratios, as previously suggested by *Tipper et al.* [2006a], which with further work, will help to better constrain the sources and processes cycling Ca during weathering. It is particularly striking that these seasonal changes are observed in the rivers that are most concentrated for Ca, and hence of most significance for the supply of Ca to the oceans. The seasonal response in the processes causing fractionation could have implications for how $\delta^{44}\text{Ca}$ may respond to changing climate over longer time-scales such as glacial-interglacial periods where the hydrological cycle is significantly re-organized. Continental storage of Ca (and carbon) is thought to be 35–40% higher in interglacial periods [*Adams and Post*, 1999] and could influence the Ca isotope composition of rivers. However, although very small seasonal variations are observed in some rivers, the overall homogeneity of the data makes the average $\delta^{44}\text{Ca}$ of the Ca flux to the oceans from weath-

ering well constrained, and is of particular use in bringing new constraints to the oceanic budget of Ca.

4. Significance for the Oceanic Budget of Ca

[20] Rivers provide the principal source of Ca to the modern oceans and the magnitude of the flux supplied by rivers is known with much greater certainty than the output flux of Ca via carbonate [*Milliman*, 1993]. Therefore a precise determination of their average Ca isotope composition provides a critical constraint to the oceanic balance of Ca, which has a pivotal role in the regulation of the global carbon cycle. A number of studies have already attempted to use Ca isotope ratios to reconstruct the oceanic Ca concentration in the past with somewhat conflicting conclusions [*De La Rocha and DePaolo*, 2000; *DePaolo*, 2004; *Fantle and DePaolo*, 2007; *Farkas et al.*, 2007; *Sime et al.*, 2007; *Griffith et al.*, 2008]. There are four main variables in such reconstructions, (1) the Ca isotope composition of the inputs to the oceans, (2) the balance of these fluxes to and from the oceans, (3) the fractionation factor between seawater and the material recording the Ca isotopic composition of seawater (bulk carbonate, forams, phosphates or sulphates for example), and (4) the proportion of Ca in the various Ca sinks (such as the proportion of calcite to aragonite which have differing Ca isotope compositions). Below, the average Ca isotope composition of the riverine input to the oceans is determined, one of the critical variables in modeling of Ca isotopes in the ocean system.

4.1. The $\delta^{44}\text{Ca}$ of the Modern Riverine Flux to the Oceans

[21] The rivers analyzed in this study constitute approximately one third of the total Ca supplied to the oceans from

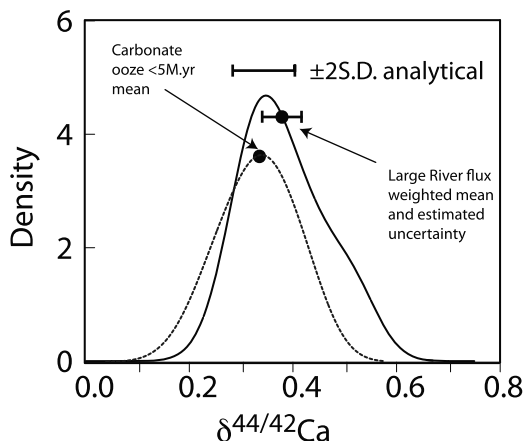


Figure 4. Probability density function (smoothed with a bandwidth of 0.05‰) of carbonate ooze (dashed line, representative of the bulk output of Ca from the oceans; data from *De La Rocha and DePaolo* [2000], *Fantle and DePaolo* [2005, 2007], and *Sime et al.* [2007]) and the largest rivers in the world (solid line).

the continents (or about 50% of the riverine flux), and it is therefore possible to calculate a robust estimate of the Ca isotope composition of global runoff. A flux-weighted mean is the most appropriate measure of the average of the Ca isotope composition of continental runoff, taking into account both the concentration of Ca and the discharge of each river:

$$\overline{\delta^{44}Ca_{riv}} = \frac{\sum_{i=1}^n F_i C_i \delta^{44}Ca_i}{\sum_{i=1}^n F_i C_i} \quad (1)$$

where F_i is the discharge in an individual river and C_i is the concentration of Ca in an individual river.

[22] The flux-weighted mean has a $\delta^{44}Ca$ value of 0.38‰. This compares favorably to the discharge-weighted mean estimated by *Schmitt et al.* [2003a] of 0.39‰, based on only eight measurements, in spite of the fact that a flux-weighted mean is more appropriate. A flux-weighted mean using the same eight rivers as *Schmitt et al.* [2003a] yields a $\delta^{44}Ca$ of 0.47‰, considerably different from discharge-weighted estimate by *Schmitt et al.* [2003a] and from the present estimate based on 22 large rivers (17 from the present study, with additional data from the Ganges, Lena, Rhine, Kolima and Yana taken from *Tipper et al.* [2008a], *Zhu and Macdougall* [1998] and *Schmitt et al.* [2003a]).

[23] The uncertainty on $\delta^{44}Ca_{riv}$ ($\sigma_{\delta^{44}Ca_{riv}}$) was estimated as 0.04‰ similar to the standard deviation of the large river data (0.07‰), assuming that the distribution of unsampled rivers is similar to the sampled rivers (see Text S1 for details). This does not take into account uncertainty in discharge and concentration but given that the estimate is based on 22 large rivers, the associated uncertainty is probably smaller than analytical uncertainty.

[24] In the modern system, the $\delta^{44}Ca$ of the total flux of Ca to the oceans is largely buffered by the riverine flux of Ca, because the riverine flux is between five and fifteen times greater than the hydrothermal flux of Ca [e.g., *Holland, 2005*; *Von Damm, 1990*; *Wilkinson and Algeo, 1989*]. Ca isotope measurements on hydrothermal fluids from both the East Pacific Rise and the Mid-Atlantic Ridge [*Schmitt et al., 2003a*; *Amini et al., 2008*] have $\delta^{44}Ca$ values averaging $0.43 \pm 0.04\text{‰}$, very similar to mid-ocean ridge basalts (mean $\delta^{44}Ca$ of $0.49 \pm 0.17\text{‰}$ [*Zhu and Macdougall, 1998*; *Skulan et al., 1997*; *DePaolo, 2004*]). The high temperature and riverine Ca fluxes therefore have the same $\delta^{44}Ca$ values to within 0.05‰, not resolvable with current analytical uncertainties. The isotopic composition of the total Ca flux to the oceans will therefore be invariant from the proportion of Ca that is supplied to the oceans via rivers and hydrothermal fluids. In the case that the riverine flux is only five times in excess of the hydrothermal flux [e.g., *Wilkinson and Algeo, 1989*], the $\delta^{44}Ca$ of the total Ca flux to the oceans would be 0.39‰ and in the case the riverine flux of Ca is in excess of the hydrothermal flux by a factor of 15 [e.g., *Holland, 2005*], the $\delta^{44}Ca$ of the total flux to the oceans would be 0.38‰, both values being indistinguishable from the riverine $\delta^{44}Ca$ (at the current level of analytical uncertainty).

4.2. Modern and Recent Output of Ca From the Oceans

[25] The output of Ca from the oceans is best represented by bulk carbonate. Specific organisms, such as foraminifera, brachiopods or belemnites have carbonate tests with variable fractionation factors from seawater [*Heuser et al., 2005*; *Sime et al., 2007*; *Farkaš et al., 2006, 2007*; *Steuber and Buhl, 2006*] and as such are not representative of the bulk Ca sink. Here the $\delta^{44}Ca$ of the modern riverine input of Ca is compared to the recent (<5 M.yr) Ca isotope data on bulk carbonate ooze and limestone of *Fantle and DePaolo* [2007], *Sime et al.* [2007], *Fantle and DePaolo* [2005] and *De La Rocha and DePaolo* [2000]. The data sources are described in more detail in Text S1.

[26] The riverine and bulk carbonate ooze (<5 M.yr) Ca isotope data have been represented as a probability density function (Figure 4), to allow the distributions of data to be compared. The probability density functions of carbonate ooze from the last 5 M.yr and modern large rivers are remarkably similar, with the peaks of both distributions having almost identical $\delta^{44}Ca$ values. The mean of the carbonate data (0.33 ± 0.13 , 2S.D.) is within uncertainty of $\delta^{44}Ca_{riv}$. This is a remarkable result, given that the data have been generated by two different analytical techniques, in two separate laboratories. This implies that the Ca isotopic composition of the inputs and outputs of Ca from the oceans are the same, and that the maximum difference between the $\delta^{44}Ca$ values of the inputs and outputs is the associated uncertainty.

[27] Below, we apply the same model used by *De La Rocha and DePaolo* [2000], *DePaolo* [2004], *Fantle and DePaolo* [2005] and *Sime et al.* [2007] to demonstrate that for a maximum difference between the $\delta^{44}Ca$ values of the sources and sinks of Ca of an analytical uncertainty of $\pm 0.04\text{‰}$, the input and output fluxes can only differ by up to 15%.

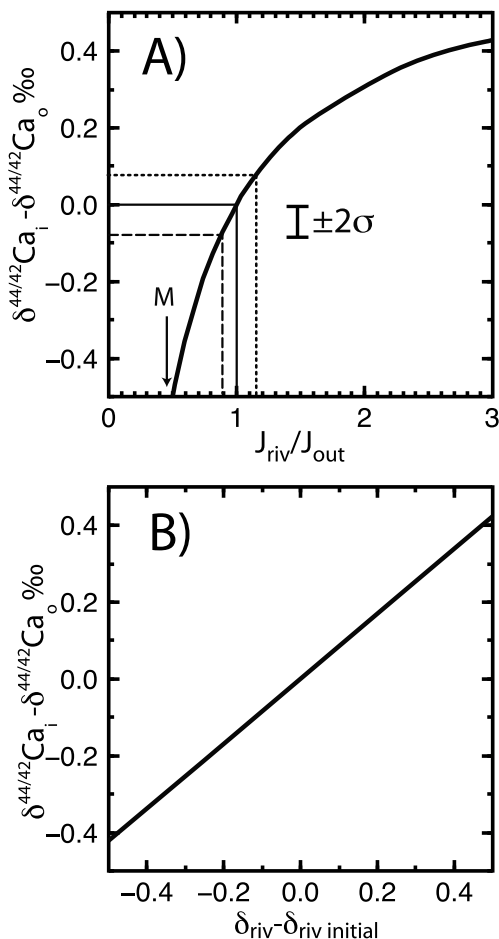


Figure 5. The sensitivity of Ca isotopes in the oceans (expressed as the difference between the Ca isotopic composition of the input and output, y axis) as a function of (a) the imbalance between the magnitude of the input and output fluxes (expressed as J_{riv}/J_{out}) and (b) to a change in the isotopic composition of the riverine input (expressed as $\delta_{riv} - \delta_{riv\ initial}$).

4.3. Constraining the Maximum Modern Oceanic Imbalance of Ca

[28] The oceanic budget of Ca is controlled by the inputs and outputs of Ca to and from the oceans, in addition to the buffering capacity of the oceans (dependent on the size of the oceanic reservoir of Ca). In a true steady state ocean, the inputs and outputs have identical magnitudes and isotopic compositions. In this case, the oceanic mass of Ca, and its isotopic composition are constant in time. A pseudo steady-state ocean is equally plausible, where the isotopic composition of seawater remains constant, but is maintained by a difference in both the magnitudes and isotopic compositions between the inputs and outputs, and hence by changing the mass of Ca in the oceanic reservoir. In the modern oceans, the oceanic Ca concentration is 10.2 mmol/L [Holland, 1984], with a δ^{44}_{42} Ca value of 0.93‰ [Hippler et al., 2003; Tipper et al., 2008b]. Changes in the size and isotopic com-

position of the oceanic reservoir of Ca can be expressed mathematically as:

$$\frac{dN_{zCa}}{dt} = \sum ({}^zJ_i - {}^zJ_o) \quad (2)$$

where z refers to the isotope of Ca in question, N refers to the number of moles of any given isotope in the oceans at time t , and zJ_i and zJ_o are the input and output fluxes of zCa . By combining two equations for ${}^{44}Ca$ and ${}^{42}Ca$ it can be shown that:

$$\begin{aligned} \frac{d(N_{Ca}\delta^{44}_{42}Ca)}{dt} &= J_i\delta^{44}_{42}Ca_i - J_o\delta^{44}_{42}Ca_o \\ &= J_i\delta^{44}_{42}Ca_i - J_o(\delta^{44}_{42}Ca_{sw} + \Delta_{sed}) \end{aligned} \quad (3)$$

where J_o and J_i and the total input and output fluxes of Ca from the oceans, N_{Ca} is the total mass of oceanic Ca, $\delta^{44}_{42}Ca_i$ is the isotopic composition of the input of Ca to the oceans, $\delta^{44}_{42}Ca_{sw}$ is the isotopic composition of seawater, and Δ_{sed} is the bulk fractionation between carbonate and seawater. The boundary conditions are the modern N_{Ca} and seawater $\delta^{44}_{42}Ca$ values, and bulk fractionation factor of 0.63‰ (determined as the difference in $\delta^{44}_{42}Ca$ between modern carbonates and seawater) [DePaolo, 2004; Sime et al., 2007]. Equation (3) was solved numerically at stepwise time intervals, in response to a perturbation in either the magnitude of the input/output fluxes or the isotopic composition of the input, and the system allowed to return to a pseudo-steady-state solution (time invariant $\delta^{44}_{42}Ca_{sw}$, but time-dependent N_{Ca}). This is reached typically after one Myr., but depends on the residence time of Ca in the oceans which is variable in the solutions, because of the varying concentration of Ca in the oceans. More details of the solutions are provided in Text S1. The sensitivity of the system has been expressed as the difference between the isotopic composition between the inputs and outputs ($\delta^{44}_{42}Ca_i - \delta^{44}_{42}Ca_o$; see Figure 5, y axis), a measure of the deviation of the oceanic Ca budget from steady state.

[29] First, the sensitivity is illustrated for a system where the input and output fluxes are not in balance (expressed as J_{riv}/J_{out}) (Figure 5a). In the case where $J_{riv} < J_{out}$, the supply of Ca is limited and continued precipitation of marine carbonate leads to a decrease of Ca in the oceans, and a Rayleigh style fractionation of Ca isotope ratios in the ocean carbonate system. This causes a large increase in the isotopic compositions of both seawater and carbonate (provided that the bulk fractionation factor does not change during such a perturbation). In the case where $J_{riv} > J_{out}$, the Ca concentration of the oceans increases, and slowly the Ca with an isotopic composition of modern seawater, is mixed with Ca having an isotopic composition of the input (rivers), lowering the $\delta^{44}_{42}Ca$ value of seawater. The isotopic response of Ca to changes in the input flux is strongly non-linear, implying that relatively small imbalances between the input and output fluxes can induce quite large changes in the isotope ratios. The dashed line in Figure 5a illustrates that up to 10% imbalance in the oceanic Ca fluxes is possible if the input Ca flux has an isotopic composition lower than the output by the uncertainty on the $\delta^{44}_{42}Ca$ of the flux-

weighted mean ($\pm 0.04\%$). If the input flux has an isotopic composition greater than that of the output by the uncertainty, the imbalance in Ca fluxes is 15% (dotted line). In the case where the output of Ca from the oceans exceeded the input of Ca from the oceans by a factor of two, a possibility suggested by Milliman [1993] based on a detailed compilation of data of the carbonate sink (labeled M in Figure 5a), a difference of ca. 0.5‰ would be predicted between the $\delta^{44}\text{Ca}$ of the inputs and outputs of Ca. The Ca isotope data do therefore rule out such a hypothesis (on timescales similar to the residence time of Ca in the modern system, ca. 1 M.yr), and imply that either a missing water source of Ca to the oceans has been neglected (groundwater) or that the carbonate sink of Ca from the oceans has been overestimated [Milliman, 1993]. We note that this predicted difference of 0.5‰ is greater than the entire spread of the Ca isotope data for large rivers at high water stand. A significant imbalance between the input and output fluxes cannot be ruled out altogether however. If the weathering system has been perturbed on a time-scale much shorter than the residence time of Ca (such as variations on a glacial-interglacial time-scale), Ca in the ocean-carbonate system will not yet have responded, because of the buffering potential of the oceans with respect to Ca.

[30] Although the response of the Ca isotope composition of the ocean-carbonate system is strongly non-linear for an imbalance in the magnitudes of the input and output fluxes, the response is linear to a perturbation in the isotopic composition of the input (Figure 5b) (such as secular variation in $\delta^{44}\text{Ca}$ for example) or variation in the bulk fractionation factor (such as a shift from calcite to aragonite seas). The implication is that a small shift in the riverine input will be matched by a shift of the same magnitude in the ocean carbonate system. In contrast, if the imbalances in the fluxes are to cause variation in the isotopic composition of the ocean-carbonate system, an imbalance of ca. 10% is required to cause 0.1‰ change in the Ca isotope composition of the oceans.

[31] The above sensitivity test of Ca in the oceans is one of the simplest possible, because there is no feedback between the concentration of Ca, and the output flux of Ca from the oceans, of the form:

$${}^zJ_o(t) \propto {}^zN(t) \quad (4)$$

[32] A feedback of this form is expected to occur in nature (though is unlikely linear because the flux of carbonate from the oceans also depends on the carbonate ion, which is more likely to limit the output, rather than the concentration of Ca, at least on geologically short time-scales). This feedback is essentially equivalent to a changing carbonate compensation depth, and depends on rivers supplying both Ca and HCO_3^- to the oceans. The inclusion of such a feedback would serve to dampen the trends that are presented here, returning the oceanic balance of Ca to a steady state, meaning that the calculations presented here have extreme magnitudes.

[33] The simple suggestion above, that the Ca in the modern ocean-carbonate system must be relatively closely balanced is in stark contrast to some other workers who have suggested a more dynamic system [Fantle and DePaolo,

2005; Griffith *et al.*, 2008] based on Ca isotope reconstructions, but in agreement with other workers who have proposed a relatively stable system [Schmitt *et al.*, 2003a; Holland, 2005]. The critical assumption above is that the bulk carbonate ooze really is representative of the bulk output. Milliman [1993] argues that the main carbonate sink from the modern oceans is not via deep carbonate oozes, but rather is via shallow water carbonates in reefs, banks and tropical shelves, as aragonite and high magnesium-calcite. If correct, the $\delta^{44}\text{Ca}$ of the main Ca sink from the oceans could differ by up to 0.2‰ from that of the bulk carbonate ooze [Böhm *et al.*, 2006; Gussone *et al.*, 2005] compromising the simple interpretation above. However, the coincidence in $\delta^{44}\text{Ca}$ between the riverine data set presented here, and the carbonate data set of De La Rocha and DePaolo [2000]; Fantle and DePaolo [2005, 2007] and Sime *et al.* [2007] is remarkable, and lends itself to the simple conclusion that the $\delta^{44}\text{Ca}$ of the main inputs and outputs from the oceans are very similar. In this case the isotope data constrain that any differences between the input and output fluxes of Ca from the oceans is likely to be less than 10–15% in the modern system. Although such an imbalance might seem small, this would easily be enough to account for the proposed three-fold variations in oceanic Ca concentrations over the Tertiary [Horita *et al.*, 2002]. It would appear to be a very fortuitous coincidence that the principal input and outputs of Ca had very similar isotopic compositions if the system was far from steady state, and although the interpretation is non-unique, the data seem to strongly suggest that the oceanic balance of Ca, must be close (if not necessarily at) steady state. The isotopic composition of the riverine flux of Ca therefore brings a significant mass balance constraint to the oceanic budget of Ca.

5. Conclusions

[34] Ca isotope ratios were measured in a global compilation of 52 water samples, including 17 of the largest rivers in the world. These rivers account for more than one third of the total input of Ca into the oceans in the present day. They drain a range of tectonic, climatic and geological environments. To assess variability between samples, more than one sample was analyzed from each basin, in many cases, including samples from different water stages. The Ca isotope data show no systematic relationship with lithology (consistent with previous data sets). However, the range in $\delta^{44}\text{Ca}$ values from the large rivers coincides well with the range in $\delta^{44}\text{Ca}$ values of limestones, consistent with much of riverine Ca being derived from limestone weathering. Additional variability could be induced by the large range in evaporite Ca isotope compositions and by fractionation during weathering. The range in the $\delta^{44}\text{Ca}$ of the large rivers is very small (0.27‰). This small variation enables the flux-weighted mean of the $\delta^{44}\text{Ca}$ of continental runoff to be reliably estimated at $0.38 \pm 0.04\%$.

[35] Riverine Ca provides the main input of Ca to the oceans and the data enable the marine budget of Ca to be refined. The average riverine $\delta^{44}\text{Ca}$ is within uncertainty of the main output of Ca from the oceans (bulk carbonate ooze younger than 5Myr, with mean $\delta^{44}\text{Ca}$ of 0.33 ± 0.13 , 2S.D.). The similarity in the $\delta^{44}\text{Ca}$ values of the inputs and

outputs from the oceans data strongly suggests that the oceanic budget of Ca must be close to steady state, and that the input and output fluxes are unlikely to differ by more than 15%. The ocean-carbonate system could however have been perturbed by a transient event with a time-scale much shorter than the residence time of Ca (ca. 1 M.yr), in which case the ocean-carbonate system will not yet have responded. An imbalance in the oceanic budget of Ca of 10–15% in the modern system would easily be sufficient to account for large changes in the Ca concentration of seawater over geological time-scales. Although the interpretation is not unique, the data do constrain one of the main variables in the modern oceanic budget of Ca.

[36] **Acknowledgments.** E. Tipper is supported by a Marie-Curie Inter-European-Fellowship at ETH Zürich for research on global budgets of Ca and Mg. The time-series from the Irrawady and Salween were collected by the Dept. of Meteorology and Hydrology in Yangon. River samples from this study were very kindly donated from the collection of J. Edmond by E. Boyle. D. Calmels provided a suite of samples from the Jura mountains in France and many helpful discussions on carbonate weathering. S. Rad provided major element data on sample AN03-17. M. Caddick collected sample 1U from the Sutlej. Helpful discussions are acknowledged with J. L. Birck, D. Calmels, J. West, J. Bouchez, and the attendees of the seawater discussion group at ETH. C. Bouman and J. Schwieters from Thermo provided invaluable advice for setting up the measurement of Ca isotope ratios on the Neptune at IPGP. The research was supported by the Leverhulme trust and NERC. This is IPGP contribution 3050.

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