

Environmental geochemistry of calcium isotopes: Applications of a new stable isotope approach*

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Abstract This paper summarizes isotope fractionation mechanism, analytical method and applications in environmental geochemistry of calcium isotopes. Calcium isotopic composition can be used to constrain material sources and study geological and environmental processes as the isotopic composition of calcium ($\delta^{44}\text{Ca}$) and fractionation processes depend on geochemical circumstances in nature. Recently, thanks to current advances in analytical technology of calcium isotopes, calcium isotopes are broadly used in biological and geochemical studies, such as the mechanism of plants imbibing nutrients through their roots, calcium transport in the environmental ecosystem, calcium cycle in oceans and paleo-oceans and paleo-climate. The elementary data show that $\delta^{44}\text{Ca}$ values vary from -2.88% to 0.92% in natural samples.

Key words calcium isotope; fractionation; advances and applications

1 Introduction

In nature, calcium has six naturally occurring stable isotopes with atomic mass units (amu) and the abundances of ^{40}Ca (96.941%), ^{42}Ca (0.647%), ^{43}Ca (0.135%), ^{44}Ca (2.086%), ^{46}Ca (0.004%) and ^{48}Ca (0.187%) are presented in this paper. These analytical results of calcium isotopes are often expressed in per mil defined as follows: $\delta^{42}\text{Ca} = [(^{42}\text{Ca}/^{40}\text{Ca})_{\text{sample}} / (^{42}\text{Ca}/^{40}\text{Ca})_{\text{standard}} - 1] \times 1000$ and $\delta^{44}\text{Ca} = [(^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}} / (^{44}\text{Ca}/^{40}\text{Ca})_{\text{standard}} - 1] \times 1000$. From $\delta^{44}\text{Ca}$ values, we get information on the fractionation processes occurring during biological and physical-chemical processes (Marshall and DePaolo, 1982, 1989; Marshall et al., 1986; Nelson and McCulloch, 1989; Shih et al., 1994; Fletcher et al., 1997; Nägler and Villa, 2000; Zhu and MacDougall, 1998; Russell et al., 1978; Skulan et al., 1997; Skulan and DePaolo, 1999), but also on a possible ^{40}Ca excess resulting from β -decay of ^{40}K (Marshall and DePaolo, 1982, 1989; Marshall et al., 1986; Nelson and McCulloch, 1989; Shih et al., 1994; Fletcher et al., 1997; Nägler et al., 2000). $\delta^{42}\text{Ca}$ values only reflect fractionation processes.

The present lack of data is due to the fact that thermal ionization measurements of calcium are difficult

because it is a low-mass element with a relatively large mass dispersion of its isotopes. Recently, thanks to new advances in analytical technology of calcium isotopes, calcium isotopes are widely applied in geochemical studies, such as the mechanism of plants imbibing nutrients through their roots, calcium transport in the environmental ecosystem, calcium cycle in oceans, paleo-oceans and paleo-climate.

2 Measurement techniques of calcium isotopes and international standard normalization

A major improvement in the precise Ca isotope measurement technique is the application of a double spike by Coleman (1971) and Russell et al. (1978) who first used a $^{42}\text{Ca}/^{48}\text{Ca}$ double spike for more accurate measurement of the Ca isotopic composition. They expressed the measured Ca isotope ratios as $\delta(^{40}\text{Ca}/^{44}\text{Ca})$ values $\{ \delta(^{40}\text{Ca}/^{44}\text{Ca}) = [(^{40}\text{Ca}/^{44}\text{Ca})_{\text{sample}} / (^{40}\text{Ca}/^{44}\text{Ca})_{\text{standard}} - 1] \times 1000 \}$ by normalizing the measured ^{40}Ca intensity to ^{44}Ca . A Ca fluoride standard (CaF_2) was used, that is supposed to represent the average bulk Earth. Skulan et al. (1997, 1999) redefined the $\delta^{44}\text{Ca}$ notation by normalizing the measured ^{44}Ca intensity to $\delta^{40}\text{Ca}$ $\{ \delta^{44}\text{Ca} = [(^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}} / (^{44}\text{Ca}/^{40}\text{Ca})_{\text{standard}} - 1] \times 1000 \}$.

2.1 Thermal ionization mass spectrometry (TIMS)

Generally, using the "peak jumping method"

masses 40, 41, 42, 43, 44 and 48 were measured in sequence on a single Faraday cup. Disadvantage of this time consuming method is the small sample throughput in combination with a reduced internal statistical precision (Skulan et al., 1997). Recently, Heuser et al. (2002) present a new technique using a multicollector thermal ionization mass spectrometer (MC-TIMS) in combination with a modified double spike technique, improving the statistical uncertainties (internal reproducibility) of Ca isotope measurements and the average sample throughput.

2.2 Multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS)

Other mass spectrometries like diode laser resonance ionization mass spectrometry and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) (Halicz et al., 1999) have also been employed for Ca isotope analysis. The main problem involved in the ICP-MS measurements is isobaric interference with the argon isotope $^{40}\text{Ar}^+$ on mass 40 or $^{12}\text{C}^{16}\text{O}_2^+$ on mass 44. In order to overcome this problem, recent progress in the measurement of Ca isotopes using ICP-MS has been made by using collision or reaction cells to remove interfering $^{40}\text{Ar}^+$ (Boulyga and Becker, 2001). Fietzke et al. (2004) reported a new technique for the measurement of $^{44}\text{Ca}/^{40}\text{Ca}$ isotope ratios on MC-ICP-MS using the so-called "cool plasma" technique. In contrast to the TIMS technique, Ca isotope measurements on MC-ICP-MS can be performed by the bracketing standard technique and do not require a Ca double spike because the mass bias in the plasma is rather stable as compared to the mass-fractionation in the TIMS ion source. This reduces the effort to chemical preparations without any loss of precision and accuracy for the Ca isotope measurements.

2.3 Sample preparation and international standard normalization

Sample preparation of calcium isotopes involving the following steps:

(1) Water samples were filtered using 0.2 μm Nylon filters and acidified to pH equal to 1. One-mL aliquots of these samples were evaporated till dryness, redissolved in 1.5 N HCl, and centrifuged.

(2) The powdered apatite grains were treated with 0.5 N acetic acid in order to remove Sr-rich calcite overgrowths and rinsed with distilled water prior to dissolution in 6 N HCl, evaporated to dryness, redissolved in 1.5 N HCl and centrifuged.

Then, the powdered carbonate rock samples were dissolved in double-distilled HCl, evaporated to dryness, redissolved in 1.5 N HCl and centrifuged.

(3) The plant samples were also powdered, digested for one week in hot (150°C) concentrated HNO_3 , evaporated to dryness, redissolved in 1.5 N HCl and centrifuged.

(4) A chromatographic clean-up for Ca was then carried out, for all the samples on a 0.6 cm internal diameter quartz column filled with Temex 50W-X8 (200 – 400 mesh; 1 mL). 1.5 N HCl was used to separate successively Ca and Sr after removing interfering isotopes of Mg and K.

Note that following Hippler et al. (2003) and the discussion at the EUG-EGS-AGU Joint Assembly in Nice in 2003, with members from various European laboratories measuring Ca isotope fractionation, most of them to apply NIST SRM 915a for normalization and to use the following δ -notation for all Ca data are presented:

$$\delta^{44/40}\text{Ca} = \left[\left(\frac{^{44}\text{Ca}}{^{40}\text{Ca}} \right)_{\text{sample}} / \left(\frac{^{44}\text{Ca}}{^{40}\text{Ca}} \right)_{\text{NIST SRM 915a}} - 1 \right] \times 1000 \quad (\text{Eisenhauer et al., 2003}).$$

3 Fractionation mechanism of Ca isotopes in nature

Natural fractionation of Ca isotopes in surface processes was reported to be relatively small (Heumann and Lieser, 1970, 1972; Heumann et al., 1982; Stahl and Wendt, 1968). Natural variations in Ca-isotope ratios may be introduced by the beta-decay of the potassium isotope ^{40}K (half-life: 1.277×10^9 a), increasing the relative abundance of ^{40}Ca . The amount of this increase can be used to date igneous and metamorphic rocks (Marshall and DePaolo, 1982, 1989; Marshall et al., 1986; Shih et al., 1994; Fletcher et al., 1997; Nägler et al., 2000).

Furthermore, Ca-isotope variations may be introduced by kinetic fractionation due to diffusion and chemical exchange reactions. Nägler et al. (2000) and Zhu and MacDougall (1998) found a temperature dependence of Ca-isotope fractionation during calcium carbonate (CaCO_3) precipitation. These authors observed that with increasing temperature the heavier isotope (^{44}Ca) would become enriched relative to ^{40}Ca . While the fractionation of Ca at this temperature is different from that of other stable isotope systems like oxygen ($\delta^{18}\text{O}$), carbon ($\delta^{14}\text{C}$) and boron ($\delta^{11}\text{B}$) where the light isotopes become enriched relative to the heavier ones with increasing temperature. Most likely, the different behaviors of Ca during temperature-dependent fractionation are related to the fact that Ca is controlled by kinetic fractionation rather than by equilibrium fractionation.

To understand the opposite fractionation behavior

of the $^{18}\text{O}/^{16}\text{O}$ and the $^{44}\text{Ca}/^{40}\text{Ca}$ isotope systems, two possible isotope fractionation processes have to be taken into account (Gussone Nikolaus et al., 2003): (1) equilibrium isotope fractionation due to vibrational characteristics of the light and heavy isotopes related to covalent atomic bonding, and (2) kinetic isotope fractionation due to different transport reaction characteristics of the light and heavy isotopes during diffusion across the boundary layer between a solution and a solid (O'Neil, 1986; O'Neil et al., 1969; Bigeleisen and Mayer, 1947; Urey, 1947). Kinetic isotope fractionation occurs at any boundary layer from one phase to another (e.g. liquid/solid, liquid/enzyme) because lighter isotopes always tend to diffuse faster than heavier isotopes, which results in an enrichment of the lighter isotopes in the product phase. In contrast, equilibrium fractionation occurs as a consequence of covalent atomic bonding (Gussone Nikolaus et al., 2003). During molecule formation the incorporation of heavier isotopes is preferred because covalent atomic bonds formed with heavier isotopes show larger bonding energies and, hence, are more stable than covalent bonds formed with lighter isotopes (O'Neil, 1986; O'Neil et al., 1969). As a consequence of the covalent bonding with C and H atoms, the $\delta^{18}\text{O}$ values of the dissolved carbonate species CO_2 , HCO_3^- , and CO_3^{2-} always tend to be heavier than the $\delta^{18}\text{O}$ composition of the surrounding bulk solution (e.g. seawater). For example, at 19°C the isotope fractionation of H_2O versus $\text{CO}_2(\text{aq})$, HCO_3^- , and solid CaCO_3 is 58‰, 34‰, and 29‰, respectively (Zeebe, 1999).

In contrast, elements like Ca tend to form ionic rather than covalent bonds in carbonate crystals (O'Neil, 1986). Therefore, Ca isotope fractionation is only affected by kinetic isotope fractionation but not by equilibrium fractionation because no vibration bonding modes are active (O'Neil et al., 1969). In general, at fluid-solid interactions both kinetic and equilibrium fractionation processes are temperature-dependent. At lower temperatures, equilibrium fractionation tends to enrich the heavier isotopes in the more stable molecules whereas kinetic fractionation tends to enrich the lighter isotopes in the product phase (Gussone Nikolaus et al., 2003). Consequently, the isotope systems like $\delta^{18}\text{O}$ controlled by equilibrium fractionation are an inverse function of temperature, whereas the isotope systems like $\delta^{44}\text{Ca}$, controlled by kinetic fractionation are positively related to temperature.

4 Advances and applications of the fraction of calcium isotopes in biological and environmental research

4.1 Mechanism of plants imbibing nutrient elements through their roots

For obvious reasons, it is a necessity for the plant to be in control of uptake, release, and exchange of solutes. One primary function of fine roots in most terrestrial plants is the uptake of mineral nutrients (Kottke and Oberwinkler, 1986). In principle, there are two simple, not necessarily exclusive, ways for nutrient uptake and transport by roots, namely the apoplastic and symplasmic routes.

The simplest model for the uptake of nutrients by roots is to assume that nutrients traverse the apoplast by diffusion, facilitated by the flow of water in the transpiration stream. This rather simplistic view of transport via the "bulk flow" requires a more or less free radial access from the rhizosphere across the root into the xylem vessels. In this case, the only driving forces required would be diffusion and the transpiration stream. This model, however, appears to be inconsistent with some observations concerning nutrient uptake. In the roots of many higher plants, relevant amounts of hydrophobic material are incorporated into the otherwise hydrophilic walls of certain cells, particularly in the characteristic casparian bands, present in the structurally distinguished cell layer, the endodermis (Zeier et al., 1999).

In many tree species, such as spruce, the endodermis is of particular importance since the roots do not show any sign of typical exodermal structure. Since the early sixties, Van Fleet (1961), Bonnett (1968) and Clarkson and Robards (1975) have raised the question of whether or not the endodermis acts as a diffusion barrier to the free passage of water and ions. If this were the case, water and solutes would have to pass through at least two membranes in order to cross the endodermal cells (Clarkson, 1996), which would offer extensive mechanisms to control entry and transport, e.g. through ion channels and aquaporins, as well as protection against leakage of water and solutes from the xylem. Peterson and Enstone (1996) suggested that the endodermis might be traversed via "general" endodermal cells or, in a more specialized way, via dedicated, i.e., passage cells.

Is the casparian band the postulated diffusion barrier for the passage of water and solutes into and out of the roots, as suggested by previous work (Perumalla and Peterson, 1986; Peterson et al., 1993)? Recently, Arnd J. Kuhn et al. (2000) used the stable isotopes ^{44}Ca and ^{24}Mg to follow the path of ions of the same elements into the mycorrhizal roots of intact small spruce trees. It is a direct and minimally invasive method, combining a functional and structural ap-

proach that minimizes physiological disturbances, such as changes in osmotic or hydrostatic pressure or ionic composition caused, for example, by root amputation. After investigating the kinetics of entry and the path of main calcium and magnesium ions into the roots and the functional significance of the endodermis, Arnd J. Kuhn et al. (2000) showed that there exists a free apoplastic path for divalent cations in the cortex and that the endodermis is a major barrier to the further passage of Mg and Ca into the xylem. For the first time the complete kinetics of tracer ions was monitored at the cellular level by microbeam techniques in combination with the stable isotope ^{44}Ca .

4.2 Calcium transport in the environmental ecosystem

Calcium (Ca) is one of the most abundant elements in the lithosphere and plays a major role in many geological and biological processes (Rubin et al., 1985). The important role of calcium (Ca) in biologic processes is based on its chemical versatility, which is related to its highly adaptable coordination geometry, its divalent charge, modest binding energies, fast reaction kinetics, and its inertness in redox reactions (Williams, 1974, 1989).

Table 1. Calcium isotopic composition of rock and biological samples

	Sample	$\delta^{44}\text{Ca}$	$\pm 2\sigma$	[Ca] (%)
Rock sample	Mauna Kea tholeiitic basalt	-0.16	± 0.12	7.46
	Mauna Kea alkalic basalt	0.34	± 0.25	6.23
	Unzen dacite (1992 eruption)	-0.15	± 0.22	3.49
	Unzen dacite (1994 eruption)	0.02	± 0.08	3.51
	Shasta dacite (Black Butte)	0.12	± 0.24	3.82
	Shasta dacite, hornblende	0.11	± 0.21	8.25
	Shasta dacite, plagioclase	-0.27	± 0.06	10.17
	Inyo rhyolite, Wilson Butte	0.09	± 0.20	0.38
	Mid-ocean ridge basalt (Indian O.)	-0.16	± 0.19	8.44
	Mid-ocean ridge basalt (Indian O.)	-0.23	± 0.10	8.07
	Holocene carbonate ooze	0.06	± 0.14	37.42
	Miocene carbonate ooze	-0.37	± 0.15	38.21
	Eocene chalk	-0.12	± 0.21	37.08
	Jurassic chalk, Scaglia Rossa, Italy	-0.12	± 0.26	39.90
	Jurassic chalk, Scaglia Rossa, Italy	0.09	± 0.08	35.84
	Seawater	San Diego	0.92	± 0.18
Biological sample	Shallow, warm water foram. (<i>Alveolinella sp.</i>)	0.49	± 0.01	33.30
	Foram., from 3000' depth	0.09	± 0.17	18.40
	Deep ocean limpet (<i>Bathycyanea sp.</i>)	-0.4	± 0.01	40.60
	Shallow tropical marine snail (<i>Conus puncticulatus</i>)	-0.43	± 0.12	39.20
	Anchovy	-0.23	± 0.17	35.60
	Starfish, Big Sur, Ca. (<i>Pisaster ochraceus</i>)	0.13	± 0.08	34.30
	Sea otter cortical bone (<i>Enhydra lutra</i>)	-0.86	± 0.22	37.90
	Unweaned Dali's porpoise (<i>Phocoenoides dalli</i>) whole bone	-1.91	± 0.13	34.20
	Adult Dali's porpoise whole bone	-2.3	± 0.06	24.30
	Adult Dali's porpoise outer cortical bone	-2.49	± 0.26	34.10
	Tropical land snail (<i>Drymaeus sp.</i>)	-1.5	± 0.17	40.20
	Juvenile pond turtle (<i>Pseudemys scripta</i>)	-1.27	± 0.04	37.10
	Adult pond turtle (<i>Pseudemys scripta</i>)	-1.14	± 0.06	36.00
	Domestic dog (<i>Canis familiaris</i>)	-1.75	± 0.13	37.20
	Ostrich (<i>Struthio camelus</i>)	-1.29	± 0.14	35.80
	Juvenile deer whole bone (<i>Odocoileus sp.</i>)	-2.88	± 0.06	35.80
	Adult deer outer cortical bone (<i>Odocoileus sp.</i>)	-2.29	± 0.11	35.60
	Adult deer whole bone (<i>Odocoileus sp.</i>)	-2.32	± 0.24	36.30
	Alligator mississippiensis cortical bone	-2.73	± 0.08	36.00
	Juvenile dinosaur (<i>Edmontosaurus sp.</i>)	-0.91	± 0.18	35.80
Adult dinosaur cortical bone (<i>Edmontosaurus sp.</i>)	-0.79	± 0.12	35.60	

Note: All of the Ca isotope data are from Skulan et al., 1997.

It has long been suspected that fractionation oc-

curing during geochemical, especially biological, cyc-

ling should cause calcium isotopic abundances in natural materials to vary in an orderly way (Corless, 1968; Stahl and Wendt, 1968). Variations in calcium isotopic composition in nature were found previously (Russell et al., 1978). Compared with better-known isotope systems, the detection of such variation has proved elusive and there are relatively few useful data on calcium isotopes in geological materials and for biological materials.

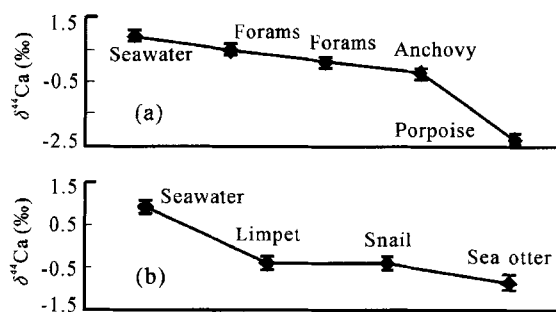


Fig. 1. Variation of $\delta^{44}\text{Ca}$ in two marine food-chains.

DePaolo et al. (1995), using a double spike approach similar to that of Russell et al. (1978), measured Ca isotopic compositions in a variety of natural samples and concluded that biological fractionation would cause Ca to become isotopically lighter. They also found that oceanic carbonate sediments have lower $^{44}\text{Ca}/^{40}\text{Ca}$ than the seawater from which they had been precipitated. Measurements of $^{44}\text{Ca}/^{40}\text{Ca}$, expressed as $\delta^{44}\text{Ca}$, were made on igneous rocks and on shell and bone materials from modern organisms to investigate the magnitude and origins of calcium isotopic fractionation in nature (Skulan et al., 1997). The results document a span of 4‰, in $\delta^{44}\text{Ca}$ (Table 1), measured with the double spike technique to a precision of $\pm 0.15\%$. Preliminary data suggest that calcium becomes isotopically lighter as it moves through marine food chains (Fig. 1).

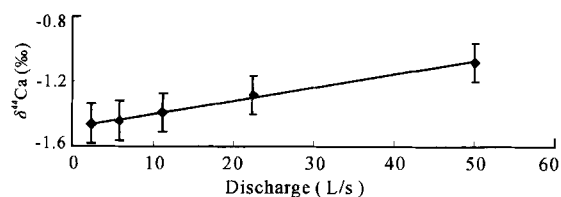


Fig. 2. The variation of river $\delta^{44}\text{Ca}$ vs. the discharge.

In marine environment, biological activity is largely responsible for removing calcium from seawater (Ferris et al., 1994; Stumm, 1992; Berner et al., 1983), this discrimination depletes the ocean of light calcium and is probably mainly responsible for the high $\delta^{44}\text{Ca}$ of seawater. The high seawater value is almost

certainly not the result of an input of isotopically heavy calcium. The variation of Ca isotopic composition in MORBs: $\delta^{44}\text{Ca} = -0.16\%$ – -0.23% ; carbonates: $\delta^{44}\text{Ca} = -0.27\%$ – -0.12% ; and volcanics: $\delta^{44}\text{Ca} = -0.23\%$ – -0.34% , strongly suggesting that no major source of marine calcium has so high $\delta^{44}\text{Ca}$ as seawater (Table 1).

In the terrestrial environment, Skulan et al. (1997) analyzed four terrestrial herbivores: a snail (*Drymaeus sp.*), a Cretaceous dinosaur (*Edmontosaurus sp.*), an ostrich (*Struthio camelus*), and a deer (*Odocoileus sp.*). The $\delta^{44}\text{Ca}$ values of the first three range from -0.8% to -1.5% . These are not unreasonable values for animals feeding on plants whose source calcium probably has a $\delta^{44}\text{Ca}$ value close to the geologic average of zero. On the other hand, they cannot explain why the $\delta^{44}\text{Ca}$ of deer bone (-2.3% to -2.9%) is so low. Regional variation in $\delta^{44}\text{Ca}$ of calcium entering continental food chains, or differences in the extent to which various terrestrial plants fractionate calcium isotopes, might explain this apparent anomaly, but without more data they cannot be sure. Besides, the low $\delta^{44}\text{Ca}$ (-2.7%) of *Alligator mississippiensis* bone makes sense in light of the carnivorous habits and freshwater environment of this animal. *Alligator* $\delta^{44}\text{Ca}$ is also about 1.5‰ lower than the $\delta^{44}\text{Ca}$ value of the freshwater turtles (-1.2%), as might be expected given that alligators commonly eat turtles (Grenard, 1991). The domestic dog (*Canis*) bone had lower $\delta^{44}\text{Ca}$ than deer, but given the omnivorous diet of most domestic dogs. This means nothing (the dog was an old individual and was included in order to test a possible effect of age on $\delta^{44}\text{Ca}$).

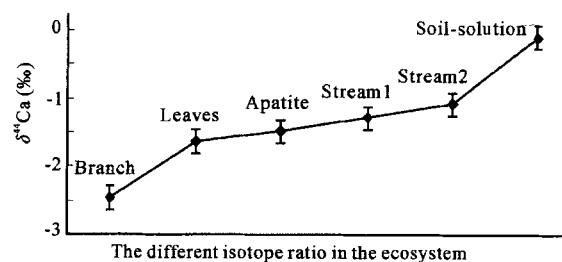


Fig. 3. Different $\delta^{44}\text{Ca}$ ratios in plants, rocks, river waters and soil solution.

At the scale of a small watershed (Aubure, Vosges, France), Schmitt et al. (2003a) found waters at high flow rates are depleted in light ^{40}Ca compared to waters at low flow rates (Fig. 2). The $\delta^{44}\text{Ca}$ of the five analyzed samples continuously increase from $-1.46\% \pm 0.13\%$ to $-1.08\% \pm 0.17\%$, when the discharge increases from 2.33 to $50 \text{ L} \cdot \text{s}^{-1}$ (Table 1).

The two vegetation samples (beech leaves and

branch) and one apatite sample also collected at the outlet of the Aubure watershed are enriched in light ^{40}Ca isotope ($\delta^{44}\text{Ca} = -1.63\text{‰} \pm 0.20\text{‰}$, $-2.46\text{‰} \pm 0.23\text{‰}$ and $-1.48\text{‰} \pm 0.10\text{‰}$, respectively) compared to a soil solution sampled at 10 cm depth under the beech grove ($\delta^{44}\text{Ca} = -0.11\text{‰} \pm 0.19\text{‰}$). It is especially interesting to notice that, at the Aubure watershed scale, the $\delta^{44}\text{Ca}$ of the outlet water samples, corresponding to different discharge rates, plot in between the values of the soil solution (for high discharge rates) and the plants (for low discharge rates) (Schmitt et al., 2003a) (Fig. 3). The apatite presents for its part a similar $\delta^{44}\text{Ca}$ value as that of the low discharge rate water. As a result, the soil solution is least fractionated compared to seawater, whereas the beech branch ($\delta^{44}\text{Ca} = -2.46\text{‰} \pm 0.23\text{‰}$) is the most fractionated sample. The river flux changes due to the variation of the proportion of waters resulting from chemical alteration of rocks and biologically fractionated soil solutions (Schmitt et al., 2003a) (Fig. 3). Calcium isotopes could therefore be an important tool to quantify the impact of the plants and the biosphere on the river water chemistry.

Systematic analysis of the biological samples indicates that biological processing of calcium discriminates against heavy isotopes and that biological fractionation is the primary generator of calcium isotopic fractionation in nature.

4.3 Calcium cycle in the ocean

Previous studies on the oceanic Ca cycle involved either Ca concentrations (Wilkinson and Algeo, 1989; Berner and Berner, 1995; Elderfield and Schultz, 1996; De Villiers, 1998.) or Ca isotopic composition (Skulan et al., 1997; Zhu and MacDougall, 1998; De La Rocha and DePaolo, 2000). On the basis of their isotopic analysis, Skulan et al. (1997) and De La Rocha and DePaolo (2000) concluded that present-day seawater was at steady-state condition. However, a systematic investigation of $^{44}\text{Ca}/^{40}\text{Ca}$ ratios in the oceanic Ca cycle (Zhu and MacDougall, 1998) indicated that the average Ca isotopic composition of input was quite different from that of output (the Ca weathering flux could be greater than the sedimentation one), suggesting that the present ocean was not in a steady state with respect to Ca (Table 2-a). Besides, De La Rocha and DePaolo (2000) proposed that significant variations in the isotopic composition of marine calcium occurred over the last 80 million years. In the same way, these variations reflected deviations in the balance between inputs of calcium to the ocean from weathering and outputs.

Such a result disagrees with previous studies

based on the analysis of Ca concentrations (Berner and Berner, 1995). Differences in the interpretation of the Ca isotope data certainly result from the limited number of available Ca isotope data, especially for the weathering flux. Indeed, the latter has been much less documented for Ca isotopes than the carbonate sedimentation (Skulan et al., 1997; Zhu and MacDougall, 1998; De La Rocha and DePaolo, 2000; Halicz et al., 1999; Nägler et al., 2000). The Ca isotopic compositions of continental and oceanic weathering fluxes were previously assumed to be close to those of average igneous rocks from the continents and oceanic basins (Skulan et al., 1997; Zhu and MacDougall, 1998; De La Rocha and DePaolo, 2000). Only few water samples have been studied. Furthermore, few hydrothermal vent values are available.

Table 2-a. Calcium isotope data for calcium cycle in the ocean

Sample	[Ca] ($\times 10^{-6}$)	$\delta^{44}\text{Ca}$	$\pm 2\sigma$	N
River input				
Amazon S302	24.9	-1.33	± 0.06	1
Orinoco OR451	5.3	-1.17	± 0.16	2
Orinoco OR750	104	-1.14	± 0.06	2
Yangtze C40	41.4	-0.63	± 0.07	4
Yangtze GB9	7.2	-1.71	± 0.23	2
Yangtze GB13	11.6	-1.33	± 0.14	2
Yangtze GB18	12.4	-1.68	± 0.05	2
Yangtze GB20	6.4	-1.49	± 0.19	2
LenaUL 102		-1.19	± 0.09	2
Aldan UL 101		-0.98	± 0.09	2
Yana YN 101		-1.18	± 0.17	2
Kolyma KY 120		-0.88	± 0.22	2
Hydrothermal input				
MORB PROTEA D8		-0.69	± 0.21	2
MORB D27-3		-0.59	± 0.17	2
MORB D12-29		-0.54	± 0.26	2
Holocene carbonate output				
Carbonate ooze ODB 806B		-2.61	± 0.11	2
Carbonate ooze INMD 113Bx		-1.93	± 0.06	2
Carbonate ooze P6408-1		-2.21	± 0.09	2
Carbonate ooze INMD 038P		-1.93	± 0.13	2
Carbonate ooze INMD 059Bx		-2.64	± 0.07	2
Carbonate ooze INMD 067Bx		-1.88	± 0.23	2
Tropical coral IVA1b		-1.84	± 0.22	2

Note: Calcium isotope data are from the following source: S302, Palmer and Edmond, 1992; OR451 and OR750, Edmond et al., 1996; C40, Ca concentration from Zhu and MacDougall, 1998; GB9, GB13, GB18 and GB20, Krishnaswami et al., 1992; and all the other samples, Zhu and MacDougall, 1998.

In order to constrain the Ca isotopic flux to the oceans and to discuss the oceanic Ca budget, it should include the analysis of (1) Ca isotopes in continental waters on a regional scale, and (2) the determination

of $\delta^{44}\text{Ca}$ values of some major rivers and hydrothermal vents. Schmitt et al. (2003a) found the $\delta^{44}\text{Ca}$ variation of river samples ranges from 0.5‰ to 1‰ without any relationship with the lithology of the watershed or the climate (Table 3). Similarly, the $\delta^{44}\text{Ca}$ value of hydrothermal vents is also uniform and close to the mean value of river waters. Consequently, the ^{44}Ca flux to the ocean should remain rather constant through time with a mean of $-1.1‰ \pm 0.2‰$. This value confirms that the Ca budget of the present-day seawater is in steady state (Table 2-b).

Table 2-b. Calcium isotope data for calcium cycle in the ocean

Sample	$\delta^{44}\text{Ca}$	$\pm 2\sigma$	[Ca] mmol/L
World river			
Amazon ^①	-1.44	± 0.07	0.14
Ganges (BCP65) ^②	-0.72	± 0.17	1.42
Indus (AK 63 = 25) ^③	-1.16	± 0.24	0.79
Huanghe ^①	-0.82	± 0.18	1.18
Hydrothermal vent			
ND 09 D ^④	-0.63	± 0.18	7.2
ND 17 D ^④	-1.09	± 0.19	43.6
PL 10 G2 ^④	-0.78	± 0.16	66
Foraminifera			
C 5378 ^④	-1.00	± 0.21	$40 (\times 10^{-9})$
C 5379 ^④	-0.90	± 0.16	$40 (\times 10^{-9})$

Note: ① Gaillardet et al. (1999) for Amazon and Huanghe; ② Galy (1999) for Ganges; ③ Karim (1999) for Indus; ④ Schmitt et al., 2003a.

In conclusion, the present study finally confirms that the present-day ocean is in steady state with regard to Ca isotopes and concentrations. Calcium isotopes are then the potential tracers to quantify the response time of the ocean to reach new steady-state conditions after such a perturbation.

4.4 Paleo-ocean and paleo-climate

The Ca isotopic composition of modern seawater collected worldwide at various depths is constant (Zhu and MacDougall, 1998; De La Rocha and DePaolo, 2000; Schmitt et al., 2003a). This is due to the Ca residence time (~ 1 Ma; Broecker and Peng, 1982; Zhu and MacDougall, 1998) which is long compared to the mixing time of ocean water (10^3 years). Therefore, paleo-oceans were likely homogeneous with respect to Ca isotopic composition at a given time.

The $\delta^{44}\text{Ca}$ values of carbonate sediments of different ages show a systematic variation of the magnitude roughly coincident with major climatic events inferred from other records (De La Rocha and DePaolo, 2000). Furthermore, these $\delta^{44}\text{Ca}$ data reflect variations in the $\delta^{44}\text{Ca}$ of paleoseawater and indicate sub-

stantial variability in the global Ca^{2+} cycle.

Table 3. The relationship of $\delta^{44}\text{Ca}$ of the rivers with the lithology of the watershed

River name	[Ca] mmol/L	$\delta^{44}\text{Ca}$	$\pm 2\sigma$	Geology
Amazon				
Amazon at Iquitos	0.55	-1.33 ^①	± 0.06	A, E
Amazon at mouth Orinoco	0.14	-1.14 ^②	± 0.07	Mouth
Orinoco at Bolivar	0.13	-1.17 ^①	± 0.16	Mouth
Cojedes at Sucre	2.6	-1.14 ^①	± 0.06	A, E
Ganges-Indus				
Pilang gad at mouth	0.18	-1.71 ^①	± 0.23	HH
Bhagirathi at head	0.29	-1.33 ^①	± 0.14	HH
Balganga at mouth	0.31	-1.68 ^①	± 0.05	HH
Jola gad at mouth	0.16	-1.49 ^①	± 0.19	HH
Ganges at mouth	1.42	-0.72 ^②	± 0.17	Mouth
Indus at mouth	0.79	-1.16 ^②	± 0.24	Mouth
Siberian river				
Lena at Aldan	0.39	-1.19 ^①	± 0.09	P, S
Aldan at mouth	0.32	-0.98 ^①	± 0.09	P, S, V
Yana at mouth	0.26	-1.18 ^①	± 0.17	Mouth
Kolyma at mouth	0.3	-0.88 ^①	± 0.22	Mouth
Chinese rivers				
Yangtze at mouth	0.79	-0.63 ^①	± 0.07	Mouth
Huanghe at mouth	1.18	-0.82 ^②	± 0.18	Mouth

Note: A. Accretionary zone; E. evaporites; HH. High Himalayas; P. platform; S. shield; V. Verkhoyansh foldbelt. ① Zhu and MacDougall, 1998; ② Schmitt et al., 2003a.

Temperature appears to influence fractionation in some species of foraminifera (Skulan et al., 1997; Zhu and MacDougall, 1998; De La Rocha and DePaolo, 2000; Nägler et al., 2000). It is not clear how much or how widespread this phenomenon is Skulan et al. (1997) published, for the first time, the data on the variation of $\delta^{44}\text{Ca}$ values in marine carbonate sediments (carbonate ooze, chalk) over the last 160 Ma. Additional data covering the last 80 Ma were published by De La Rocha and DePaolo (2000). Furthermore, Calcium isotopes have been used as a tracer of marine paleotemperatures (Nägler et al., 2000). Recently, Adrian Immenhauser et al. (2005) applied three different paleo-temperature proxies ($\delta^{44}\text{Ca}$, Mg/Ca and $\delta^{18}\text{O}$) to study Cretaceous seawater temperature seasonality. On a qualitative basis, all the three proxies reflect the same cyclical trend and thus yield robust evidence for seasonal fluctuations in Late Cretaceous surficial seawater temperature. This suggests the successful application of the new $\delta^{44}\text{Ca}$ temperature proxy to fossil mollusk calcite.

However, such bulk sediments may yield misleading results because they can contain extremely fine-grained components such as coccoliths that may be highly fractionated with respect to Ca isotope ratios

during biomineralization and that tend to recrystallize more easily even during slight diagenesis than foraminifera or phosphorites (Zhu and MacDougall, 1998; DePaolo and Finger, 1991). Therefore, the best phase to use (e. g. foraminifera, bulk carbonate, carbonate fine fraction) for the reconstruction of the Ca isotopic composition of seawater through time has not yet been agreed upon (Schmitt et al., 2003b). Such fractionation between marine carbonate sediments (carbonate ooze, chalk.) and seawater is expected, but the extent and mechanism causing this fractionation need to be investigated further.

4.5 CaCO₃ biomineralization

Marine organisms play an important role in global Ca cycling; they take up Ca and other elements from seawater, and transport them by various mechanisms into the carbonate lattices of their skeletons. The biogenic CaCO₃ minerals are expected to reflect both the composition and temperature of the seawater in which the organisms lived. Those organisms producing CaCO₃ biominerals, foraminifera, and corals have been most exploited (Lear et al., 2000; Mitsuguchi et al., 1996; Fallon et al., 1999). However, observations on these carbonates often differ from those to be expected from straightforward consideration of inorganic chemical and isotope equilibria (Cohen et al., 2001; Nurnburg et al., 1996; McConnaughey, 1989; McConnaughey et al., 1997). Such differences are often termed "vital effects" and need to be recognized when using proxy observations on biogenic carbonate to infer environmental parameters.

Compared to other stable isotope studies (McConnaughey, 1989; McConnaughey et al., 1997; Erez, 1978; Kuile et al., 1989) and various elemental abundances in these CaCO₃ minerals (Cohen et al., 2001; Nurnburg et al., 1996; Elderfield and Schultz, 1996) that are a routine part of the characterization of oceanographic variables in climate studies, little attention has been paid to the stable isotopes of Ca and Mg.

In order to address the outstanding questions concerning the processes of biomineralization of marine organisms, and to provide a fuller evaluation of their potential as proxies for environmental parameters, recently Changa et al. (2004) determined the natural variation of Ca and Mg stable isotopes of carbonates in carbonate skeletons of perforate foraminifera and reef corals together with Mg/Ca ratio to assess the influence of biomineralization processes. The results for coral aragonite suggest its formation, in terms of stable isotope behavior, approximating to inorganic precipitation from a seawater reservoir. In contrast, the results for foraminifera calcite suggest a marked biological control on

Mg isotope ratios presumably related to its low Mg content compared with seawater (Changa et al., 2004).

It is well known that the Ca isotopic composition of biogenic carbonates is offset from that of the dissolved Ca in seawater from which they were precipitated, due to isotope fractionation during Ca uptake and biomineralization. However, the extent to which the above factors affect the Ca isotopic composition of biogenic carbonates has not been resolved. In particular, there is debate over whether there is interspecific variability in the magnitude of Ca isotope fractionation by foraminifera; to what degree this fractionation is temperature-dependent, and whether some species show a much greater sensitivity to temperature than others (Zhu and MacDougall, 1998; De La Rocha and DePaolo, 2000; DePaolo, 2004; Nägler et al., 2000; Gussone et al., 2003; Changa et al., 2004). With the aim of clarifying the temperature-dependence of calcium isotope fractionation in different species of planktonic foraminifera, Sime et al. (2005) have investigated the influence of temperature on calcium (Ca) isotope fractionation during biomineralization through the paired analyses of $\delta^{44/42}\text{Ca}$ (via MC-ICP-MS) and $\delta^{18}\text{O}$ on the calcite tests of 12 species of planktonic foraminifera from coretop sediments. Samples were collected from a suite of box-cores from the sites between 60°N and 30°S in the North Atlantic and West Indian oceans, spanning a range in sea surface temperature of 9 – 27°C. However, no significant correlation between temperature and Ca enrichment factor was observed in any of the 12 species of foraminifera investigated. The influence of temperature on e was close to zero for the combined non-*globorotalid* species, -0.07 ± 0.10 K (e versus 1000/K; $0.0008\text{‰} \pm 0.0012\text{‰} \text{ }^\circ\text{C}$). The results suggest that the theoretically expected relationship between the Ca enrichment factor and temperature can be obscured by, as yet, unquantified metabolic and physiological processes in nature.

5 Conclusions

Present research on Ca isotopes in nature has been performed on different scales. It has shown that:

(1) Measurements of $^{44}\text{Ca}/^{42}\text{Ca}$, expressed as $\delta^{44}\text{Ca}$, were made on different rocks and seawater and on shell/bone material from organisms to investigate the magnitude and origin of calcium isotope fractionation in nature. The results document a span of $\sim 4\text{‰}$ in $\delta^{44}\text{Ca}$.

(2) Since no ^{40}Ca excess resulting from ^{40}K radioactive decay is recorded, the small variation among measured $\delta^{44}\text{Ca}$ values represents mass-dependent

fractionation that is affected by kinetic fractionation only. Systematic analysis of biological samples indicates that biological processing of calcium discriminates against heavy isotopes, and that biological fractionation is the primary generator of calcium isotope fractionation in nature. So it is necessary to conduct research on biogeochemistry cycle of the calcium isotopes.

(3) The isotopic composition of calcium ($\delta^{44}\text{Ca}$) and its fractionation processes depend on geochemical circumstances in nature. Therefore, the calcium isotopic composition can be used to indicate material sources and study geological processes such as the successful application of the new $\delta^{44}\text{Ca}$ temperature proxy for paleo-ocean and paleo-climate, which is coincident with major climatic events inferred from other records. Besides, it can also be used as an important tool to quantify the impact of plants and biosphere on the river water chemistry, including the variation of river $\delta^{44}\text{Ca}$ vs. the discharge, different $\delta^{44}\text{Ca}$ ratios in plants, rocks, river waters and soil solution, and the variation of $\delta^{44}\text{Ca}$ in food-chains in nature.

At present, little research on calcium isotopic geochemistry has been conducted at home (Han Guili and Liu Congqiang, 2001) though calcium isotopes should be broadly used in many geochemical studies due to its recent advances in analytical technology.

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