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## Calcium isotope fractionation in calcite and aragonite

NIKOLAUS GUSSONE,<sup>1,\*</sup> FLORIAN BÖHM,<sup>2</sup> ANTON EISENHAUER,<sup>2</sup> MARTIN DIETZEL,<sup>3</sup> ALEXANDER HEUSER,<sup>2</sup> BARBARA M. A. TEICHERT,<sup>1</sup> JOACHIM REITNER,<sup>4</sup> GERT WÖRHEIDE,<sup>4</sup> and WOLF-CHRISTIAN DULLO<sup>2</sup><sup>1</sup>DFG Forschungszentrum Ozeanränder der Universität Bremen, Leobener Str. D-28359 Bremen, Germany<sup>2</sup>Leibniz-Institut für Meereswissenschaften, IFM-GEOMAR, Wischhofstr. 1-3, D 24148 Kiel, Germany<sup>3</sup>Institute of Applied Geosciences, Graz University of Technology, A-8010 Graz, Rechbauerstrasse 12, Austria<sup>4</sup>Geowissenschaftliches Zentrum Göttingen, Goldschmidtstr. 1-3, D 37077 Göttingen, Germany

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**Abstract**—Calcium isotope fractionation was measured on skeletal aragonite and calcite from different marine biota and on inorganic calcite. Precipitation temperatures ranged from 0 to 28°C. Calcium isotope fractionation shows a temperature dependence in accordance with previous observations:  $1000 \cdot \ln(\alpha_{cc}) = -1.4 + 0.021 \cdot T$  (°C) for calcite and  $1000 \cdot \ln(\alpha_{ar}) = -1.9 + 0.017 \cdot T$  (°C) for aragonite. Within uncertainty the temperature slopes are identical for the two polymorphs. However, at all temperatures calcium isotopes are more fractionated in aragonite than in calcite. The offset in  $\delta^{44/40}\text{Ca}$  is about 0.6‰. The underlying mechanism for this offset may be related to the different coordination numbers and bond strengths of the calcium ions in calcite and aragonite crystals, or to different Ca reaction behavior at the solid-liquid interface. Recently, the observed temperature dependence of the Ca isotope fractionation was explained quantitatively by the temperature control on precipitation rates of calcium carbonates in an experimental setting (Lemarchand et al., 2004). We show that this mechanism can in principle also be applied to  $\text{CaCO}_3$  precipitation in natural environments in normal marine settings. Following this model, Ca isotope fractionation in marine Ca carbonates is primarily controlled by precipitation rates. On the other hand the larger Ca isotope fractionation of aragonite compared to calcite can not be explained by different precipitation rates. The rate control model of Ca isotope fractionation predicts a strong dependence of the Ca isotopic composition of carbonates on ambient  $\text{CO}_3^{2-}$  concentration. While this model is in general accordance with our observations in marine carbonates, cultured specimens of the planktic foraminifer *Orbulina universa* show no dependence of Ca-isotope fractionation on the ambient  $\text{CO}_3^{2-}$  concentration. The latter observation implies that the carbonate chemistry in the calcifying vesicles of the foraminifer is independent from the ambient carbonate ion concentration of the surrounding water. Copyright © 2005 Elsevier Ltd

### 1. INTRODUCTION

The equilibrium isotope partitioning between minerals and fluids can vary with the chemical composition and bond character of the mineral. This is well known for the oxygen and carbon isotope fractionation between minerals and aqueous fluids (O'Neil, 1986; Kim and O'Neil, 1997).

For instance, the fractionation of oxygen and carbon isotopes differs between  $\text{CaCO}_3$  polymorphs. In aragonite  $^{18}\text{O}$  is enriched by 1.0‰ and  $^{13}\text{C}$  by 1.7‰ relative to calcite (Romanek et al., 1992; Böhm et al., 2000). In this case the vibrational behavior of the carbonate ions is influenced by the structure of the crystal lattice and the atomic coordination numbers. The denser aragonite lattice with its  $\text{Ca}^{(9)}\text{O}$  coordination enhances the fractionation of oxygen and carbon compared to calcite ( $\text{Ca}^{(6)}\text{O}$  coordination).

The isotope fractionation effects mentioned above are mainly caused by the thermodynamic (vibrational) behavior of the C-O bonds in the carbonate ion ( $\text{CO}_3^{2-}$ ).

In contrast to oxygen isotopes the fractionation mechanisms of Ca isotopes between aqueous Ca and solid  $\text{CaCO}_3$  are less well understood. The Ca-O bond in  $\text{CaCO}_3$  has an ionic character (covalent contribution of 20.6%) and is about four times weaker than the C-O bond (Reeder, 1983). Accordingly, ther-

modynamic Ca isotope fractionation is expected to be small (O'Neil, 1986). Nevertheless, Gussone et al. (2003) observed a small but resolvable difference in Ca isotope fractionation between aqueous solution and solid for calcite and aragonite. This indicates that the mechanisms of Ca isotope fractionation in  $\text{CaCO}_3$  may be influenced by the crystal lattice structure, i.e., by the bonding environment and coordination of calcium with oxygen.

In this study we evaluate three different models for Ca isotope fractionation in light of the Ca isotope offset between aragonite and calcite and the  $\delta^{44/40}\text{Ca}$ -temperature relationship observed for natural and synthetic carbonate samples.

#### 1.1. Kinetic Isotope Fractionation and Diffusion

It was shown by several studies that heavier Ca isotopes are depleted in the solid phase relative to the fluid (cf. Skulan et al., 1997; Zhu and Macdougall, 1998; Skulan and DePaolo, 1999; De La Rocha and DePaolo, 2000; DePaolo, 2004). Based on this observation Gussone et al. (2003) proposed a kinetic Ca isotope fractionation model for carbonate precipitation. This model quantitatively explained the two different  $\delta^{44/40}\text{Ca}$ -temperature relationships observed in foraminiferal species and stressed the importance of aquocomplexes for diffusive Ca isotope fractionation in aqueous solutions.

\* Author to whom correspondence should be addressed (gussone@uni-bremen.de).

Table 1. Sample locations of the benthic biota (sponges and brachiopods).

Sample	Species	Location	Depth (m)	Temp. (°C)	Source <sup>b</sup>
DW 398	<i>Vaceletia</i> sp.	Lifou, New Caledonia	300 <sup>a</sup>	16.2	$\delta^{18}\text{O} = 1.5\text{‰}$ $\delta_{\text{w}} = 0.6\text{‰}$
DW546	<i>Vaceletia</i> sp.	Wallis et Futuna	200 <sup>a</sup>	23.0	$\delta^{18}\text{O} = 0.2\text{‰}$ $\delta_{\text{w}} = 0.9\text{‰}$
DW54	<i>Vaceletia</i> sp.	Norfolk Ridge, New Caledonia	300 <sup>a</sup>	17.0	$\delta^{18}\text{O} = 1.2\text{‰}$ $\delta_{\text{w}} = 0.5\text{‰}$
V1	<i>Vaceletia crypta</i>	Astrolabe Reef, Fiji	8	26.4	WOA98
V4	<i>Vaceletia crypta</i>	Lizard Island, Great Barrier Reef	10	26.8	WOA98
Ce95-1	<i>Ceratoporella nicholsoni</i>	Jamaica, Caribbean	20	27.1	$\delta^{18}\text{O}^{\text{c}} = -0.8\text{‰}$ $\delta_{\text{w}} = 0.8\text{‰}$
Ce96	<i>Ceratoporella nicholsoni</i>	Jamaica, Caribbean	20	27.1	$\delta^{18}\text{O}^{\text{c}} = -0.8\text{‰}$ $\delta_{\text{w}} = 0.8\text{‰}$
Pb19	<i>Ceratoporella nicholsoni</i>	Pedro Bank, Caribbean	125	25.7	$\delta^{18}\text{O}^{\text{c}} = -0.4\text{‰}$ $\delta_{\text{w}} = 0.9\text{‰}$
RS11	<i>Astrosclera willeyana</i>	Gulf of Aqaba, Red Sea	30	26.1	$\delta^{18}\text{O} = 0.6\text{‰}$ $\delta_{\text{w}} = 2.0\text{‰}$
AwMac	<i>Acanthochaetetes wellsi</i>	Mactan, Cebu	40	27.6	WOA98
Aw92	<i>Acanthochaetetes wellsi</i>	New Caledonia, Coral Sea	8	24	Böhm et al. 1996
AwLi	<i>Acanthochaetetes wellsi</i>	Lizard Island, Great Barrier Reef	15	26	WOA98
316282	<i>Thecidellina</i> sp.	Osprey Reef, Coral Sea	30	26.9	WOA98
BP-Mad	Gen. et spec. indet.	Madeira	7	20	WOA98
CrRck	<i>Waltonia inconspicua</i>	South New Zealand	1	14	WOA98
SJI1	<i>Terebratalia transversa</i>	San Juan Island, Washington	5	10	WOA98
SJI2	<i>Terebratalia transversa</i>	San Juan Island, Washington	5	10	WOA98
PL1	Articulated coralline red alga	Monterey Bay, California	beach	14	WOA98

<sup>a</sup> Dredged samples, depth estimate.

<sup>b</sup> Source for temperature estimates: WOA: World Ocean Atlas (Conkright et al., 1998);  $\delta^{18}\text{O}$ : calculated from  $\delta^{18}\text{O}$  values measured on sample splits (V-PDB) and local seawater composition ( $\delta_{\text{w}}$ , V-SMOW).

<sup>c</sup> Böhm et al. (2000).

## 1.2. Equilibrium Fractionation

In contrast to the model of kinetic isotope fractionation, Bullen et al. (2003) and Marriott et al. (2004) proposed that Ca isotope fractionation in carbonates may be caused under equilibrium conditions. In their models the covalent bonding of Ca in a Ca-aquocomplex ( $\text{Ca}_{\text{aq}}$ ) is stronger than in a carbonate mineral. As heavier isotopes are energetically preferred by stronger bonds this effect could lead to the observed  $^{44}\text{Ca}$  depletion of the solid carbonates.

## 1.3. Equilibrium Fractionation Affected by Coprecipitation

The model of Lemarchand et al. (2004) proposes that equilibrium isotope fractionation between dissolved Ca and solid  $\text{CaCO}_3$  is overprinted by an increasing amount of unequilibrium Ca incorporated into the crystal with increasing precipitation rate. This model is in accord with the interpretation of experimental and theoretical results by Zhang et al. (1988), which proposed that the equilibrium Ca isotope fractionation would easily be overwhelmed by coprecipitation of unequilibrium Ca, due to its very low energetic yield. An increasing amount of coprecipitation with increasing precipitation rate was also found for trace element incorporation into carbonate minerals (cf. Lorens, 1981; Watson, 2004).

The aim of this study is to investigate the role of vital effects, thermodynamic and kinetic isotope fractionation and precipitation kinetics for Ca isotope systematics in calcite and aragonite. In order to address this question we measured the  $\delta^{44/40}\text{Ca}$  of various biogenic and inorganic aragonite and calcite samples.

## 2. SAMPLE MATERIAL AND ANALYTICAL METHODS

### 2.1. Samples and Sample Preparation

Samples of the planktic foraminifer *Turborotalia quinqueloba* (low magnesium calcite, LMC) were collected in the Norwegian Sea and the North Atlantic using net catches, covering a temperature range from  $-0.4$  to  $10^\circ\text{C}$ . Pteropods (planktic gastropods, aragonite), were collected from a multicorer core top during cruise SO 164 of the research vessel SONNE in the Caribbean at a present sea surface temperature of  $27.5^\circ\text{C}$  (Nürnberg et al., 2003). Sclerosponges (*Ceratoporella nicholsoni*, *Vaceletia* spp. and *Astrosclera willeyana* (aragonite), *Acanthochaetetes wellsi* (high magnesium calcite: HMC)) and brachiopods (*Terebratalia transversa*, *Waltonia inconspicua*, *Thecidellina* sp., LMC) were collected by scuba diving, dredging and during dives with the submersible Jago (Table 1). Articulated coralline red algae were collected at Monterey Bay, California, representing a temperature of about  $14^\circ\text{C}$ . Water temperatures were either taken from the World Ocean Atlas (Conkright et al., 1998) or calculated from oxygen isotopes measured on sample splits. The oxygen isotopic composition of the local waters was calculated from salinities (Conkright et al., 1998).

Inorganic calcite and aragonite were precipitated using a gas diffusion method as described in Dietzel and Usdowski (1996) and Dietzel et al. (2004). The precipitation rates of the inorganic aragonite were calculated by taking the surface of the inner PE-membrane of the precipitation-setup as a first order approximation of the surface on which the carbonate precipitated. To calculate the precipitation rate of the sclerosponge *C. nicholsoni* we recalculated the value given in Haase-Schramm et al. (2003) taking into account a surface area about twice as large as the living sponge surface, according to the roughly  $45^\circ$  angle of the skeletal growth surfaces in the sponge calices. Precipitation rates of *A. wellsi* were estimated based on the measured skeleton density of  $1.1 \text{ g/cm}^3$ , linear growth rates between  $0.5$  and  $1.5 \text{ mm/yr}$  (Böhm et al., 1996; Fallon et al., 2003) and assuming an effective growth surface of two times the living surface.

Subsamples from sclerosponge skeletons were obtained using a dental drill. The drill samples, *T. quinqueloba* shells, pteropods and inorganic precipitates were dissolved in  $2.5 \text{ N HCl}$ , dried down and redissolved in  $2.5 \text{ N HCl}$ . The brachiopod shells and red alga were bleached with  $10\%$  sodium hypochlorite solution for several days and washed three times in ultrapure water. The cleaned shells were dissolved in a mixture of  $2.5 \text{ N HCl}$  and  $30\% \text{ H}_2\text{O}_2$ , dried and redissolved in  $2.5 \text{ N HCl}$ .

## 2.2. Assessment and Calculation of Open Ocean Carbonate Data

To evaluate the influence of temperature on the marine carbonate system we used surface water data (upper 50 m) for temperature, salinity, dissolved inorganic carbon (DIC) and total alkalinity (TA). This data is obtained from the Geochemical Ocean Sections Study (GEOSECS, östlund et al., 1987), a global survey carried out in 1972–1973 (Atlantic Ocean), 1973–1974 (Indian Ocean) and 1977–1978 (Pacific Ocean). The dataset is available from the IRI/LDEO Climate Data Library (<http://ingrid.ldeo.columbia.edu>). Carbonate ion concentrations ( $[\text{CO}_3^{2-}]$ ) were calculated from DIC, pH and TA data using the algorithm of Ware et al. (1991) and the constants in the  $\text{CO}_2\text{-H}_2\text{O}$  system of Millero (1995) ( $K_0$ ,  $K_w$ ), Millero et al. (2002) ( $K_1$ ,  $K_2$ ) and Dickson (1990) ( $K_B$ ). To separate the influences of temperature and salinity the  $[\text{CO}_3^{2-}]$  was recalculated after normalizing DIC and TA to a constant salinity of 35 psu.

## 2.3. Calcium Isotope Analysis and Conversion between Different Ca Isotope Notations

Calcium isotope ratios were determined on a Finnigan MAT 262 RPQ<sup>+</sup> and Finnigan Triton T1 thermal-ionization-mass-spectrometer at the IFM-GEOMAR, following the method described in Heuser et al. (2002). The isotope variations of Ca are expressed as  $\delta^{44/40}\text{Ca}$  values ( $\delta^{44/40}\text{Ca} [\% \text{ SRM915a}] = ((^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}} / (^{44}\text{Ca}/^{40}\text{Ca})_{\text{SRM 915a}} - 1) \cdot 1000$ ), as proposed by Eisenhauer et al. (2004). An inter-laboratory comparison of the in-house  $\text{CaF}_2$ , NIST SRM 915a and seawater standards is given in Hippler et al. (2003):  $\Delta^{44/40}\text{Ca}_{(\text{Seawater-NISTSRM 915a})} = 1.88\%$ ,  $\Delta^{44/40}\text{Ca}_{(\text{CaF}_2\text{-NISTSRM 915a})} = 1.44\%$ . The average  $2\sigma_m$  of our samples is 0.12‰ (30 ppm/amu) (amu = atomic mass units) determined by repeated aliquot measurements of various sample materials.

Recent advances in calcium isotope analysis by MC-ICPMS lead to the use of several different isotope ratios to express Ca isotope fractionation. Up to now  $^{44}\text{Ca}/^{42}\text{Ca}$ ,  $^{44}\text{Ca}/^{40}\text{Ca}$  and  $^{48}\text{Ca}/^{42}\text{Ca}$  are reported and in the future the use of additional ratios is possible (Halicz et al., 1999; Boulyga and Becker, 2001; Fietzke et al., 2004; Marriott et al., 2004; Soudry et al., 2004; Wieser et al., 2004). These different approaches, using isotope ratios with mass differences of 2, 4 and 6 amu, hinder the direct comparison of Ca-isotope data. We therefore express our data in a new notation ( $\delta^{\text{mu}}\text{Ca}$ ) which expresses the Ca isotope fractionation per one atomic mass unit relative to the SRM 915a standard (in ppm ( $10^{-6}$ )). The superscript mu refers to the fractionation per one atomic mass unit. Generally a small difference results from a conversion by applying either a kinetic or an equilibrium fractionation law.  $\delta^{\text{mu}}\text{Ca}$  [ppm/amu SRM915a] =  $((^{a}\text{Ca}/^{b}\text{Ca})_{\text{sample}} / (^{a}\text{Ca}/^{b}\text{Ca})_{\text{standard}} - 1) \cdot (f) \cdot 10^6$  (with  $f = (\ln(b/(b+1)))/(\ln(b/a))$  assuming kinetic isotope fractionation and  $f = a/((b+1) \cdot (a-b))$  if equilibrium fractionation is assumed (Matsuhisa et al., 1978; Young et al., 2002)). The fractionation factor  $\alpha$  can be converted to  $\alpha_{\text{mu}}$  in analogy to  $\delta^{\text{mu}}\text{Ca}$  as  $\alpha_{\text{mu}} = \alpha^{\ln(b/(b+1))/\ln(b/a)}$  (assuming kinetic isotope fractionation) or  $\alpha_{\text{mu}} = \alpha^{a/((b+1) \cdot (a-b))}$  (for equilibrium fractionation) with  $\alpha_{a/b} = (^{a}\text{Ca}/^{b}\text{Ca}_{\text{solid}}) / (^{a}\text{Ca}/^{b}\text{Ca}_{\text{fluid}})$ . At present it can not finally be concluded whether  $\delta^{\text{mu}}\text{Ca}$  and  $\alpha_{\text{mu}}$  values based on the kinetic or equilibrium fractionation law are better suited to describe Ca isotope mass fractionation. Considering present day analytical precision, both approaches yield equal values within uncertainty. The  $\delta^{\text{mu}}\text{Ca}$  and  $\alpha_{\text{mu}}$  values listed in Table 2 are calculated using the equilibrium fractionation law. Using the  $\delta^{\text{mu}}\text{Ca}$  notation a specific sample has one distinct  $\delta$  and  $\alpha$  value, regardless of which isotope ratio it is based on. For better comparison we will present our data as  $\delta^{44/40}\text{Ca}$  and  $\alpha$  ( $\alpha_{44/40}$ ) as well as  $\delta^{\text{mu}}\text{Ca}$  and  $\alpha_{\text{mu}}$  (Table 2).

## 3. RESULTS

### 3.1. Temperature Dependence

The fractionation factors of the measured carbonate samples define two distinct temperature dependent Ca isotope fractionation arrays (Fig. 1). Both arrays have similar slopes (Eqns. 1-5), but are offset by about 0.6‰ in  $\delta^{44/40}\text{Ca}$  (150 ppm/amu).

The array defined by the aragonite samples is more depleted in  $^{44}\text{Ca}$  relative to  $^{40}\text{Ca}$  and includes sclerosponges (*C. nichol-*

*soni*, *Vaceletia* spp., *A. willeyana*), pteropods and inorganically precipitated aragonite.

Biogenic aragonite:

$$1000 \cdot \ln(\alpha) = -1.89 \pm 0.13 + (0.017 \pm 0.006) \cdot T(^{\circ}\text{C});$$

$$R^2 = 0.80, p < 0.001, n = 14 \quad (1a)$$

$$10^6 \cdot \ln(\alpha_{\text{mu}}) = -473 \pm 33 + (4.3 \pm 1.4) \cdot T(^{\circ}\text{C}) \quad (1b)$$

Inorganic aragonite (Gussone et al., 2003):

$$1000 \cdot \ln(\alpha) = -1.94 \pm 0.06 + (0.015 \pm 0.002) \cdot T(^{\circ}\text{C});$$

$$R^2 = 0.92, p < 0.001, n = 30 \quad (2a)$$

$$10^6 \cdot \ln(\alpha_{\text{mu}}) = -483 \pm 15 + (3.7 \pm 0.4) \cdot T(^{\circ}\text{C}) \quad (2b)$$

The small differences between biogenic and inorganic aragonite are not significant within the analytical uncertainty and are therefore not interpreted here.

The array defined by calcitic materials is less depleted in  $^{44}\text{Ca}$  and includes sclerosponges (*A. wellsi*), planktic foraminifera (*Orbulina universa*, *Turborotalia quinqueloba*), brachiopods, a red alga and inorganic calcite. In our data there is no systematic Ca isotope difference between low and high-Mg calcites.

Biogenic calcite samples (without *O. universa*):

$$1000 \cdot \ln(\alpha) = -1.39 \pm 0.17 + (0.026 \pm 0.01) \cdot T(^{\circ}\text{C});$$

$$R^2 = 0.76, p < 0.001, n = 13 \quad (3a)$$

$$10^6 \cdot \ln(\alpha_{\text{mu}}) = -351 \pm 45 + (6.6 \pm 2.6) \cdot T(^{\circ}\text{C}) \quad (3b)$$

*O. universa* (Gussone et al., 2003):

$$1000 \cdot \ln(\alpha) = -1.39 \pm 0.07 + (0.019 \pm 0.003) \cdot T(^{\circ}\text{C});$$

$$R^2 = 0.91, p < 0.001, n = 18 \quad (4a)$$

$$10^6 \cdot \ln(\alpha_{\text{mu}}) = -348 \pm 18 + (4.8 \pm 0.8) \cdot T(^{\circ}\text{C}) \quad (4b)$$

Inorganic calcite of Marriott et al. (2004) ( $\alpha_{44/42}$  recalculated to  $\alpha_{44/40}$ ):

$$1000 \cdot \ln(\alpha) = -1.02 \pm 0.25 + (0.015 \pm 0.013) \cdot T(^{\circ}\text{C});$$

$$R^2 = 0.73, p < 0.02, n = 6 \quad (5a)$$

$$10^6 \cdot \ln(\alpha_{\text{mu}}) = -256 \pm 62 + (3.8 \pm 3.2) \cdot T(^{\circ}\text{C}) \quad (5b)$$

The fractionation trend of the calcite samples is identical within uncertainty to the previously published monospecific calibration curve of *O. universa* and similar to the data of Marriott et al. (2004). The small deviation from the latter data may be caused either by an inter-laboratory bias due to different analytical and data reduction procedures or it may be due to the different experimental set up and conditions during precipitation, which are considerably different with respect to salinity (cation concentrations) and precipitation rate.

Table 2. Calcium isotope fractionation in biogenic and inorganic calcium carbonate samples.<sup>a</sup>

1	2	3	4	5	6	7	8	9
Sample	T [°C]	$\delta^{44/40}\text{Ca}$ ‰ SRM915a	$\alpha$	1000 ln( $\alpha$ )	$\delta^{\text{mu}}\text{Ca}$ ppm/amu SRM915a	$\alpha_{\text{mu}}$	$10^6 \ln(\alpha_{\text{mu}})$	Mineralogy
<i>Vaccetia</i> spp.								
DW398-1	16.2	0.34	0.99846	-1.54	91	0.99959	-413	aragonite
DW546-1	23.1	0.40	0.99852	-1.48	107	0.99960	-397	aragonite
DW546	23	0.39	0.99851	-1.49	105	0.99960	-400	aragonite
DW54-1	17	0.23	0.99835	-1.65	62	0.99956	-443	aragonite
DW54	17.1	0.24	0.99836	-1.64	64	0.99956	-440	aragonite
V1-6	26.4	0.46	0.99858	-1.42	124	0.99962	-381	aragonite
V4-6	26.8	0.43	0.99855	-1.45	116	0.99961	-389	aragonite
<i>Ceratoporella nicholsoni</i>								
Ce95-1	27.1	0.51	0.99863	-1.37	137	0.99963	-368	aragonite
Ce96-304	27.1	0.41	0.99853	-1.47	110	0.99961	-395	aragonite
Pb19-401	25.7	0.42	0.99854	-1.46	113	0.99961	-392	aragonite
<i>Astrosclella willeyana</i>								
RS11	26.1	0.42	0.99854	-1.46	113	0.99961	-392	aragonite
<i>Acanthochaetetes wellsi</i>								
AwMac	27.6	1.02	0.99914	-0.86	274	0.99977	-231	HMC
Aw92	24	1.21	0.99933	-0.67	325	0.99982	-180	HMC
AwLi	26	1.18	0.99930	-0.70	317	0.99981	-188	HMC
Pteropods								
SO7-3/1	27.5	0.49	0.99861	-1.39	132	0.99963	-373	aragonite
SO7-3/2	27.5	0.44	0.99856	-1.44	118	0.99961	-387	aragonite
SO7-3/3	27.5	0.44	0.99856	-1.44	118	0.99961	-387	aragonite
Brachiopods								
316282	26.9	1.19	0.99931	-0.69	325	0.99982	-180	LMC
BP-Mad	20	1.05	0.99917	-0.83	277	0.99977	-228	LMC
CrRck	14	0.82	0.99894	-1.06	223	0.99972	-282	LMC
SJI1	10	0.92	0.99904	-0.96	250	0.99975	-255	LMC
SJI2	10	0.97	0.99909	-0.91	263	0.99976	-242	LMC
<i>Turborotalia quinqueloba</i>								
23523-2	10.2	0.50	0.99862	-1.38	135	0.99963	-370	LMC
37/25	2.5	0.44	0.99856	-1.44	117	0.99961	-387	LMC
23515	-0.4	0.52	0.99864	-1.36	140	0.99964	-365	LMC
37/53	1	0.41	0.99853	-1.47	110	0.99960	-395	LMC
Inorganic calcite								
ac1	25	0.24	0.99909	-0.91	65	0.99976	-244	calcite
ac3	25	0.05	0.99890	-1.10	13	0.99970	-296	calcite
Articulated coralline red alga								
PL1	14	1.05	0.99917	-0.83	282	0.99978	-223	HMC

<sup>a</sup> Column 4: fractionation factor  $\alpha = ({}^{44}\text{Ca}/{}^{40}\text{Ca})_{\text{solid}}/({}^{44}\text{Ca}/{}^{40}\text{Ca})_{\text{fluid}}$ . Fluid is seawater ( $\delta^{44/40}\text{Ca}$ : 1.88 ‰ SRM 915a) for all carbonates except for samples ac1 and ac3 (fluid:  $\delta^{44/40}\text{Ca}$ : 1.15 ‰ SRM 915a). Column 6:  $\delta^{\text{mu}}\text{Ca}$  [ppm/amu SRM915a] =  $(({}^{\text{a}}\text{Ca}/{}^{\text{b}}\text{Ca})_{\text{sample}}/({}^{\text{a}}\text{Ca}/{}^{\text{b}}\text{Ca})_{\text{SRM915a}} - 1) \cdot (1/(a-b)) \cdot 10^6$ ) and a, b being the masses of the respective Ca isotopes. Column 7: fractionation factor  $\alpha_{\text{mu}} = \alpha^{[a/(b+1)(a-b)]}$  (assuming equilibrium isotope fractionation) with  $\alpha = ({}^{\text{a}}\text{Ca}/{}^{\text{b}}\text{Ca}_{\text{cc}})/({}^{\text{a}}\text{Ca}/{}^{\text{b}}\text{Ca}_{\text{fluid}})$  and a, b being the masses of the respective Ca isotopes. Column 9: Mineralogy: HMC: high magnesium calcite; LMC: low magnesium calcite.

### 3.2. Relationship between Carbonate Chemistry and Ca-Isotope Fractionation in the Present-Day Ocean

The GEOSECS surface water stations cover a latitudinal range from 69°S to 54°N, a temperature range from -1.5 to 29.7°C, salinities from 32.6 to 40.4 psu (practical salinity units), DIC (dissolved inorganic carbon) from 1.84 to 2.18 mmol/kg and TA (total alkalinity) from 2.20 to 2.52 mEq/kg. The resulting carbonate ion concentrations range from 0.10 to

0.28 mmol/kg and show a highly significant correlation to water temperature (Fig. 2):

$$[\text{CO}_3^{2-}] (\text{mmol/kg}) = (0.113 \pm 0.006) + (0.0053 \pm 0.0003) \cdot T(^{\circ}\text{C});$$

$$R^2 = 0.87, p = 0, n = 222(6)$$

Salinity has only a minor influence on  $[\text{CO}_3^{2-}]$ . Normalization

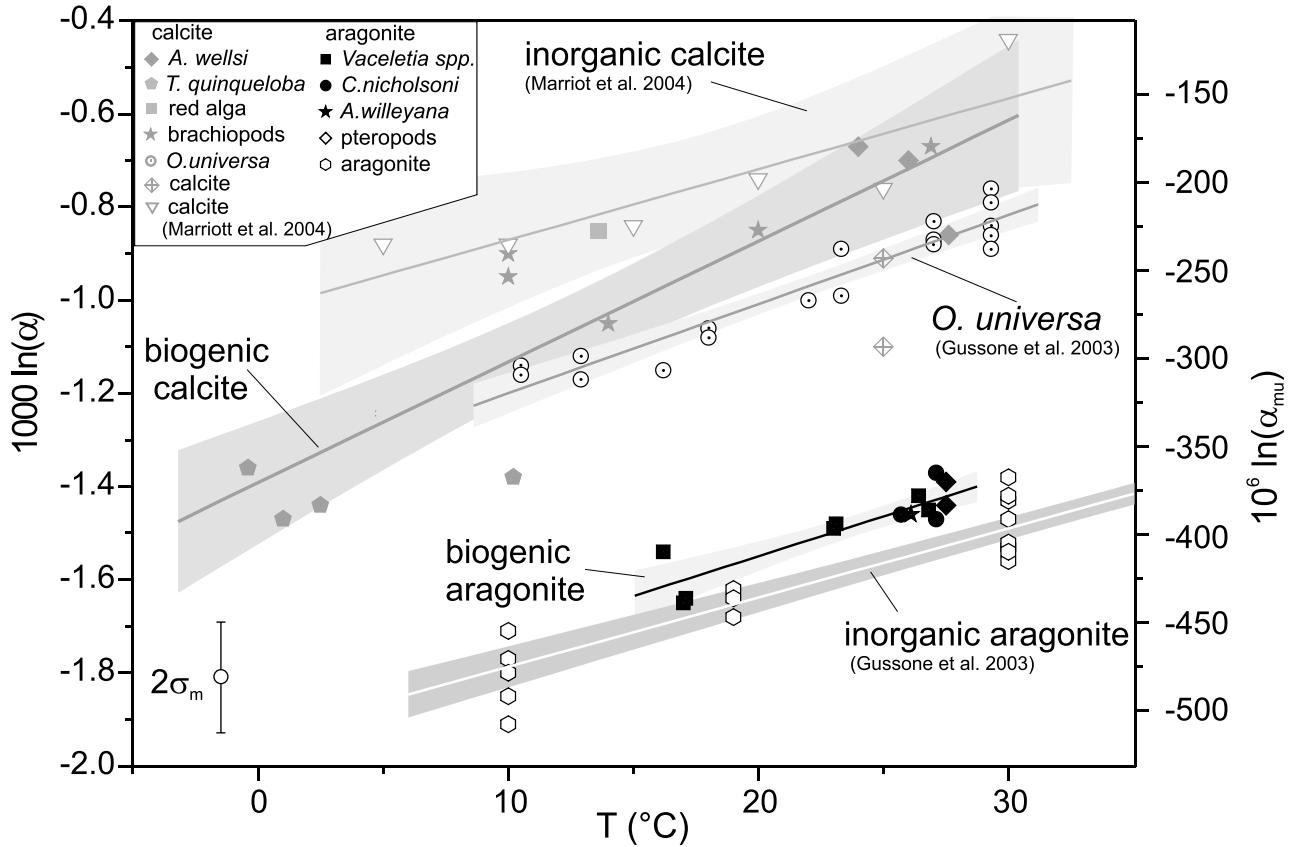


Fig. 1. Temperature dependent Ca isotope fractionation of different aragonitic and calcitic carbonates: aragonite samples (black symbols) are more enriched in <sup>40</sup>Ca than calcite samples (gray symbols). The offset is about 0.6‰ (150 ppm/amu). All fractionation-temperature trends have similar slopes of about 0.02‰/°C (5 ppm/amu · °C<sup>-1</sup>).

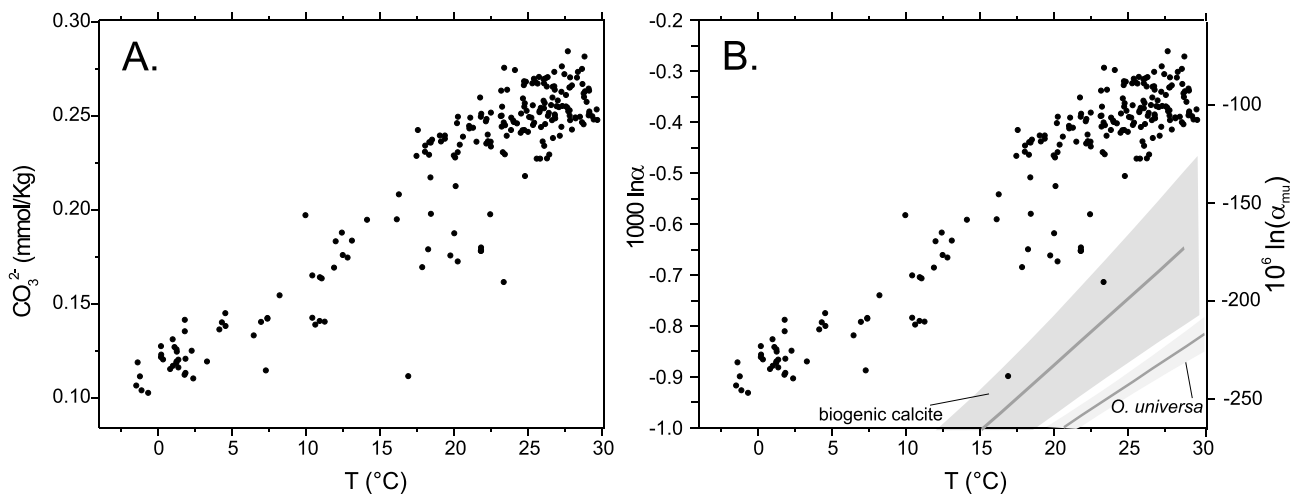


Fig. 2. (A) Carbonate ion (CO<sub>3</sub><sup>2-</sup>) concentration in open ocean surface waters (0–50 m) as a function of temperature. The CO<sub>3</sub><sup>2-</sup> concentration was calculated from DIC (dissolved inorganic carbon) and TA (total alkalinity) from GEOSECS data. (B) Calculated calcium isotope fractionation for calcite precipitated from waters with respective CO<sub>3</sub><sup>2-</sup> concentration (after Lemarchand et al., 2004). The calculated 1000 · lnα values show a temperature dependence of 0.02‰/°C which is identical within error with the observed temperature calibration. There is an offset of about 0.5‰ between observed and calculated fractionation values.

of the data to a constant salinity (35 psu) changes the regression only slightly to:

$$[\text{CO}_3^{2-}](\text{mmol/kg}) = (0.119 \pm 0.005) \\ + (0.0049 \pm 0.0003) \cdot T(^{\circ}\text{C}); \\ R^2 = 0.87, p = 0, n = 222 \quad (7)$$

The observed correlation between  $[\text{CO}_3^{2-}]$  and temperature is not an artifact of the temperature dependence of the carbonic acid system parameters used in our calculations. This can be demonstrated by calculating  $[\text{CO}_3^{2-}]$  from DIC and TA with constant (temperature-invariant) carbonic acid system parameters (15°C). The resulting relation does not differ significantly from Eqn. 6:

$$[\text{CO}_3^{2-}](\text{mmol/kg}) = (0.119 \pm 0.006) \\ - (0.0050 \pm 0.0003) \cdot T(^{\circ}\text{C}); \\ R^2 = 0.85, p = 0, n = 222 \quad (8)$$

Therefore the observed correlation reflects variations in the measured DIC/TA ratio, an actual property of ocean surface waters.

We derive a relation between the Ca isotope fractionation in calcite ( $1000 \cdot \ln(\alpha_{\text{cc}})$ ) and carbonate ion concentration by calculating a regression through the data of Lemarchand et al. (2004), experiments A and B:

$$1000 \cdot \ln(\alpha_{\text{cc}}) = -(1.31 \pm 0.12) \\ + (3.69 \pm 0.59) \cdot [\text{CO}_3^{2-}](\text{mmol/kg}); \\ R^2 = 0.94, p = 0, n = 14 \quad (9)$$

Combining Eqns. 6 and 9 yields a temperature dependent calcium isotope fractionation equation for calcite in marine surface waters:

$$1000 \cdot \ln(\alpha_{\text{cc}}) = -(0.89 \pm 0.14) + (0.020 \pm 0.003) \cdot T(^{\circ}\text{C}) \\ (10)$$

The slope of Eqn. 10 is in accordance with the empirical relationship for marine calcites (Eqn. 11, combining the data of Eqns. 3 and 4), but  $1000 \cdot \ln(\alpha_{\text{cc}})$  is offset by about 0.5‰:

$$1000 \cdot \ln(\alpha_{\text{cc}}) = -(1.39 \pm 0.1) + (0.021 \pm 0.005) \cdot T(^{\circ}\text{C}) \\ (11)$$

#### 4. DISCUSSION

Our Ca isotope measurements clearly show an offset between calcitic and aragonitic samples of about 0.6‰ (150 ppm/amu). Biogenic aragonites show less scatter of  $\alpha$  or  $\alpha_{\text{mu}}$  values compared to the biogenic calcite samples (Fig. 1 and Table 2). The stronger scatter of the calcites may be partially explained by the more sophisticated calcification mechanisms that allow the precipitation of Mg-poor calcite in modern seawater (e.g., brachiopods and planktic foraminifera). The high Mg content of modern seawater favors the precipitation of either Mg-rich calcite or aragonite. Therefore, organisms that form skeletons of low-Mg calcite need to actively control the chemical composition of their calcifying fluid.

In order to elucidate the mechanisms which are responsible for the smaller Ca isotope fractionation in calcite relative to aragonite, we investigate the processes which are involved in calcium carbonate precipitation. Further, we will discuss the three currently available models of Ca isotope fractionation in  $\text{CaCO}_3$  (kinetic, equilibrium, and disequilibrium fractionation) and their compatibility with our key observations: 1. the Ca isotope offset between aragonite and calcite; 2. the similar relation between temperature and Ca-isotope fractionation in natural and cultured biogenic as well as inorganic  $\text{CaCO}_3$  precipitates; 3. the independence of Ca isotope fractionation from the ambient  $\text{CaCO}_3$  saturation state in foraminiferal calcite (Gussone et al., 2003).

#### 4.1. $\text{CaCO}_3$ Crystal Growth and Isotope Fractionation

The high  $[\text{Ca}^{2+}]/[\text{CO}_3^{2-}]$  ratio of seawater causes calcite surfaces to be positively charged due to adsorption of  $\text{Ca}^{2+}$  ions at the crystal surface. The crystal grows by adsorption of  $\text{CO}_3^{2-}$  onto these  $\text{Ca}^{2+}$  sites and subsequent addition of  $\text{CaCO}_3$  to the crystal lattice. The crystal growth rate is therefore proportional to the number of available  $\text{Ca}^{2+}$  surface sites and the  $\text{CO}_3^{2-}$  concentration ( $[\text{CO}_3^{2-}]$ ) in the fluid (Zuddas and Mucci, 1998). Surface sites are always sufficiently available, due to the high  $\text{Ca}^{2+}$  concentration in seawater, and thus the crystal growth is limited by  $[\text{CO}_3^{2-}]$ . This growth model was used by Lemarchand et al. (2004) to explain their observation that Ca isotope fractionation between dissolved Ca and calcite is independent from  $[\text{Ca}^{2+}]$  but strongly dependent on the carbonate ion concentration, because  $\text{CO}_3^{2-}$  controls the oversaturation. Their Ca isotope fractionation model (in the following abbreviated by “LWP model”) implies that at low crystal growth rates Ca incorporation into  $\text{CaCO}_3$  involves an isotope fractionation. At very high growth rates Ca is exchanged between fluid and crystal without noticeable isotope effects. Increasing proportions of such unfractionated Ca in the crystal at increasing growth rates leads to the observed correlation between  $\delta^{44/40}\text{Ca}$  and  $[\text{CO}_3^{2-}]$  (Lemarchand et al., 2004). The same mechanism was proposed by Zhang et al. (1988) to explain the observed lack of a significant Ca isotope fractionation in natural calcites compared to their theoretically derived  $^{44}\text{Ca}/^{40}\text{Ca}$  equilibrium fractionation of  $-3\text{‰}$  to  $-18\text{‰}$  between Ca-aquocomplexes ( $\text{Ca}(\text{H}_2\text{O})_6^{2+}$ ) and calcite.

The empirically determined temperature dependence of Ca isotope fractionation in  $\text{CaCO}_3$  (Gussone et al., 2003) is explained by the LWP model (Lemarchand et al., 2004) as an effect of growth rate variations in response to varying carbonate ion concentrations, which results from the temperature dependence of the carbon acid speciation (e.g., Millero, 1995), showing an increase in  $[\text{CO}_3^{2-}]$  with increasing temperatures (Fig. 2a). Hence higher temperatures lead to higher  $[\text{CO}_3^{2-}]$  in the fluid, leading to higher precipitation rates, which cause, according to the model, the incorporation of a larger proportion of unfractionated Ca into the crystals and thus diminish Ca isotope fractionation with increasing temperature (Fig. 2b).

To evaluate the consequences of the experimental LWP model for the temperature dependence of Ca isotope fractionation in the open ocean, we further investigate the effects of salinity, ionic strength and inhibitors in the ocean.

As shown by Zuddas and Mucci (1998) the precipitation rate

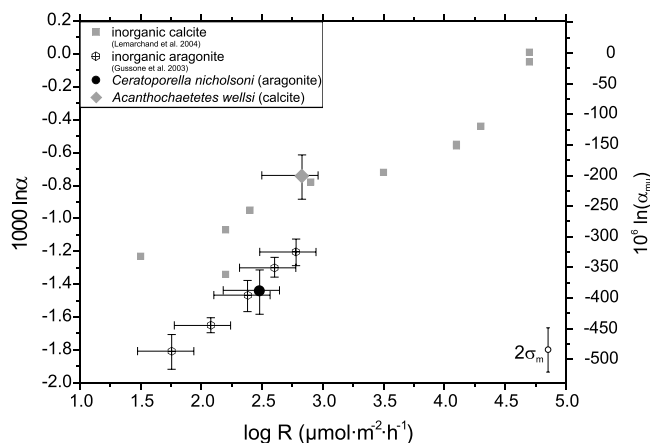


Fig. 3. Calcium isotope fractionation ( $1000 \cdot \ln\alpha$ ) as a function of the precipitation rate ( $\mu\text{mol} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ). The offset between calcite and aragonite at the same precipitation rate is about  $0.6\text{‰}$  (150 ppm/amu). Horizontal error bars indicate  $\pm 50\%$  variation of the precipitation rates.

(R) of calcite and therefore the calcium isotope fractionation in the LWP model depends not only on  $[\text{CO}_3^{2-}]$  but also on the ionic strength of the ambient fluid. Higher ionic strength favors faster precipitation. The salinity variations of marine surface waters as reflected in the GEOSECS data have only a minor influence on  $[\text{CO}_3^{2-}]$ , but through the ionic strength effect can cause R to vary by a factor of up to 30. This effect needs to be considered for the interpretation of Ca isotope fractionation in marine carbonates with respect to the model of Lemarchand et al. (2004). A linear regression through their data indicates that Ca isotope fractionation of calcite ( $\alpha_{\text{cc}}$ ) varies as a function of the precipitation rate R:

$$1000 \cdot \ln(\alpha_{\text{cc}}) = -1.91 + 0.37 \cdot \log(R) (\mu\text{mol}/\text{m}^2/\text{h}) \quad (12)$$

With that relation, the salinity and ionic strength variations reflected in the GEOSECS data can cause variations of  $1000 \cdot \ln(\alpha_{\text{cc}})$  of up to  $0.5\text{‰}$  (125 ppm/amu). However, this effect leads to only a slight change (about 15%) of the slope in Eqn. 10, because salinity and temperature in marine surface waters are only weakly correlated ( $r^2 = 0.3$ ).

Combining the LWP model with the GEOSECS data (Eqn. 10) predicts a  $0.5\text{‰}$  (125 ppm/amu) smaller fractionation ( $0.5\text{‰}$  heavier  $\delta^{44/40}\text{Ca}$ -values) than the observed isotope values in marine calcite materials (Fig. 2b, Eqns. 3 and 4). This offset does not necessarily contradict the LWP model. In fact it can be explained by Ca isotope fractionation controlled by precipitation rate. Zuddas and Mucci (1994) observed that calcite precipitation occurs 25 times slower in seawater than in an artificial  $\text{NaCl-CaCl}_2$  solution of identical  $\text{CaCO}_3$  saturation, probably due to influences from  $\text{Mg}^{2+}$  ions, sulfate and other inhibitors. As the fractionation Eqn. 10 is derived from laboratory experiments in  $\text{NH}_4\text{Cl-CaCl}_2$  solutions, its application to natural seawater precipitates affords a correction for the reduced precipitation rate. According to Eqn. 12 the 25-fold lower precipitation rate should translate into Ca isotope fractionation that yields  $0.5\text{‰}$  lighter  $\delta^{44/40}\text{Ca}$  for calcite precipitated from seawater compared to  $\text{NH}_4\text{Cl-CaCl}_2$  solutions. The latter value can quantitatively explain the observed offset be-

tween predicted (Eqn. 10) and observed (Eqn. 11) Ca-isotope fractionation (Fig. 2). These results support the model, that Ca isotope fractionation may be controlled by  $[\text{CO}_3^{2-}]$  via the precipitation rate. However, it is also apparent that in the present ocean there is a strong linkage between temperature and  $[\text{CO}_3^{2-}]$  and hence precipitation rate and Ca isotope composition of marine carbonates. The scatter in the T- $\text{CO}_3^{2-}$  relation in marine surface waters (Fig. 2a) might also partially explain the scatter in the T -  $\delta^{44/40}\text{Ca}$  data of marine carbonate samples (Fig. 1).

## 4.2. Controls of Ca Isotope Fractionation in Polymorphic $\text{CaCO}_3$ Modifications

Considering the influence of precipitation rate on the Ca isotope fractionation in calcite opens the question, whether the observed Ca isotope fractionation between aragonite and calcite is simply a consequence of the different precipitation rates of both polymorphs. Zhong and Mucci (1989) measured precipitation rates of aragonite and calcite in seawater and found that at identical Ca and carbonate ion concentrations aragonite precipitates about 3 times faster than calcite. Following Lemarchand et al. (2004) the faster precipitation would lead to a roughly  $0.1\text{‰}$  (25 ppm/amu) smaller fractionation of aragonite compared to calcite, which is contradictory to our observations. At similar growth rates, the inorganic precipitates of aragonite (Gussone et al., 2003) are roughly  $0.6\text{‰}$  (150 ppm/amu) more fractionated than the calcite precipitates of Lemarchand et al. (2004) (Fig. 3, Table 3).

A straightforward comparison of the precipitation rates between the different setups is difficult. The inorganic calcite precipitation rates of Lemarchand et al. (2004) were theoretically calculated from the solution chemistry following the approach of Zuddas and Mucci (1994), which takes the reactive crystal surface area into account. In contrast, the precipitation rates of the inorganic aragonites (Gussone et al., 2003; Dietzel et al., 2004) were calculated by using the surface area of the growth substrate as an approximation of the reactive surface. This approach reveals a reasonable approximation, because the aragonite crystals in this experiment grew as a dense isopachous crust of needles. The same applies for the calcification rate estimates of the biogenic aragonite and calcite from sclerosponges.

Despite these large uncertainties, a comparison of the precipitation rates is possible because of the logarithmic rate relationship (Eqn. 12) that is quite insensitive to uncertainties in the rate values. The fractionation difference of  $0.6\text{‰}$  between

Table 3. Approximated precipitation rates (R).

Sample	T (°C)	R ( $\mu\text{mol}/\text{h}/\text{m}^2$ )	Log(R)
<i>C. nicholsoni</i>	26	310	2.49
<i>A. wellsi</i>	25	630	2.80
Aragonite <sup>a</sup>	10	60	1.76
Aragonite <sup>a</sup>	19	120	2.08
Aragonite <sup>a</sup>	30	240	2.38
Aragonite <sup>a</sup>	40	400	2.60
Aragonite <sup>a</sup>	50	600	2.78

<sup>a</sup> Inorganic aragonite (Dietzel et al., 2004; Gussone et al., 2003).

Table 4. Mineralogical, physical and chemical properties of calcite and aragonite.

Property	Calcite	Aragonite
Crystal structure	trigonal, $\bar{3}2/m$ , ditrigonal scalenohedral	orthorhombic, $2/m 2/m 2/m$ , dipyramidal
Elementary cell dimensions	a = 4.990 Å, c = 17.061 Å	a = 4.96 Å, b = 7.97 Å, c = 5.74 Å
Ca coordination	Ca <sup>16l</sup> O	Ca <sup>19l</sup> O
Ca-O distance	2.36 Å	2.53 Å
Density	2.710 g/cm <sup>3</sup>	2.947 g/cm <sup>3</sup>
Solubility Product	$3.36 \times 10^{-9}$ mol <sup>2</sup> /L <sup>2</sup>	$6.0 \times 10^{-9}$ mol <sup>2</sup> /L <sup>2</sup>
1000ln( $\alpha_{\text{solid-fluid}}$ ) <sup>18</sup> O/ <sup>16</sup> O, 25°C <sup>a</sup>	28.3‰ (14.95‰/amu)	29.2‰ (15.43‰/amu)
1000ln( $\alpha_{\text{solid-fluid}}$ ) <sup>13</sup> C/ <sup>12</sup> C, 25°C <sup>b</sup>	1.0‰	2.7‰
1000ln( $\alpha_{\text{solid-fluid}}$ ) <sup>44</sup> Ca/ <sup>40</sup> Ca, 25°C <sup>c</sup>	-0.9‰ (-0.24‰/amu)	-1.6‰ (-0.43‰/amu)

<sup>a</sup> H<sub>2</sub>O-CaCO<sub>3</sub> (Kim and O'Neil, 1997; Böhm et al., 2000).

<sup>b</sup> HCO<sub>3</sub><sup>-</sup>-CaCO<sub>3</sub> (Romanek et al., 1992).

<sup>c</sup> Ca<sub>aq</sub>-CaCO<sub>3</sub>, *O. universa* calcite and inorganic aragonite (Gussone et al., 2003).

calcite and aragonite corresponding to a 20–25 times faster precipitation, is too large to be explained only by a systematic error due to the different approaches for precipitation rate determination. Additionally, calcitic and aragonitic sclerosponges which have similar precipitation rates, exhibit the typical offset of about 0.6‰ (Fig. 3). These considerations show that different precipitation rates cannot explain the observed offset in Ca isotope fractionation between aragonite and calcite.

Instead we suggest that Ca isotope fractionation in different CaCO<sub>3</sub> polymorphs is mineralogically controlled. This can be either due to the different vibrational behavior of Ca in aragonite and calcite crystals (equilibrium fractionation sensu Marriott et al., 2004, and Zhang et al., 1988) or due to differences in the surface chemistry of the two polymorphs (sensu Watson, 2004).

The observed <sup>44</sup>Ca depletion in the crystal relative to the fluid was previously interpreted either as kinetic isotope fractionation (cf. Gussone et al., 2003) or as equilibrium fractionation (cf. Bullen et al., 2003; Lemarchand et al., 2004; Marriott et al., 2004). The equilibrium fractionation model is based on the assumption, that Ca has stronger covalent bonds in a hydration sphere than in the carbonate lattice. Hence heavy Ca is preferentially kept in solution while the carbonate crystal is enriched in light Ca. Decreasing fractionation with increasing temperature, which is typical for equilibrium isotope fractionation, can then lead to the positive correlation with temperature.

The observed different fractionation of calcite and aragonite is also compatible with the equilibrium fractionation model. Calcium isotope fractionation between calcite and aragonite could arise from the different Ca-O bond strengths in these modifications. The Ca-O bonds are about 60% stronger in the calcite structure than in aragonite (Zheng, 1999). Therefore, <sup>44</sup>Ca should be enriched in calcite relative to aragonite. This prediction matches our observation of less fractionated, isotopically heavier Ca isotopes in calcite compared to aragonite.

In contrast, the model of kinetically dominated Ca isotope fractionation is based on the assumption that due to the dominantly ionic character of the Ca-O bonds, there is no significant energetic advantage of the <sup>44</sup>Ca-O bonds in the Ca-aquocomplex compared to that in the crystal. It explains the observed fractionation and its temperature dependence with kinetic effects during the transport of Ca-aquocomplexes across a thin boundary layer between the fluid and the crystal surface. This

boundary layer may include a near-surface region sensu Watson (2004). Considering the different crystal structures, bond strengths and activation energies of aragonite and calcite (Table 4), different kinetic behavior of Ca ions at the surface of these crystals is expected. Taking this into account, the observed difference in calcium isotope fractionation between aragonite and calcite may be compatible with the kinetic fractionation model.

Finally, the model of Lemarchand et al. (2004) proposes a Ca isotope equilibrium fractionation for calcite of about -1.5‰ which is overprinted in the crystal by disequilibrium effects. The observed temperature dependence in calcite is explained by increasing admixture of unequilibrated Ca from the solution due to faster precipitation rates at higher temperatures. The same mechanism should apply to the inorganic aragonite precipitates, which show a similar temperature dependence as indicated by the LWP model (Gussone et al., 2003). Application of the LWP model would imply that the inorganic aragonite partly formed from isotopically unequilibrated Ca. However, Dietzel et al. (2004) showed that the incorporation of trace elements (Sr, Ba) in this aragonite follows the Nernst distribution law and therefore occurred under equilibrium conditions. Although there is a general difference between chemical and isotopic equilibrium, we propose that Ca isotopes should equilibrate similar to the element/Ca ratio, since precipitation of Ca from the solution does not involve slow, complex reactions (breaking up of covalent bonds) as it is the case for carbon or oxygen in the carbonate ions. This would imply that these inorganic aragonites precipitated in Ca isotopic equilibrium and that a different mechanism than proposed by the LWP model would be responsible for the observed temperature dependence, e.g., temperature-dependent equilibrium fractionation. Further experiments at very low precipitation rates will be necessary to solve this contradiction.

The LWP model can explain the observed temperature dependence of  $\delta^{44/40}\text{Ca}$  in calcium carbonates. However there is a discrepancy concerning the [CO<sub>3</sub><sup>2-</sup>]-dependence of Ca isotope fractionation in inorganic calcite observed by Lemarchand et al. (2004) with what we observed in the foraminiferal species *Orbulina universa* (Gussone et al., 2003) (Fig. 4). *O. universa* calcite shows a temperature dependent Ca isotope fractionation of about 0.02‰/°C in agreement with the LWP model, but does not exhibit a significant dependence of  $\delta^{44/40}\text{Ca}$  on ambient [CO<sub>3</sub><sup>2-</sup>] over a range from 0.137 to 0.530 mmol/kg. This lack



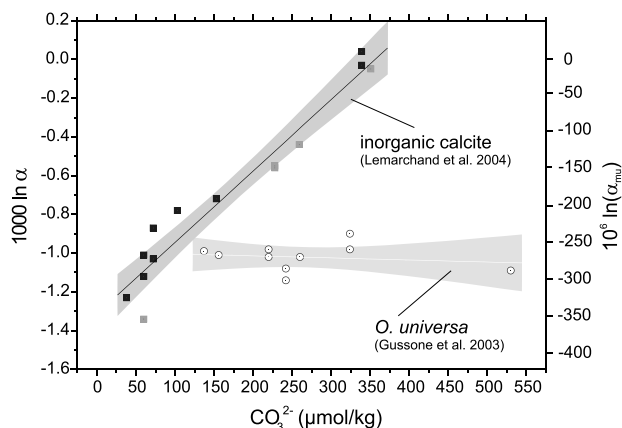


Fig. 4. Calcium isotope fractionation ( $1000 \cdot \ln \alpha$ ) of *O. universa* (Gussone et al., 2003) and inorganically precipitated calcite (Lemarchand et al., 2004) as a function of  $\text{CO}_3^{2-}$ . Inorganic calcite shows a strong decrease of Ca isotope fractionation (increasing  $1000 \cdot \ln \alpha$ ) with increasing carbonate concentration, while the planktonic foraminifer *O. universa* shows no significant variation.

of  $[\text{CO}_3^{2-}]$  dependence can only be reconciled with the findings of Lemarchand et al. (2004) by assuming that the carbonate chemistry in the foraminifer vesicle where precipitation takes place is controlled by biological processes and is largely independent from the ambient water chemistry. Consequently calcite growth in the foraminifer vesicle is not directly limited by the ambient  $[\text{CO}_3^{2-}]$ . This decoupling of internal and external carbonate chemistry does not generally contradict the interpretation of the temperature dependence of *O. universa* by the LWP model, because the dissociation of the carbonate species in the vesicles of *O. universa* is affected by temperature in the same way as in the ambient water.

Alternatively these results might indicate that the rate dependent fractionation mechanism is not dominating the Ca isotope fractionation in *O. universa*. However at present it can not be concluded, whether equilibrium, kinetic, rate-dependent or additional biological fractionation is responsible for the Ca isotope signal in *O. universa*.

Additionally, further mechanisms for Ca isotope fractionation beyond the LWP model are necessary to explain the presence of a much stronger temperature dependence of Ca isotopes in certain foraminifera species cf. (Zhu and Macdougall, 1998; Nägler et al., 2000; Gussone et al., 2004).

## 5. SUMMARY AND CONCLUSION

Calcite and aragonite exhibit a systematic difference in calcium isotope composition of about 0.6‰ (150 ppm/amu). This difference can not be explained by different saturation states and precipitation rates of both minerals. Instead it is most likely based on thermodynamic crystal properties. However, the currently small theoretical and experimental data base for the thermodynamic behavior of Ca isotopes in the  $\text{Ca}_{\text{aq}}\text{-CaCO}_3$  system is pending further amelioration.

The close agreement in the relation between temperature and Ca isotope fractionation of calcite and aragonite as well as of marine biogenic and experimental inorganic precipitates points to an universal mechanism controlling Ca isotope fractionation

in calcium carbonates. A possible mechanism is the temperature dependence of the dissociation constants of the carbonate species as suggested by the LWP model. Data from marine surface waters show that this model is generally applicable to marine calcium carbonates, if the effects of ionic strength and growth inhibitors like  $\text{Mg}^{2+}$  on precipitation rates are considered.

Ca isotope data of *Orbulina universa* show no dependence on the ambient  $[\text{CO}_3^{2-}]$  but do exhibit the temperature dependence indicated by the LWP model. This observation implies a biological mechanism controlling the carbonate chemistry in the calcifying vesicles of *O. universa*.

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