doi:10.1016/S0016-7037(03)00100-5

Variations of the ^{44}Ca/^{40}Ca ratio in seawater during the past 24 million years: Evidence from δ^{44}Ca and δ^{18}O values of Miocene phosphates

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Abstract—The Ca isotope variation of 11 Miocene and Pleistocene, authigenic, marine phosphates is rather small compared to the corresponding variation in δ^{18}O values. The δ^{44}Ca values are not correlated with the δ^{18}O values and, therefore, they are not temperature controlled. It is likely that the δ^{44}Ca values of the phosphorites reflect the variation in the δ^{44}Ca values of paleo-seawater but, in contrast to Sr, not the isotopic composition of seawater itself. Furthermore, Ca and Sr isotopic compositions are decoupled with decreasing stratigraphic age of the phosphate peloids with Sr isotopic compositions changing to more radiogenic values while Ca isotopic compositions remain rather stable. All samples have δ^{44}Ca values below present-day seawater values, suggesting that phosphate formation discriminates against heavy Ca isotopes.

Phosphorites and carbonaceous sediments have a similar Ca isotopic variation during the Miocene. A systematic and more or less constant shift between marine carbonates and phosphates is observed: the phosphate samples are slightly less enriched in ^{40}Ca compared to carbonates. This shift has been related to a mineral-dependent kinetic mass fractionation during precipitation from seawater. The rather stable δ^{44}Ca value for the 19 to 9 Ma old phosphorites points to a constant δ^{44}Ca fractionation of about 1.1 between seawater and phosphorites during the past and suggests steady-state conditions for the Mid-Miocene seawater (sedimentation flux equals erosion flux).   *Copyright © 2003 Elsevier Science Ltd*

1. INTRODUCTION

Following the demonstration of biologic fractionation (Skulan et al., 1997; Zhu and MacDougall, 1998) Ca isotopes have been used as a tracer of biomineralisation (Skulan and DePaolo, 1999), of the global calcium cycle (De La Rocha and DePaolo, 2000), and of marine paleotemperatures (Nägler et al., 2000). Of special importance is the observation that biologic fractionation discriminates against heavy isotopes and that this phenomenon plays a major role in regulating the Ca isotopic composition of terrestrial calcium. Therefore, biologic activity not only removes calcium from seawater (Ferris et al., 1994; Stumm and Morgan, 1981; Berner et al., 1983) but also depletes the ocean in the light calcium isotopes. 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., 2001). 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.

Ca isotope geochemistry is in many ways still in its infancy. Only a few fractionation factors are known for biomineralisation processes (Skulan et al., 1997; Skulan and DePaolo, 1999; Halicz et al., 1999; De La Rocha and DePaolo, 2000) and, while 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 by exactly how much nor how widespread this phenomenon is. 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 is not yet agreed upon. Skulan et al. (1997) published for the first time data on the variation of δ^{44}Ca values in marine carbonate sediments (carbonate ooze, chalk. . .) over the last 160 Ma. Additional data covering the last 80 Ma have been published by De La Rocha and DePaolo (2000). 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 biomineralisation and that tend to recrystallise more easily even during slight diagenesis than foraminifers or phosphorites (Zhu and MacDougall, 1998; DePaolo and Finger, 1991). Therefore, we propose to test the suitability of another material, marine phosphorite peloïds, for the reconstruction of the Ca isotopic composition of seawater. The phosphorite peloïds used for this study originate from different continental platforms (North Carolina, California, Peru, and Malta island). It has been shown that these authigenic phosphorites formed in Sr and Nd isotopic equilibrium with seawater (McArthur et al., 1990; Stille, 1992; Stille et al., 1994; Stille et al., 1996; Riggs et al., 1997; Riggs et al., 2000). Hence these apatites are likely to be suitable for reconstruction of the evolution of the Ca isotopic composition in seawater during the Miocene. Since there is a strong Ca isotope fractionation between marine sediments such as limestone, chalk, gypsum, and carbonate ooze and seawater (Russell et al., 1978; Skulan et al., 1997; Halicz et al., 1999), such fractionation between phosphorites and seawater is also expected, and the extent and mechanism causing this fractionation remains to be investigated. Further, O isotope fractionation measured in phosphorites reflects variation of temperature as well as changes in δ^{18}O values of

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Table 1. Strontium isotopic age data, Ca, Sr, and O isotopic composition of 11 phosphates and calculated paleotemperatures.

Sample	Location	Embayment	Sr age (Ma)[a]	$^{87}Sr/^{86}Sr$[e]	$\delta^{44}Ca$	$2\sigma_{mean}$[f]	$\delta^{42}Ca$	$2\sigma_{mean}$[f]	No. measurements	$\delta^{18}O$[g]	T (°C)[h]
Pho 5682	Peru		0.48[d]	0.70915(2)[d]	−1.08	0.11	−0.49	0.05	2	—	—
Pho 5553	California	Monterey	9.90[d]	0.70886(2)[d]	−0.98	0.17	−0.41	0.10	1	24.0	8.2[i]
Pho 5554			16.75[d]	0.70868(2)[d]	−1.06	0.14	−0.56	0.07	2	17.3	32.7[j]
OB 53–14	North Carolina	Onslow Bay	9.00[b]	0.70888(1)[b]	−1.10	0.11	−0.55	0.10	1	23.3	11.2[i]
OB 3–7			10.78[b]	0.70884(1)[b]	−1.12	0.16	−0.51	0.10	1	—	—
OB 24-9			18.50[b]	0.70858(1)[b]	−0.88	0.14	−0.46	0.10	1	23.6	5.6[j]
OB 64-20			19.04[b]	0.70854(1)[b]	−1.08	0.27	−0.56	0.13	4	23.3	6.9[j]
GH 8.5R		Aurora section	18.76[b]	0.70856(1)[b]	−0.91	0.14	−0.44	0.10	1	—	—
FG 41	Malta	Ir Rih Bay Section	17.08[c]	0.70870(1)[c]	−0.86	0.18	−0.33	0.14	2	22.4	10.8[j]
FG 17			21.98[c]	0.70840(1)[c]	−0.53	0.14	−0.24	0.08	2	22.0	12.5[j]
FG 8			24.30[c]	0.70826(1)[c]	−0.76	0.16	−0.46	0.08	4	21.2	15.9[j]

[a] The Sr age dates were obtained by using the regression analysis of Hodell et al. (1991) with estimated errors of ±0.48 Ma at the 80% CI and ±0.74 Ma at the 95% CI.

[b] Riggs et al. (2000); [c] Jacobs et al. (1996); [d] this study.

[e] Uncertainties (2σ of the mean) of the $^{87}Sr/^{86}Sr$ ratios are in parenthesis.

[f] For more than one measurement, uncertainties (2σ of the mead) refer to the external reproducibility.

[g] $1\sigma = 0.2‰$.

[h] Paleotemperatures were calculated using the equation of Longinelli and Nuti (1973): $t = 111.4 − 4.3*(\delta^{18}O − \delta^{18}O_{sw})$, where $\delta^{18}O$ and $\delta^{18}O_{sw}$ refer to the oxygen isotope compositions of the phosphate and seawater, respectively.

[i] $\delta^{18}O_{sw} = 0‰$ SMOW.

[j] $\delta^{18}O_{sw} = −1‰$ SMOW.

seawater (Shemesh et al., 1983; Shemesh et al., 1988). The temperature dependence of Ca fractionation is therefore tested by analysing oxygen and calcium isotope ratios on the same samples.

2. MATERIAL AND METHODS

2.1. Sample Description

For the present study, 11 marine and authigenic Miocene and Pleistocene peloïdal phosphate grains have been analysed (Table 1). The fine sand-sized peloïds form as disseminated grains below and at the sediment–water interface in response to the degradation of organic matter in nutrient-rich, suboxic shelf environments (Jarvis et al., 1994; Riggs et al., 2000). The degradation of organic matter liberates PO_4^{3-} to solution, which together with CO_3^{2-} derived from the oxidation of organic matter, reacts with Ca^{2+} and F^- ions from seawater to form carbonate fluorapatite (francolite). The general formula for the carbonate fluorapatite is: $Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_{x-y-z}x(CO_3.F)_y(SO_4)_zF_2$ (Jarvis et al., 1994).

The presently studied samples originate from phosphate-rich sediments of the North Carolina and Peru continental margin, from carbonate platform and shelf sediments of the Maltese platform, and from the Monterey Formation in California. The two Californian samples precipitated in North Pacific seawater, the sample from Peru in South Pacific seawater, the five North Carolina samples in North Atlantic seawater, and the three samples from Malta island in Tethys seawater. The major episodes of phosphogenesis on the Malta shelf occurred between 24 and 16 Ma and can be correlated with synchronous episodes of phosphogenesis along the western North Atlantic (Jacobs et al., 1996). The ages of formation of the studied apatites range between 24 and 0.5 Ma, as deduced from their $^{87}Sr/^{86}Sr$ ratios and the contemporaneous seawater $^{87}Sr/^{86}Sr$ curve (Hodell et al., 1991). The peloïdal phosphate grains (Fig. 1a) manifest stronger chemical stability than other phosphate materials, such as bones, teeth, and vertebrae (Riggs et al., 2000). Only the Californian samples are less well preserved and show a rough and corroded surface (Fig. 1b). A previous study suggests that some of the Miocene Monterey Formation phosphorites have been diagenetically altered at various stages of burial (Kastner et al., 1990).

2.2. Analytical Methods

The phosphate peloidal grains were hand-picked to 99% clean under a binocular microscope. Powdered samples were treated with 0.5 N
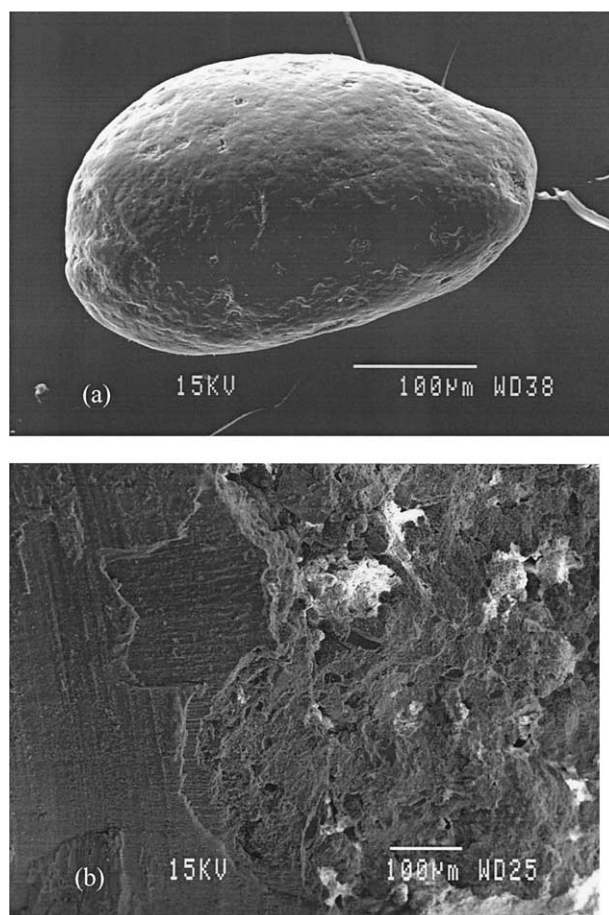

Fig. 1. Electron scanning microscopy pictures of (a) well preserved North Carolina apatite grain and (b) less well preserved apatites from California presenting a rough surface.

Table 2. $\delta^{44}Ca$ (‰) in $CaCO_3$ standards.

	Russell et al., 1978[a]	This study[b]
Johnson Matthey, Lot no. 9912	-1.0 ± 0.2 ($n = 1$)	-1.42 ± 0.11 ($n = 4$)
Johnson Matthey, Lot no. 4064	-12.8 ± 0.3 ($n = 9$)	-13.49 ± 0.19 ($n = 3$)
Standard Reference Material (SRM) 915a	—	-1.89 ± 0.08 ($n = 2$)

[a] Compared to the CaF_2 standards.
[b] Compared to the seawater standard.

acetic acid to remove Sr-rich calcite overgrowths and rinsed with distilled water before dissolution in 6 N HCl (Stille et al., 1996). Approximately 20 μg of sample was analysed following techniques described in detail by Schmitt et al. (2001). The phosphates were dissolved in bidistilled HCl, evaporated to dryness, redissolved in 1.5 N HCl, and centrifuged before being loaded on AG 50W-X8 (200–400 mesh) ion-exchange resin in a 0.6 cm diameter quartz column. 1.5 N HCl was used to remove interfering isotopes of Sr, Mg, and K. Fractionation effects occurring during the chromatographic clean-up were found to be comparable to earlier published values (Russell and Papanastassiou, 1978; up to 3‰ per amu). Therefore, the Ca yield is 100% to avoid significant fractionation of Ca isotopes. No matrix-dependent changes of column calibration were observed. The calcium peak was regularly checked by column calibration using the chemical matrix of the phosphate peloids and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis (with a detection limit of 0.005 mg/L and a precision better than 5%). A drift in the calibration was never recorded. Nevertheless, to avoid ageing of the resin, it was systematically changed after 10 column runs. The procedural blank was $\sim$0.25 μg Ca, which is more than 1500 times smaller than the smallest processed sample. Blank corrections were, therefore, negligible for all samples.

Each sample was separated in two aliquots containing 10 μg of Ca. One of the aliquots was mixed with a ^{43}Ca-^{48}Ca tracer. The aliquots were loaded with H_3PO_4 on Ta filaments and introduced in a vacuum generator (VG) sector thermal ionization mass spectrometry (TIMS) instrument for mass spectrometric analysis. Most of the samples were analysed at least twice including chemical preparation and separation.

Because radioactive decay of ^{40}K may cause small variations in radiogenic ^{40}Ca, a double spike technique including two mass spectrometer runs for each sample has been applied: one for a spiked aliquot and another for an unspiked one, at an ion current of $6.0 \pm 1.2 * 10^{-11}$ A for the most abundant isotope ^{40}Ca. The running procedures on the mass spectrometer as well as the data reduction and fractionation correction have been described previously (Russell et al., 1978; Galer, 1999; Schmitt et al., 2001). According to the nomenclature of previous studies, analytical results are presented in terms of delta values in per mil defined as the difference between $^{44}Ca/^{40}Ca$ or $^{44}Ca/^{42}Ca$ of a sample and a standard.

However, the standard routinely measured is not ultrapure $CaCO_3$ as used by Skulan et al. (1997) but the present-day seawater isotopic composition which has been shown to be uniform within the analytical reproducibility of previous studies (Zhu and MacDougall, 1998; Schmitt et al., 2001). In addition, three carbonate standards, including the Standard Reference Material (SRM) 915a have also been measured and show coherent values with those obtained by Russell et al. (1978) (Table 2). A detailed study on a set of Ca standard material provides consistent $\delta^{44}Ca$ ratios within statistical uncertainties in three European laboratories (Bern, GEOMAR, Strasbourg) and suggest that seawater and NIST 915a are potential common calcium reference materials (Hippler et al., accepted). An Atlantic seawater sample has been chemically processed 15 times to determine the external reproducibility of the whole analytical procedure. The 15 measurements yield a $^{44}Ca/^{40}Ca$ ratio of 0.022151 ± 0.000004, where uncertainty is the two sigma deviation (Fig. 2). The analytical precision achieved by this procedure is also 0.20‰ (2σ at the 95% confidence level).

Referring the measured values to seawater as a common standard allows one to compare data from different laboratories (Zhu and MacDougall, 1998; Schmitt et al., 2001; Hippler et al., accepted). Using the seawater isotopic composition defined earlier (Schmitt et al.,

2001), analytical results are expressed in terms of $\delta^{44}Ca$ and $\delta^{42}Ca$ (in permil) defined as:

$$\delta^{44}Ca = \{(^{44}Ca/^{40}Ca)_{sample}/0.022151 - 1\} \cdot 10^3$$

and

$$\delta^{42}Ca = \{(^{44}Ca/^{42}Ca)_{sample}/3.272 - 1\} \cdot 10^3$$

$\delta^{44}Ca$ yields information on fractionation processes but also on possible ^{40}Ca excess resulting from ^{40}K decay (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), whereas $\delta^{42}Ca$ only reflects fractionation processes. The Ca isotope data are given in Table 1.

To measure the Sr isotopic composition, 400 ng of cleaned phosphate samples were dissolved in 6N HCl, evaporated to dryness, redissolved in 4N HCl, and centrifuged before being loaded on 1 mL AG 50W-X12 (200–400 mesh) anion exchange resin in quartz columns using HCl and ammonium citrate as eluents. The $^{87}Sr/^{86}Sr$ ratios were measured on a VG Sector mass spectrometer using dynamic multicollection mode (Steinmann and Stille, 1997). Peloidal phosphate model ages were calculated using the regression equations for the $^{87}Sr/^{86}Sr$ isotopic compositions of seawater as a function of age developed by Hodell et al. (1991). Within the age ranges of 0 to 2.5, 16 to 8 and 24 to 16 million years ago (interval N-I, N-V, and N-VI, respectively, of Hodell et al., 1991), the Sr-derived ages have a stratigraphic resolution for the 95% confidence interval of ± 0.56 Ma, ± 1.36 Ma and ± 0.74 Ma, respectively (Hodell et al., 1991). The Sr isotope data are given in Table 1.

Oxygen isotope compositions have also been measured on eight phosphate samples at the University of Tübingen. Approximately 15 mg were analysed following techniques described in detail in Vennemann et al. (2002), adapted after Crowson et al. (1991) and O'Neil et al. (1994). Samples were soaked for 12 h in 2.5% NaOCl to remove soluble organic matter, washed several times in distilled water, and then soaked for 48 h in NaOH to remove humic acids. After several rinse cycles with distilled water, the phosphate was dissolved in HF, the
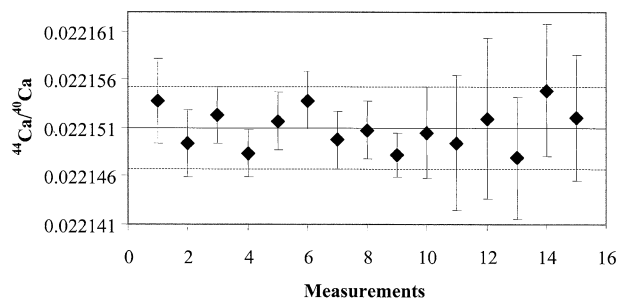

Fig. 2. External reproducibility of 15 measurements of an Atlantic seawater sample. The different values correspond to different measurements as well as to different chemical separations. The mean value as well as the 2σ deviation (45.145 ± 0.009) are given and represented by the straight line and the dashed lines, respectively. This value is close to that published earlier (45.143 ± 0.003; Schmitt et al., 2001) which was taken as a standard value in this present study.
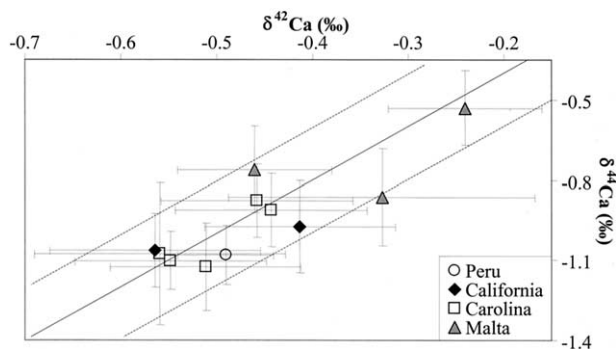
Fig. 3. $\delta^{44}Ca$ vs. $\delta^{42}Ca$ diagram. All the 11 phosphate samples plot along the mass fractionation straight line defined as $\delta^{44}Ca = 2.\delta^{42}Ca \pm 0.2$.

eluate neutralised with KOH and subsequently precipitated as Ag_3PO_4 by addition of an ammoniacal silver nitrate solution. Filtered, washed and dried crystals of Ag_3PO_4 were reacted with known amounts of graphite in sealed silica tubes to produce CO_2. The oxygen isotope composition of the CO_2 was measured on a Finnigan MAT 252 mass spectrometer. Oxygen isotope compositions of hydroxyapatite are expressed in the δ-notation ($\delta^{18}O$) in permil relative to Standard Mean Ocean Water (SMOW). Replicate analyses of the phosphorite NBS-120c from Florida gave values of 21.8‰ ± 0.2‰ (1σ, n = 2) during the course of these analyses. Our in-house standards HA (synthetic hydroxyapatite) and GW-1 (recent shark tooth material) had $\delta^{18}O$ values of 17.6 ± 0.2% (1σ, n = 2) and 22.2 ± 0.2 (1σ, n = 2), respectively The $\delta^{18}O$ values of the samples and corresponding temperatures are given in Table 1.

3. RESULTS

3.1. Spatial and Temporal Variations

In a $\delta^{44}Ca$ vs. $\delta^{42}Ca$ diagram the samples plot along a mass fractionation line defined as $\delta^{44}Ca = 2*\delta^{42}Ca \pm 0.2$ (Fig. 3). Malta FG 17 sample is the least fractionated compared to seawater, whereas the Californian Pho 5554 as well as the North Carolina samples OB 53–14, OB 3–7 and OB 64–20 are the most fractionated samples. No ^{40}Ca excess due to ^{40}K disintegration can be detected within the ±0.2‰ external reproducibility of this study. The measured Ca isotopic values are, therefore, consistent with mass-dependent fractionation and both isotopic ratios, $^{44}Ca/^{40}Ca$ and $^{44}Ca/^{42}Ca$ furnish similar information. Further discussion will consequently only rely on $\delta^{44}Ca$ to compare the results directly with those published earlier.

In Figure 4a the $\delta^{44}Ca$ values of the 11 marine phosphates are plotted against their corresponding $^{87}Sr/^{86}Sr$ values. Notable is the absence of a correlation between the $^{44}Ca/^{40}Ca$ and $^{87}Sr/^{86}Sr$ ratios (R^2 = 0.49). The $\delta^{44}Ca$ values of the studied phosphates range between −1.12 and −0.53 whereas the Sr isotopic values increase from 0.70840 to 0.70915 between 24 and 9 Ma. The samples from Carolina (16.8 to 10 Ma), California (19 to 9 Ma), and Peru (0.5 Ma) have very similar $\delta^{44}Ca$ values. The mean value of the two Californian samples (−1.02 ± 0.09) is the same as that of the five North Carolina apatites (−1.02 ± 0.10) and that from Peru (−1.08 ± 0.11). However, Malta samples (24.3 to 17.1 Ma) have slightly lower ^{40}Ca contents. Their $\delta^{44}Ca$ mean value (−0.72 ± 0.20) points to an enrichment in the heavier ^{44}Ca isotope, compared to the other

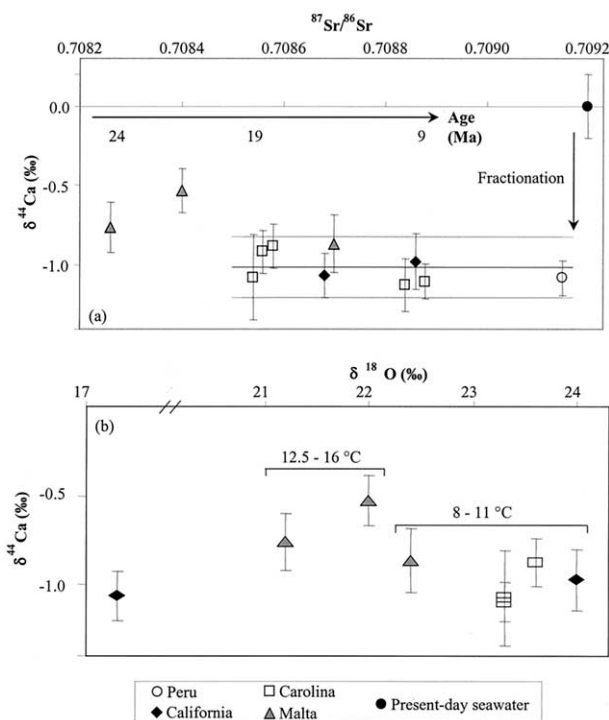Fig. 4. (a) Variation of $\delta^{44}Ca$ vs. $^{87}Sr/^{86}Sr$ in the 11 studied phosphorites and in present-day seawater The $\delta^{44}Ca$ mean value as well as the 2σ deviation (−1.2 ± 0.2, n = 9) for 9 of the 11 apatites are given and represented by the straight line and the dashed lines, respectively. (b) Variation of $\delta^{44}Ca$ vs. $\delta^{18}O$ in the studied apatites.

phosphates. All samples have moreover $\delta^{44}Ca$ values below present-day seawater, suggesting that phosphate formation discriminates against heavy Ca isotopes. This is clearly indicated by the near present-day Peru sample having a $\delta^{44}Ca$ of 1.1‰.

3.2. Temperature Variations

$\delta^{18}O$ values measured in apatites reflect variation of temperature as well as changes in $\delta^{18}O$ values of seawater (Shemesh et al., 1983; Shemesh et al., 1988; Hiatt and Budd, 2001). The onset of major glaciation in Antarctica some 14 Ma ago (Zachos et al., 2001) has caused an increase in the $\delta^{18}O$ value of seawater by ~1‰. However, this change is rather small compared to the 7‰ variation in $\delta^{18}O$ values observed for the phosphorites.

Water temperatures estimated on the basis of the oxygen isotope composition of phosphates have been calculated using the equation of Longinelli and Nuti (1973) for marine phosphates. Between 24.3 and 17.1 Ma, the $\delta^{18}O$ values of the Malta samples increase slightly from 21.2 to 22.4‰. This would correspond to cooling by ~5°C, from 15.9 to 10.8°C. The $\delta^{18}O$ values of the slightly younger North Carolina samples indicates ~5°C lower formation temperatures of 5.6 to 6.9°C. The two phosphorites from California (Pho 5553 and 5554) have different $\delta^{18}O$ values pointing to very different formation temperatures of 8.2 and 32.7°C, respectively (Table 1).

Compared to changes in $\delta^{18}O$ values, the changes in the

δ^{44}Ca values are very small (Fig. 4b). The two California samples, five North Carolina samples, and the Peru phosphate samples have within error limits identical δ^{44}Ca. δ^{18}O and δ^{44}Ca values of the three Malta samples are moreover not correlated with each other. Thus, δ^{44}Ca values of phosphorites are not temperature dependent.

4. DISCUSSION

For the phosphorites, no ^{40}Ca excess due to ^{40}K decay was observable. Therefore, their δ^{44}Ca values, 0.5 to 1.1‰ different from present-day seawater, possibly reflect processes inducing mass fractionation (Fig. 3). This fractionation could be caused by diagenesis, temperature, or precipitation kinetics. In addition, the variation of δ^{44}Ca with time might be the result of δ^{44}Ca seawater fluctuations. These different parameters are discussed below.

4.1. δ^{44}Ca and Diagenesis

It has been shown that the Sr and Nd isotopic compositions of the North Carolina and the Malta apatites were not affected by diagenetic processes (Riggs et al., 1997; Stille, 1992; Stille et al., 1994; Riggs et al., 2000; Jacobs et al., 1996). Similarly, other authors have shown that these sedimentary phosphates are mineralogically and geochemically stable in unweathered sections and that these phosphate grains retain their original geochemical and isotopic signals, even with minor diagenetic alteration (Shemesh et al., 1988; McArthur et al., 1990; Kastner et al., 1990; Compton et al., 1993; Mallinson et al., 1994). The Sr model age data on paired phosphate peloïd and foraminifera samples from the Miocene North Carolina phosphate sediments are within 0.2 Ma identical and in perfect agreement with the available biostratigraphic ages (Riggs et al., 2000). This is also valid for the apatites from the Maltese platform (Jacobs et al., 1996). Similarly, the 0.5 Ma old phosphorite from the Peru continental margin has a ^{87}Sr/^{86}Sr isotopic composition of present-day seawater. A further indication of the pristine nature of these phosphorites are their primary seawater type rare-earth element patterns (Shields and Stille, 2001).

The Californian samples, however, may have known a period of diagenesis (Kastner et al., 1990); this is especially the case for sample Pho 5554 which has a very different value of δ^{18}O compared to all other samples. Nevertheless, the Ca isotopic composition of this sample is similar to other phosphates of the same age but from other regions (e.g., Malta FG 41). Thus, it is possible that Ca isotopic compositions remain rather stable in phosphorites during diagenesis due to their high Ca concentrations (30% of the weight). Similarly, Skulan and DePaolo (1999) suggested that since the Ca is the major component of bones, the Ca isotope composition would be more resistant to diagenetic processes than other elements such as Sr or C.

4.2. δ^{44}Ca and Temperature

The δ^{44}Ca values of the eight phosphates from the North Carolina, California, and Peru continental margin remain unchanged over a period of ~19 Ma, whereas the ^{87}Sr/^{86}Sr ratios of the same samples evolve from 0.70854 (at 19 Ma) to 0.70915 (at 0.5 Ma). Only the two older Malta samples have slightly higher δ^{44}Ca values at 22 Ma and 24.3 Ma, whereas the younger 17 Ma old phosphate plots in the range of the remaining apatites from North Carolina. The δ^{18}O values of the two older Malta samples point moreover to higher formation temperatures of 12.5 to 16°C, whereas the younger phosphates point to lower temperatures ranging between 8 and 11°C.

Therefore, it cannot be excluded that the comparatively higher δ^{44}Ca values of 22 Ma and 24 Ma old apatites from Malta Island reflect a slightly warmer paleo-environment than those of the younger phosphate samples from Malta, North Carolina, and California (excluding the δ^{18}O value of Pho 5554). No correlation, however, exists in general between δ^{18}O and δ^{44}Ca values. Thus, whereas the δ^{44}Ca values remain rather stable during the past 19 Ma, the δ^{18}O values increase with decreasing stratigraphic age (Fig. 4b) and, therefore, are conform with earlier observations on biogenic apatites (Shemesh et al., 1983; Blake et al., 1997) and foraminifers (Frakes et al., 1992) that point to a general cooling during the Miocene. The average temperature difference between the North Carolina and Malta environments is ~7°C. The average difference in δ^{44}Ca between the phosphates from the same localities is 0.30‰ for δ^{44}Ca. This makes a difference of only 0.05 δ^{44}Ca per °C, which is much smaller than the change in δ^{44}Ca value of 0.24 ± 0.02‰ per °C and 0.15‰ per °C observed by Nägler et al. (2000) in the foraminifers *Globigerinoides sacculifer* and De La Rocha and DePaolo (2000) in the intertidal foraminifera *Glabratella ornatissima*, respectively.

Moreover, samples from Malta (FG 41 and FG 17) that have a rather small difference in oxygen isotope composition corresponding to ~2°C, have a relatively large difference in the δ^{44}Ca values of ~0.3‰. However, samples FG 17 and FG 8, with δ^{18}O values corresponding to a larger temperature difference of ~3.4°C, have a smaller δ^{44}Ca difference of ~0.2‰ only. Therefore, higher temperatures of formation cannot be the important mechanism leading to the higher δ^{44}Ca values in the Malta samples. Consequently, the temperature does not appear to be the main parameter controlling the δ^{44}Ca values of these phosphates.

4.3. The δ^{44}Ca Variation: A Local or Global Phenomenon?

Nineteen marine carbonate sediments (carbonate ooze, chalk. . .) covering the last 80 Ma have recently been analysed for Ca isotopic compositions (De La Rocha and DePaolo, 2000). Their δ^{44}Ca values for the period between present-day and 25 Ma were deduced from their figure and recalculated against their seawater value to compare the carbonate data with the phosphate data of this study (Fig. 5).

A systematic and more or less constant shift between marine carbonates and phosphates is observed: the carbonate samples are slightly more enriched in ^{40}Ca compared to the apatites. Only the δ^{44}Ca minimum at ~18 Ma for carbonates is not observed for the phosphate samples. More data are necessary to confirm this observation. Since the δ^{44}Ca maximum at ~22 Ma is observable for both phosphates and carbonates, one may assume that it reflects a global seawater signal which is not limited to the Tethys seawater. For samples younger than 19 Ma, the δ^{44}Ca values remain rather constant and similar to present-day values for both carbonates and phosphates within
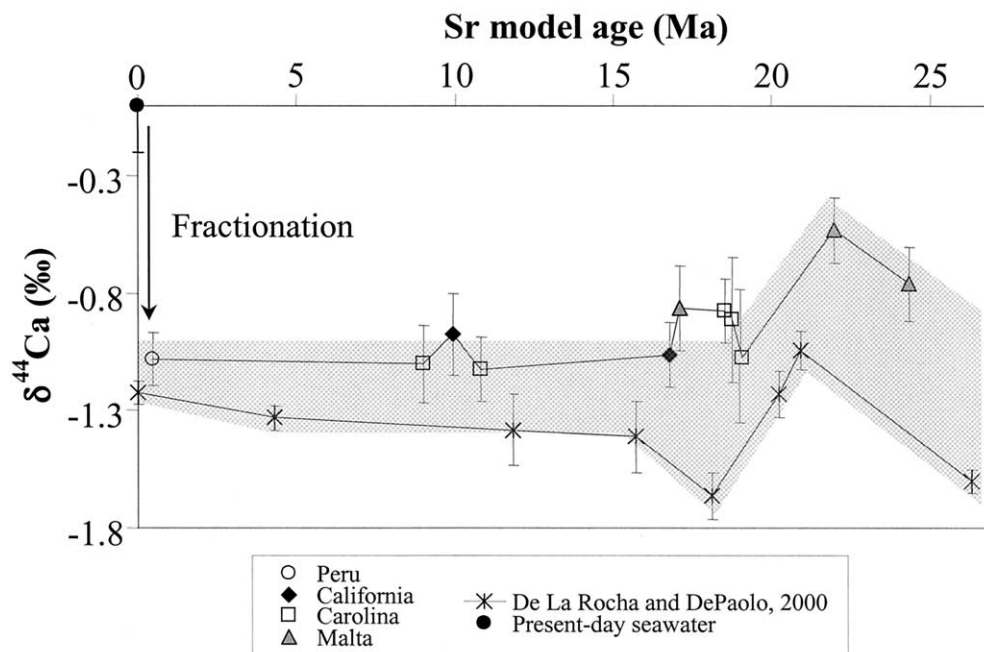
Fig. 5. Variation of δ^{44}Ca isotopic composition of apatite through geologic time (Sr model age in Ma). Comparison with the evolution of marine carbonates during the same period of time (after De La Rocha and DePaolo, 2000).

external reproducibility. The rather constant shift between δ^{44}Ca values of carbonates and phosphates might be related to a mineral-dependent kinetic mass fractionation during precipitation from seawater. If the precipitation conditions remain stable over a certain period of time, the shift between seawater and phosphate Ca isotopic composition remains also stable and the Ca isotopic composition of the phosphates only changes in response to variations in the seawater δ^{44}Ca. The fact that these marine apatites and carbonates collected at different places of the world have a rather similar isotopic variation during the past 24 Ma suggests that both phosphates and carbonates reflect the Ca isotopic variation in seawater rather than changes in the precipitation rate. This also reinforces the hypothesis of a homogeneous Ca isotopic composition of the paleoseawater at a given time during the Miocene. Of course, much more data are necessary to get more precise information about small-scale variability or stability of the Ca isotopic composition in seawater during the past 24 Ma.

4.4. The Oceanic Ca Budget

As discussed earlier, present-day seawater is in a steady state with regard to the Ca oceanic budget (Skulan et al., 1997; De La Rocha and DePaolo, 2000; Schmitt et al., submitted). The rather constant Ca isotope composition observed for both phosphates and carbonates younger than 19 Ma indicates that, similar to present-day seawater, steady-state conditions (i.e., fluxes of weathering and sedimentation remained similar) prevailed within the late Early Miocene oceans. The situation may have been different, however, during the Early Miocene (24 to 20 Ma) where carbonates and phosphates manifest a positive δ^{44}Ca excursion. During this period, major episodes of collisional tectonics took place in Asia and the western Pacific and

sea level appears to have been rising (Vail et al., 1977). Nevertheless, seafloor spreading was apparently not important and the volumes of ocean basins probably remained constant (Hays and Pitman, 1973) Thus, the Ca flux from hydrothermal activities probably did not change significantly at that time. In contrast, warming of both surface and bottom seawaters occurred during this period (Savin et al., 1975). All these conditions may have led to increased biologic carbonate precipitation. Because of the preferential incorporation of ^{40}Ca in biogenic marine calcium carbonates (Skulan et al., 1997), one would expect that the ocean becomes depleted in ^{40}Ca leading to higher ^{44}Ca/^{40}Ca ratios with time if the weathering flux remained the same. This would produce a Ca isotope excursion with increasing δ^{44}Ca values, as indicated by the two older Malta samples. This episode of marine transgression and ocean warming, however, constitutes a special case in the general cooling trend throughout the Miocene (Frakes, 1979) and the onset of polar glaciation in the Early Tertiary (Frakes, 1979; Miller et al., 1987). A consequence of this is a decreasing sea level (Miller et al., 1987) and increasing exposure of larger continental platforms to erosion with intensified Ca flux to the oceans. This increased weathering flux compensated the effects of biologic fractionation and ^{40}Ca depletion and, therefore, decreased the ^{44}Ca/^{40}Ca back to lower values (Fig. 5).

5. SUMMARY AND CONCLUSION

The Ca isotope variation of 11 Miocene and Pleistocene, authigenic and marine phosphates is rather small compared to the corresponding δ^{18}O values. The temperature does not appear to be the main parameter controlling the δ^{44}Ca values in phosphates. Similarly, Ca appears to be rather stable in phosphorites during diagenesis. Phosphorites and carbonaceous sed-

iments show a similar Ca isotopic variation during the Miocene. However, a systematic and more or less constant shift between marine carbonates and phosphates exists: the carbonate samples are slightly more enriched in ^{40}Ca compared to the apatites. At 22 Ma both phosphates and carbonates collected at different places of the world show the same positive δ^{44}Ca excursion. This suggests that the δ^{44}Ca values reflect a global seawater signal, and it is likely that the δ^{44}Ca values of the phosphates reflect the variation in the δ^{44}Ca values of paleo-seawater but, in contrast to Sr, not the isotopic composition of seawater itself. Furthermore, Ca and Sr isotopic compositions are decoupled, with Sr isotopic compositions changing to more radiogenic values while Ca isotopic compositions remain rather stable. The rather constant shift between δ^{44}Ca of carbonates and phosphates might be related to a mineral-dependent kinetic mass fractionation during precipitation from seawater. All samples have δ^{44}Ca values below present-day seawater values, suggesting that phosphate formation discriminates against heavy Ca isotopes. The rather stable calcium isotopic composition of Mid-Miocene seawater allows the application of the earlier proposed foraminifer Ca thermometer for this period of time.

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