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ScienceDirect
Earth and Planetary Science Letters 253 (2007) 96–111
EPSL
www.elsevier.com/locate/epsl

Evolution of the oceanic calcium cycle during the late Mesozoic: Evidence from $\delta^{44/40}$Ca of marine skeletal carbonates[☆]

Juraj Farkaš [a,*], Dieter Buhl [b,1], John Blenkinsop [c,2], Ján Veizer [a,3]

[a] University of Ottawa and Ottawa-Carleton Geoscience Centre, Ottawa, Canada K1N 6N5,ON
[b] Institut für Geologie, Mineralogie und Geophysik, Ruhr Universität, Bochum 44801, Germany
[c] Carleton University and Ottawa-Carleton Geoscience Centre, Ottawa, Canada K1S 5B6,ON

Received 23 January 2006; received in revised form 16 September 2006; accepted 6 October 2006
Available online 22 November 2006
Editor: H. Elderfield

Abstract

The Ca isotope compositions of 37 late Mesozoic skeletal carbonates, belemnites and brachiopods, from the Tethyan realm were analyzed by thermal (TIMS) and plasma (MC-ICP-MS) ionization mass spectrometry. A poor correlation between $\delta^{44/40}$Ca and δ^{18}O values of belemnites suggests only a weak temperature dependency for the Ca isotope composition of belemnites, likely less than 0.02‰/°C. The $\delta^{44/40}$Ca record of belemnites was therefore used to reconstruct the Ca isotope composition of paleo-seawater ($\delta^{44/40}Ca_{SW}$), based on an experimentally determined fractionation factor between seawater Ca and belemnite calcite (α_{CC-SW}) of ~0.9986. The inferred $\delta^{44/40}Ca_{SW}$ record, with an average stratigraphic resolution of 1 Ma, shows systematic temporal variation of ~0.5‰ with the Middle/Late Jurassic (~154 Ma) minimum of ~1.4‰ and a subsequent general increase to the Early Cretaceous (~124 Ma) maximum of ~1.9‰. The global nature of the $\delta^{44/40}Ca_{SW}$ record is supported by identical Ca isotope compositions of coeval (Kimmeridgian) belemnites collected from two distinct paleogeographic regions, the southern (New Zealand) and northern (Germany) margin of the Tethys Ocean. The observed late Mesozoic $\delta^{44/40}Ca_{SW}$ record was simulated using a simple Ca isotope mass balance model, and the results indicate that the variation in $\delta^{44/40}Ca_{SW}$ record can be explained by changes in oceanic input fluxes of Ca that were independent of the carbonate ion fluxes, such as the hydrothermal Ca flux or the release of Ca to the oceans via dolomitization of marine carbonates.

Keywords: calcium isotopes; belemnites; brachiopods; late Mesozoic, marine calcium cycle; seawater chemistry

[☆] Presented at the 2nd Earth System Processes (ESP2) meeting, Calgary, Canada, August 8–11, 2005; and at the 6th International Symposium on Applied Isotope Geochemistry (AIG-6), Prague, Czech Republic, September 11–16, 2005.

* Corresponding author. Tel.: +1 613 562 5800; fax: +1 613 562 5192.
E-mail addresses: jfark064@uottawa.ca (J. Farkaš), dieter.buhl@ruhr-uni-bochum.de (D. Buhl), john_blenkinsop@carleton.ca (J. Blenkinsop), jveizer@uottawa.ca (J. Veizer).
[1] Tel.: +49 234 32 23250; fax: +49 234 32 25458.
[2] Tel.: +1 613 520 2600; fax: +1 613 520 5613.
[3] Tel.: +1 613 562 5800; fax: +1 613 562 5192.

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doi:10.1016/j.epsl.2006.10.015

1. Introduction

Belemnite rostra and brachiopod shells, primarily composed of low-Mg calcite, are frequently used as carrier phases of proxies that record the physical and chemical attributes of the Mesozoic and Paleozoic oceans, such as their chemistry or isotope composition. Calcium, together with carbon and oxygen is the major component of $CaCO_3$ and has six naturally occurring isotopes ^{40}Ca, ^{42}Ca, ^{43}Ca, ^{44}Ca, ^{46}Ca and ^{48}Ca. Due to its numerous isotopes, and being the fifth most abundant element in the Earth's crust and a major constituent of biological and geological systems, it promises to be a geological tracer with a considerable potential. In terrestrial and marine environments Ca isotopes are fractionated by biological and inorganic processes that discriminate against heavy Ca isotopes [1,2]. Biological and inorganic calcification also controls the Ca removal from the ocean [2] that is balanced mostly by riverine and hydrothermal Ca input [3]. Due to the long residence time of Ca in seawater ($\tau_{Ca} \approx 1$ to 2 Ma) [4,5] relative to the short mixing time of global ocean (~1000 yr), the Ca isotope composition of modern seawater is globally homogeneous [2,6], and this likely was the case also in the geological past.

Modern marine carbonates are isotopically lighter and variably enriched in ^{40}Ca relative to present-day seawater [1,2], depending on their mineralogy [7] and precipitation kinetics such as temperature or calcification rates [8–10]. Nevertheless, the Ca isotope composition, $\delta^{44/40}Ca$, of fossil marine carbonates can potentially record secular changes in $\delta^{44/40}Ca$ of paleo-seawater, providing that the fractionation factor between seawater Ca and a carbonate phase ($\alpha_{cc/sw}$) is known. So far, only a few reconnaissance studies aimed to reconstruct the Ca isotope evolution of seawater ($\delta^{44/40}Ca_{SW}$) based on the $\delta^{44/40}Ca$ of marine carbonates or phosphates. Fantle and DePaolo [5] and De La Rocha and DePaolo [11] analyzed the Neogene (last 20 Ma) and Cenozoic (last 80 Ma) nannofossil ooze, respectively; Heuser et al. [12] the Neogene (last 24 Ma) planktonic foraminifera, Steuber and Buhl [13] the mid-Cretaceous (~80 to 125 Ma) and the Late Carboniferous (~310 Ma) marine carbonates, Böhm et al. [14] the Devonian (~365 to 415 Ma) brachiopods, and Kasemann et al. [15] the Neoproterozoic (~600 to 640 Ma) whole-rock carbonates. Two studies, Schmitt et al. [16] and Soudry et al. [17] investigated the Ca isotope composition of authigenic marine phosphates from the Miocene (~0.5 to 24 Ma) and the Cretaceous–Eocene (~46 to 114 Ma)

Table 1
The $\delta^{44/40}Ca_{NIST}$ (TIMS) values of the Middle Jurassic to Early Cretaceous belemnites

Sample	Location	Fossil name	Period[a]	Stage	Age (Ma)	$\delta^{44/40}Ca$[b] (NIST)
J138	Russia	*Pachyteuthis russiensis*	MJ	Callovian	158.4	0.35
J132	Russia	*Cylindroteuthis purosiana*	MJ	Callovian	157.7	0.28
J125	Russia	*Cylindroteuthis purosiana*	MJ	Callovian	157.4	0.12
J114	Russia	*Cylindroteuthis beaumonti*	LJ	Oxfordian	156.7	0.09
J94	Russia	*Pachyteuthis russiensis*	LJ	Oxfordian	155.7	0.11
J77	New Zealand	*Belemnopsis keari*	LJ	Kimmeridgian	153.6	0.17
J67	New Zealand	*Hibolites marwicki*	LJ	Kimmeridgian	151.1	0.26
J53	Russia	*Cylindroteuthis volgensis*	LJ	Tithonian	149.4	0.28
J16	Russia	*Cylindroteuthis volgensis*	LJ	Tithonian	147.8	0.31
K112	Germany	Species unidentified	EC	Valanginian	140.0	0.33
K111	Germany	Species unidentified	EC	Valanginian	138.6	0.29
K110	Germany	Species unidentified	EC	Valanginian	138.1	0.35
K98	Germany	Species unidentified	EC	Valanginian	136.2	0.34
K92	Germany	Species unidentified	EC	Hauterivian	135.2	0.46
K75	Germany	*Hibolites jaculoides*	EC	Hauterivian	133.1	0.47
K67	Great Britain	*Praeoxyteuthis pugio*	EC	Barremian	130.5	0.49
K45	Great Britain	*Aulacotheuthis* species	EC	Barremian	128.2	0.46
K41	Germany	*Aulacotheuthis descendens*	EC	Barremian	127.8	0.37
K35	Great Britain	*Oxyteuthis brunsvicensis*	EC	Barremian	127.4	0.42
K20	Germany	Species unidentified	EC	Barremian	126.6	0.37
K15	Great Britain	*Oxyteuthis pseudogermanica*	EC	Barremian	126.3	0.61
K11	Great Britain	*Oxyteuthis pseudogermanica*	EC	Barremian	126.2	0.48
K2	Germany	Species unidentified	EC	Aptian	124.5	0.52

[a]The following abbreviations are used: MJ = Middle Jurassic; LJ = Late Jurassic; EC = Early Cretaceous.
[b]The mean long-term external reproducibility (2σ) of the $\delta^{44/40}Ca_{NIST}$ is ±0.15‰.