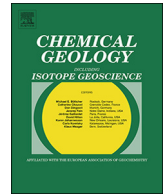




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The effect of H₂O₂ treatment on stable isotope analysis ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47}) of various carbonate minerals

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ABSTRACT

In carbonate isotopic measurements, H₂O₂ treatment is one of the most often used methods to remove organic matter contaminants from carbonate minerals for accurate analysis, but the interaction between H₂O₂ solution and carbonate minerals may also lead to analytical bias. In this study, we quantitatively tested the effect of H₂O₂ treatment for 7 types of carbonate minerals, and the influences on Δ_{47} values of calcium carbonate are systematically discussed for the first time. Most samples presented Δ_{47} offsets within the 2-SD of our analytical precision, except the methane derived authigenic carbonate (MDAC). The shift of Δ_{47} values in MDACs is attributed to the mixing effect of two types of carbonate minerals: original one and isotopically altered one, and the magnitude is determined by the differences of both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values between two endmembers. Regarding biogenic carbonate tested here, the analytical bias of H₂O₂ treatment is relative small in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, and therefore the shift of Δ_{47} values is statistically neglectable.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for most samples tested in this study became positive (up to +1.7‰) after H₂O₂ treatment. Apart from previously well discussed mechanisms, such as removal of organic contamination, isotopic fractionation during the partial dissolution and dissolution of isotopic distinct carbonate compositions in the heterogeneous minerals, we experimentally demonstrated carbon and oxygen isotopic exchanges between carbonate minerals and H₂O₂ solution for the first time. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of carbonate were influenced by isotopic exchanges with atmospheric CO₂ in the CO₂-HCO₃⁻-CO₃²⁻ system and H₂O in H₂O₂ solution, respectively. Rich transition metals in the authigenic carbonate minerals (e.g. MDAC, travertine), which catalyze H₂O₂ decomposition, can enlarge this effect by altering H₂O isotopic compositions. Though the small shift of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in biogenic carbonate observed here (up to 0.6‰) would not change scientific interpretations and conclusions in most of previous studies, cautions should be taken in the future.

Based upon our new experimental results, we suggest using a buffered H₂O₂ solution (pH ≈ 8) isolated from atmospheric CO₂ to remove potential organic contaminations in biogenic carbonate. For authigenic carbonate, H₂O₂ treatment is not recommended. If necessary, decreasing the H₂O₂ concentration, shortening the reaction time, leaving the solution in a CO₂-free environment, and adjusting the solution to a basic condition will improve the accuracy in isotopic analysis of these minerals.

1. Introduction

Isotopic compositions of biogenic and inorganic carbonates are regarded as useful paleo-environmental proxies. For instance, carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotopes in coral, foraminifera, bivalve,

gastropod and other fossils are widely applied in reconstruction of past marine and terrestrial environment (Woodruff et al., 1981; Goodfriend, 1992; Dunbar et al., 1994; Weidman and Jones, 1994; Bemis et al., 1998). Another novel and powerful tool, carbonate clumped isotope thermometry (Δ_{47}), which is defined as the anomaly of doubly

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substituted isotopologues ($^{13}\text{C}^{18}\text{O}^{16}\text{O}_2^{2-}$) in the carbonate minerals relative to the random distribution of each isotope, has also been fast developed in paleoclimate studies (Ghosh et al., 2006; Eiler, 2011). However, trace amounts of organic matter, including those involved into the skeleton of corals, covered on the surface of mollusk and ostracod shells (Walton, 1952; Boiseau and Juillet-Leclerc, 1997; Muscatine et al., 2005; Keatings et al., 2006), and mixed inside of the authigenic carbonate (Suess, 1970, 1973; Charef and Sheppard, 1984; Lebeau et al., 2014; Miyajima et al., 2018), may liberate isotopically distinct CO_2 gas (and/or other volatile organic carbon producing mass 44–46 fragments in the mass spectrometry) during carbonate H_3PO_4 digestion, potentially producing imprecise isotopic values of target carbonate minerals and impeding our understanding of past environments (Epstein et al., 1951, 1953; Charef and Sheppard, 1984; Lebeau et al., 2014).

Among various pre-treatment approaches (e.g. vacuum roasting, sodium hypochlorite, plasma ashing), hydrogen peroxide (H_2O_2) bleaching is a frequently used method for traditional $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analysis, and recently extended to clumped isotope analysis (Table S1). Although many works have discussed the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ bias involved in H_2O_2 treatment, their results and conclusions are inconsistent in magnitude and directions of isotope alterations (Table 1) (McConnaughey, 1989; Boiseau and Juillet-Leclerc, 1997; Grottoli et al., 2005; Keatings et al., 2006; Wierzbowski, 2007; Serrano et al., 2008; Feldmeijer et al., 2013; Schone et al., 2017; Roberts et al., 2018; Guo et al., 2019; Zhang et al., 2019). Some studies reported neglectable or minor effect ($< 0.2\text{‰}$) (Grottoli et al., 2005; Wierzbowski, 2007; Serrano et al., 2008; Feldmeijer et al., 2013; Schone et al., 2017; Roberts et al., 2018) while other observed larger changes in $\delta^{13}\text{C}$ and/or $\delta^{18}\text{O}$ values ($> 0.2\text{‰}$) with different directions (Boiseau and Juillet-Leclerc, 1997; Keatings et al., 2006; Guo et al., 2019; Zhang et al., 2019). The validity of this H_2O_2 pretreatment method remains unclear due to a lack of complete understanding of physical and chemical mechanisms producing the observed isotope bias, which may attribute to the removal of organic matter, partial dissolution of carbonate, precipitation of $\text{Ca}(\text{OH})_2$, isotopic exchange with the reagent, or the combination of them (Boiseau and Juillet-Leclerc, 1997; Grottoli et al., 2005; Keatings et al., 2006; Schone et al., 2017). In addition, the most recent works preliminarily tested the potential influences of H_2O_2 treatment on Δ_{47} analysis of calcium carbonate (Peral et al., 2018; Guo et al., 2019; Zhang et al., 2019). Regardless the treatment parameters (e.g. H_2O_2 concentration, time), the changes of Δ_{47} values in these preliminary studies seemed insignificant. However, given that these

studies focused on limited carbonate materials with a small dataset, further investigations on various carbonate minerals remain urgently needed for making a clear conclusion.

In this study, we tested the effect of H_2O_2 treatment on isotopic analysis ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47}) of various calcium carbonate minerals, both for biogenic and authigenic ones, and investigated their underlying mechanisms. Based on our observations and discussions, cautions and suggestions for carbonate treatments in the future are listed.

2. Materials and methods

2.1. Materials

Seven types of carbonate minerals were tested, including Carrara Marble (NBS-19), synthetic calcite, coral aragonite, gastropod aragonite (land snail), bivalve calcite, methane derived authigenic carbonate (MDAC, both aragonite and calcite), and travertine aragonite. Synthetic calcite is a commercial purchased chemical (Wako Pure Chemical Industries Ltd., Osaka, Japan). Coral samples were collected from the Holocene Numa Formation of the Boso Peninsula, central Japan (Asami and Yamaguchi, 1997). Living land snail individual (*Acusta despecta sieboldiana*) was collected in Suzukakedai, Yokohama, Japan (Zhang et al., 2014, 2018). Bivalve shells (*Calyptogena* sp.) and MDACs were recovered from the seafloor and sediment cores in Offshore-Joetsu Area in the Japan Sea and Hidaka Trough using either remotely operated vehicle (ROV) recovery or piston corers (Zhang et al., 2019). The travertine sample was collected from Pancuran Pitu, Central Java, Indonesia (Okumura et al., 2012).

2.2. Experimental

For increasing the contact area and exposing the potential organic matter sufficiently with H_2O_2 solution, carbonate samples (except for the international standard NBS-19, and land snail shell pieces) were crushed into fine powder using a mortar and pestle, well mixed, and then passed through a $40\ \mu\text{m}$ sieve (Figure S1). Due to the limited amount of fresh land snail shell used in this study ($\sim 50\ \text{mg}$), it was only crushed into coarse pieces to avoid any loss during sieving procedure.

During each measurement, 7–10 mg powder was soaked into 2 mL 10% H_2O_2 solution at room temperature ($25\ ^\circ\text{C}$) for either 18 or 48 h (Table 2). In addition, to understand reaction kinetics, a MDAC sample was treated by H_2O_2 in different concentrations (3% vs. 10%) and

Table 1
Summary of published reports on H_2O_2 treatment.

Reference	Material	Mineral	T ($^\circ\text{C}$)	H_2O_2 (%)	Time	$\Delta(\delta^{13}\text{C})$ (‰)	$\Delta(\delta^{18}\text{O})$ (‰)	$\Delta(\Delta_{47})$ (‰)
McConnaughey, 1989	Corals	aragonite	unknown	unknown	unknown	+0.02	+0.08	–
Boiseau and Juillet-Leclerc, 1997	Corals	aragonite	room T	30%	12 hr	–0.4 to +0.6	–0.4 to +0.3	–
Grottoli et al., 2005	Corals	aragonite	unknown	30%	24 hr	–0.04	–0.08	–
Keatings et al., 2006	Ostracod	calcite	80 $^\circ\text{C}$	5%	15 min	–0.5	no change	–
Wierzbowski, 2007	Synthetic aragonite	aragonite	room T	30%	12 h	–0.02	–0.14	–
	Synthetic calcite	calcite	room T	30%	12 h	–0.09 to –0.01	–0.40 to –0.02	–
	Carrara marble	calcite	room T	30%	12 h	–0.01 to –0.04	–0.46 to –0.10	–
	Bivalve	aragonite	room T	30%	12 h	+0.03 to +0.05	+0.11 to +0.14	–
	Bivalve	calcite	room T	30%	12 h	+0.06 to +0.08	0.00 to +0.01	–
	Hibolithes (fossil)	calcite	room T	30%	12 h	+0.02 to +0.06	+0.10 to +0.15	–
	Pachyteuthis (fossil)	calcite	room T	30%	12 h	+0.03	+0.17	–
Serrano et al., 2008	Foraminifera	calcite	20 $^\circ\text{C}$	30%	10 min	–0.08	–0.18	–
Feldmeijer et al., 2013	Foraminifera	calcite	unknown	10%	1 h	no change (–0.11)	no change (–0.15)	–
Schone et al., 2017	Bivalve	aragonite	room T	30%	several min	–0.05	+0.10	–
	Carrara marble	calcite	room T	30%	several min	–0.06	–0.02	–
Roberts et al., 2018	Ostracod	calcite	room T	15%	15 min	–0.003	–0.005	–
				30%	30 min	+0.02	–0.02	–
Guo et al., 2019	Land snail	aragonite	room T	10%	4 h	+0.01	+0.17	–0.005
				30%	4 h	–0.05	+0.31	+0.005
Zhang et al., 2019	MDAC	calcite & aragonite	room T	1%	4 h	+0.19	+0.08	–0.003

Table 2
Comparison of isotope results on H₂O₂ (10%) treated and untreated samples.

Sample	Mineral	Time	n	$\delta^{13}\text{C}$ (PDB, ‰)	1 s.e.	$\delta^{18}\text{O}$ (PDB, ‰)	1 s.e.	Δ_{47} , CDSES90 (‰)	1 s.e.	$\Delta(\delta^{13}\text{C})$ (‰)*	$\Delta(\delta^{18}\text{O})$ (‰)*	$\Delta(\Delta_{47})$ (‰)*
Marble	Calcite	0 h	9	1.92	0.01	-2.23	0.02	0.301	0.008			
		48 h	4	1.91	0.09	-2.05	0.05	0.297	0.007	-0.01 ± 0.09	0.19 ± 0.05	-0.004 ± 0.011
Synthetic	Calcite	0 h	3	3.84	0.01	-6.88	0.05	0.297	0.002			
		18 h	3	3.81	0.06	-6.58	0.03	0.326	0.009	-0.03 ± 0.06	0.30 ± 0.06	0.029 ± 0.009
		48 h	3	3.68	0.07	-6.41	0.06	0.322	0.004	-0.16 ± 0.07	0.47 ± 0.08	0.025 ± 0.004
Coral	Aragonite	0 h	2	-1.86	0.18	-3.96	0.07	0.654	0.001			
		18 h	2	-1.31	0.06	-3.33	0.10	0.651	0.012	0.55 ± 0.19	0.63 ± 0.12	-0.003 ± 0.012
		48 h	2	-1.28	0.06	-3.37	0.08	0.673	0.004	0.57 ± 0.19	0.59 ± 0.11	0.019 ± 0.004
Gastropoda	Aragonite	0 h	3	-13.43	0.03	-5.09	0.02	0.611	0.008			
		18 h	2	-12.98	0.12	-4.60	0.14	0.611	0.017	0.45 ± 0.12	0.50 ± 0.14	-0.001 ± 0.019
		48 h	2	-12.86	0.04	-4.63	0.01	0.617	0.001	0.57 ± 0.05	0.46 ± 0.02	0.006 ± 0.008
Bivalvia	Aragonite	0 h	2	1.09	0.02	3.27	0.04	0.659	0.001			
		18 h	2	1.22	0.07	3.51	0.06	0.665	0.001	0.13 ± 0.07	0.23 ± 0.07	0.007 ± 0.001
		48 h	2	1.27	0.12	3.61	0.01	0.663	0.014	0.18 ± 0.12	0.33 ± 0.04	0.005 ± 0.014
Travertine	Aragonite	0 h	2	3.87	0.01	-12.80	0.02	0.512	0.013			
		18 h	2	4.27	0.02	-11.81	0.06	0.512	0.005	0.40 ± 0.02	1.00 ± 0.06	0.000 ± 0.014
		48 h	2	4.39	0.02	-11.57	0.05	0.537	0.007	0.52 ± 0.02	1.24 ± 0.05	0.025 ± 0.015
MDAC-A	Aragonite	0 h	3	-49.87	0.01	3.39	0.07	0.682	0.010			
		18 h	2	-48.79	0.05	3.81	0.03	0.703	0.002	1.08 ± 0.05	0.42 ± 0.08	0.020 ± 0.010
		48 h	3	-48.83	0.26	3.69	0.08	0.717	0.004	1.04 ± 0.26	0.30 ± 0.11	0.035 ± 0.011
MDAC-C1	Calcite	0 h	4	-45.83	0.08	3.59	0.06	0.677	0.016			
		18 h	1	-44.13	-	4.97	-	0.715	-	1.70 ± 0.08	1.38 ± 0.06	0.038 ± 0.016
		48 h	1	-44.45	-	5.21	-	0.741	-	1.38 ± 0.08	1.61 ± 0.06	0.063 ± 0.016
MDAC-C2	Calcite	0 h	2	-52.93	0.02	5.27	0.01	0.683	0.006			
		48 h	2	-51.50	0.10	5.77	0.07	0.703	0.008	1.43 ± 0.10	0.50 ± 0.07	0.020 ± 0.010
MDAC-C3	Calcite	0 h	4	-28.87	0.08	5.28	0.12	0.662	0.003			
		48 h	2	-27.60	0.08	6.40	0.02	0.695	0.015	1.27 ± 0.11	1.12 ± 0.12	0.033 ± 0.015

* Errors of each variable in arithmetic calculations were propagated into the final net error.

reaction times (4, 18, 48, 72 and 96 h). After being dried in a freeze-drying machine, samples treated by H₂O₂ were then quantitatively reacted with 105% H₃PO₄ at 90 °C in a McCrete-type reaction vessel connected to a vacuum line for 20–30 min (until no bubbles came out). The generated CO₂ gas was collected simultaneously using a liquid nitrogen trap during the digestion to prevent any isotopic exchange between CO₂ and H₂O. Collected CO₂ was further separated from H₂O using the multiple-stage ethanol-dry ice distillation in the same vacuum line, after which CO₂ was injected into a gas chromatography equipped with a Supelco Q-Plot column (30 m long, 0.53 mm ID) for purification. Helium was used as the carrier gas (3 mL/min) and the column was held at -20 °C.

Purified CO₂ sample was injected into a dual-inlet isotope ratio mass spectrometer (MAT253; Thermo Fisher Scientific Inc., Bremen, Germany) at Tokyo Institute of Technology, which was equipped with 6 Faraday cups with resistor of 3×10^8 , 3×10^{10} , 3×10^{11} , 1×10^{12} , 1×10^{12} and 1×10^{12} Ω for m/z 44, 45, 46, 47, 48, 49, respectively. Each sample was measured for 80 sample-reference cycles (8 acquisitions) with the total integration time of 1280s at m/z 44 intensity of 14 V. Pressure base line (PBL) correction for obtaining the accurate peak intensity of CO₂ gases was following the protocol suggested by He et al. (2012). Δ_{48} offset was monitored to avoid any contamination of hydrocarbons. It is noted that MDAC samples without being purified via a silver wool trap presented extremely high Δ_{48} offset signals due to contamination of sulfur-bearing compounds (Zhang et al., 2019). These contaminants led to false positive Δ_{48} signal (but accurate Δ_{47} values) in MDAC measurements. Due to memory effects, following measurements may occasionally display false positive Δ_{48} signal, but the measured Δ_{47} values are accurate, which was verified in pure carbonate samples that do not contain any organic carbonate (such as NBS-19 and synthetic calcite). The detailed discussions of this issue were reported in the supporting document of Zhang et al. (2019). In this study, we carefully monitored the Δ_{48} signals and memory effects from MDAC to eliminate

any potential influence of hydrocarbons on biogenic carbonates.

Raw δ_{45} , δ_{46} , δ_{47} , δ_{48} , δ_{49} values for each measurement obtained by the IRMS were input into an online application provided by Daeron et al. (2016) for obtaining the raw $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, Δ_{47} , Δ_{48} and Δ_{49} values which were calculated in Brand et al. (2010) ¹⁷O parameters. Raw $\delta^{18}\text{O}$ values were then calculated using the acid fractionation factors: 1.00814 for calcite (Kim et al., 2015) and 1.00854 for aragonite (Kim et al., 2007), respectively. Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were calibrated by reference to NBS-19. Raw Δ_{47} values were projected into the absolute reference frame (carbon dioxide equilibrated scale, CDSES) using equilibrated CO₂ gases (25 °C and 50 °C) and heated gases (1000 °C), following Dennis et al. (2011). Either carbonate standard, equilibrated or heated CO₂ gas was analyzed routinely to monitor any shift of the calibration frame. NBS-19 was used as a laboratory standard material, and long-term (2014–2018) measurements yielded a mean Δ_{47} value of $0.391 \pm 0.016\text{‰}$ (1 σ sd, $n = 27$) (Zhang et al., 2019), indistinguishable to the accepted value ($0.392\text{‰} \pm 0.017\text{‰}$, 1 σ sd) (Dennis et al., 2011). All the clumped isotope data presented in this study were projected into the 90 °C acid digestion reference frame (Table 2).

The mineralogy of each sample, before and after H₂O₂ treatment, was identified using the X-Ray Diffractometer (XRD, Ultima IV; Rigaku Corporation). The images of sample surface were scanned by the Scanning Electron Microscope (SEM, Hitachi S-3400 N; Hitachi Ltd.).

3. Results

XRD patterns and SEM images are presented in Figs. 1 and 2, respectively. All of the studied minerals and materials, such as calcite and aragonite, presented exactly same peaks in scanned patterns before and after treatment, suggesting new mineral phase after H₂O₂ treatment was not detected by XRD. SEM images show insignificant surface changes of marble, synthetic calcite and bivalvia samples before and after H₂O₂ treatment. However, surfaces of H₂O₂-treated land snail

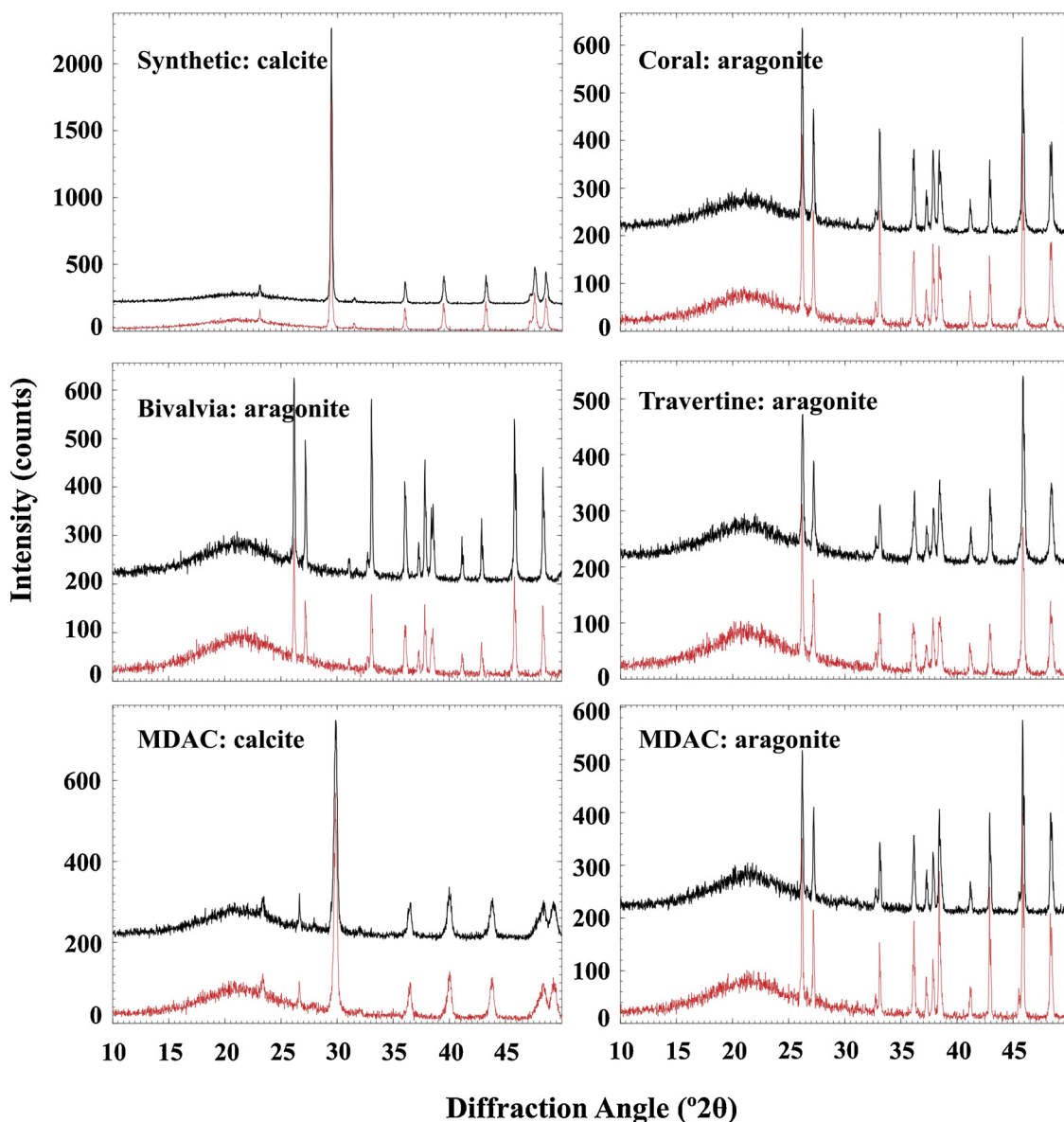


Fig. 1. XRD patterns of various carbonate materials used in this study. Untreated samples are presented in upper (black) curves while lower (red) curves represent the same samples after 48 h 10% H_2O_2 treatments.

shell, coral, travertine and MDAC samples were notably changed.

The changes of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47} values for different types of carbonate after H_2O_2 treatment are listed in Table 2 and illustrated in Fig. 3. The marble sample (NBS-19) presented insignificant changes in $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47} values after 10% H_2O_2 treatments. Synthetic calcite exhibited indistinguishable $\delta^{13}\text{C}$ and Δ_{47} (less than 2-SD measurement uncertainty) values, but enriched $\delta^{18}\text{O}$ values (large than 0.2‰).

Biogenic aragonites, e.g. coral, gastropod and bivalvia, show remarkably enriched $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values after treatment, varying from 0.13‰ to 0.57‰, and from 0.23‰ to 0.63‰, respectively. However, all the samples presented identical Δ_{47} values, with and without H_2O_2 treatment.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of authigenic carbonates (travertine and MDACs) changed dramatically after H_2O_2 treatment and their changes were as large as +1.70‰ and +1.61‰, respectively. In contrast to other types of carbonate minerals such as marble, synthetic calcite and biogenic carbonate, most of authigenic carbonate samples presented heavier Δ_{47} values after H_2O_2 treatment. Some of them exceeded the 2-SD uncertainty of our clumped isotope measurements ($\pm 0.032\text{‰}$).

4. The effect of H_2O_2 treatment: mechanisms and implications

4.1. Carbon isotope

H_2O_2 is a weak acid with a pKa of 11.7 at 25 °C (i.e. pH = 5.6 in 10% H_2O_2 solution). The most widely accepted mechanism of changes in $\delta^{13}\text{C}$ values is the isotopic fractionation due to the partial dissolution of carbonate in acidic H_2O_2 solution (Boiseau and Juillet-Leclerc, 1997; Grottoli et al., 2005; Wierzbowski, 2007; Serrano et al., 2008; Lebeau et al., 2014), which has been confirmed by the scanning electron microscope (SEM) (Boiseau and Juillet-Leclerc, 1997; Grauel et al., 2013; Falster et al., 2018). We also observed similar surface changes in this study (Fig. 2). If it was the main process causing the alteration of $\delta^{13}\text{C}$ values, the offsets should have become larger along with longer reaction time. In contrast, our observed $\delta^{13}\text{C}$ values for the same sample treated for 18 and 48 h present indistinguishable variations, suggesting $\delta^{13}\text{C}$ values approach to the steady state after 18 h treatment. Given that the magnitude of $\Delta(\delta^{13}\text{C})$ values in this study is larger than previous studies ($< 0.2\text{‰}$, Table 1), partial dissolution suggested by previous studies cannot fully explain large positive changes in our biogenic

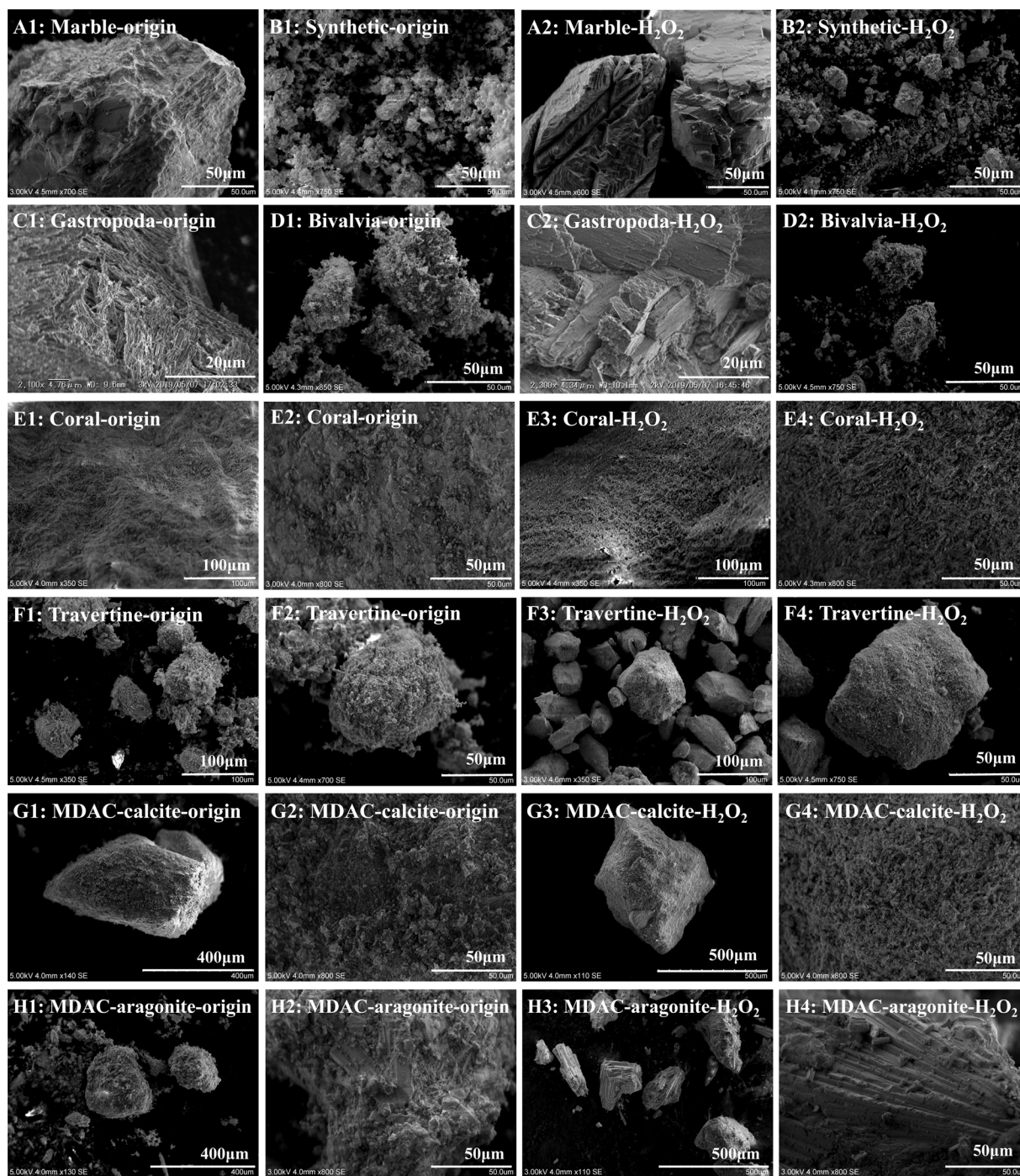


Fig. 2. Scanning electron micrographs of various minerals used in this study. Samples before and after 10% H_2O_2 treatment (labeled by 'origin' and ' H_2O_2 ', respectively) are compared. Marble, synthetic calcite and bivalvia samples show insignificant surface changes after treatment, while the surfaces of H_2O_2 -treated gastropoda (land snail) shell, coral, travertine and MDAC samples were notably changed.

and authigenic carbonate samples (Fig. 3a). An alternative explanation suggested by the literature (Boiseau and Juillet-Leclerc, 1997; Schone et al., 2017) is the dissolution of isotopic distinct carbonate composition.

We propose that another plausible explanation for positive $\Delta(\delta^{13}\text{C})$ values in biogenic carbonate is the successful removal of organic matters. The biogenic carbonate is usually mixed by the ^{13}C depleted organic matter inside the skeleton or remaining body tissue. For instance, the mollusk shells such as land snail are covered by organic matrix consisted by chitin, proteins and proteoglycans (Agoha and Mazi, 2009; Fernandez et al., 2016). These organic compounds may yield CO_2 gases

with lighter $\delta^{13}\text{C}$ values during the reaction with phosphoric acid and lead to analytical artifacts (Boiseau and Juillet-Leclerc, 1997; Grottoli et al., 2005). The organic layer can be successfully removed by the H_2O_2 treatment, as shown in SEM images (Fig. 2). Therefore, by removing these contaminations using H_2O_2 , the measured $\delta^{13}\text{C}$ values of biogenic materials, such as gastropods shell and coral skeleton, should become positive. For instance, organic carbon in coral skeletons can contribute as much as 0.7% to total carbon (Boiseau and Juillet-Leclerc, 1997). For symbiotic and nonsymbiotic corals, mean $\delta^{13}\text{C}$ values of organic carbon were determined to be -26.1‰ and -24.3‰ , respectively, and the most negative $\delta^{13}\text{C}$ value was -38.5‰ (Muscatine et al.,

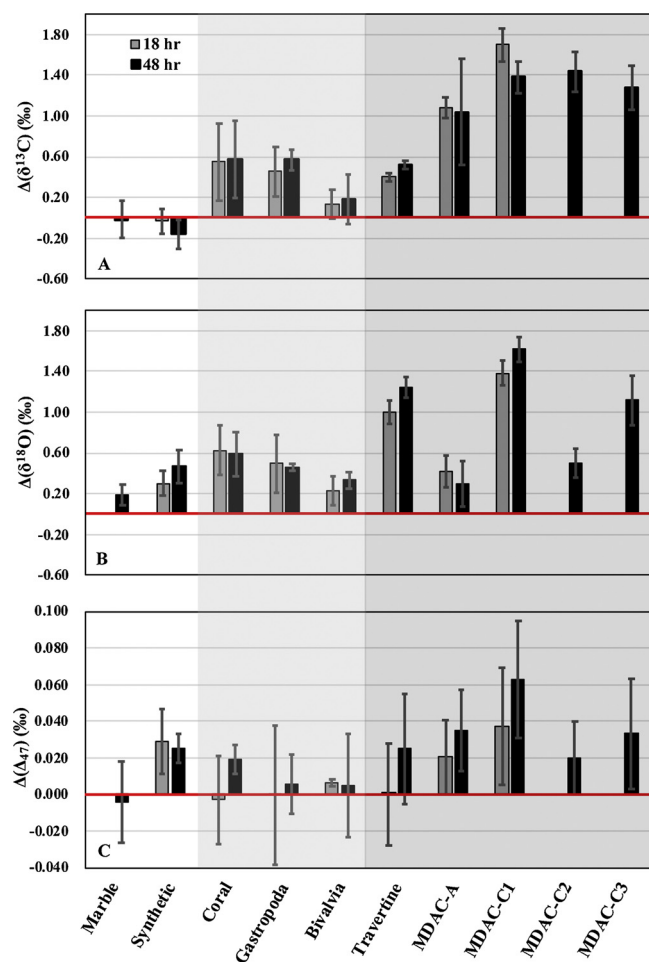


Fig. 3. Changes in isotopic values of various carbonate minerals after 10% H_2O_2 treatment. Delta values in y-axis equal to the isotope differences of (a) $\delta^{13}\text{C}$, (b) $\delta^{18}\text{O}$ and (c) Δ_{47} values between treated and untreated samples. Error bars present 2 standard errors.

2005). With these numbers, the true $\delta^{13}\text{C}$ value of carbonate may be solved by isotopic mass balance:

$$\delta^{13}\text{C}_m = x \delta^{13}\text{C}_{\text{org}} + (1-x) \delta^{13}\text{C}_{\text{carb}} \quad (1)$$

where $\delta^{13}\text{C}_m$, $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ are measured, organic and coral skeleton carbon isotope values, respectively, and x is the fraction of skeletal organic matter. If we assume all organic carbon was converted into CO_2 during acid digestion, the measured $\delta^{13}\text{C}$ value of coral skeleton can be as much as 0.26‰ less than the true value. The influence can be even larger since the previous organic extraction method underestimated the amount of organic matter (Muscatine et al., 2005).

Nevertheless, removal of organic matter cannot explain the extremely high $\Delta(\delta^{13}\text{C})$ values ($> 1\%$) in MDACs. To quantify the possible influence of organic matter on MDACs, carbonates in a MDAC sample (~ 50 mg) were removed by 12 mL of 3 M HCl, and the residue was subsequently reacted with 105% H_3PO_4 at 90 °C following the same method as described in Section 2.2. Negligible CO_2 gas (accounting for $\sim 0.01\%$ of CO_2 liberated from carbonate minerals, quantified by m/z 44 signal in the IRMS) was produced. The result suggests that the enriched $\delta^{13}\text{C}$ value observed in MDAC samples should not be attributed to the organic contamination, but is likely related to isotope effects during the H_2O_2 treatment. A plausible explanation for this positive alteration is the isotope exchange with dissolved atmospheric CO_2 in the $\text{CO}_2\text{-HCO}_3^- \text{-CO}_3^{2-}$ system. If we assume the $\delta^{13}\text{C}$ of HCO_3^- in the solution is in equilibrium with atmospheric CO_2 ($\delta^{13}\text{C} = -9.6\%$, Zhang et al., 2014), the value is estimated as -1.6% using the carbon isotopic

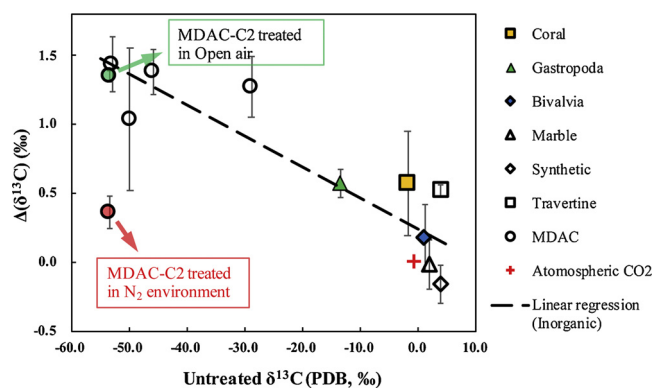


Fig. 4. Changes in $\delta^{13}\text{C}$ values of each sample against their origin $\delta^{13}\text{C}$ values, after being treated by 10% H_2O_2 for 48 h. Cross mark shows the expected value for the newly precipitated calcite via atmospheric CO_2 . The $\Delta(\delta^{13}\text{C})$ values of MDAC-C2 treated in open air (green circle) and N_2 environment (red circle) for 18 h are also plotted in the figure. Error bars present 2 standard errors.

fractionation factor between CO_2 and HCO_3^- at 25 °C (Zhang et al., 1995). The $\delta^{13}\text{C}$ value of newly precipitated carbonate phase can be further calculated to be -0.7% by adding a calcite-bicarbonate fractionation factor (0.9‰) (Rubinson and Clayton, 1969). As shown in Fig. 4, there is a clear correlation between the $\Delta(\delta^{13}\text{C})$ and original $\delta^{13}\text{C}$ values for the inorganic carbonate. Those carbonate samples with largely depleted $\delta^{13}\text{C}$ values (e.g. ca. -50% in MDACs) present large and positive shift towards the atmospheric CO_2 equilibrated carbonates after H_2O_2 treatment (Fig. 4), implying significant influences of isotopic exchange with dissolved CO_2 . To verify this hypothesis, we additionally treated a MDAC sample by 10% H_2O_2 in pure N_2 gas for 18 h to eliminate any potential influence from atmospheric CO_2 . The change of $\delta^{13}\text{C}$ value under N_2 environment ($0.36 \pm 0.06\%$), which may be a result of partial dissolution of isotopic depleted carbonate compositions at weak acidic solution, is significantly lower than the result of control experiments conducted in open air ($1.35 \pm 0.02\%$) (Fig. 4, Table S3). These results provide strong evidence to support our interpretation suggested above, although the dissolution-reprecipitation process cannot be detected by XRD because the amount of newly precipitated carbonate is lower than the XRD detection limit and/or in amorphous phase.

Consequently, mechanisms of changes in $\delta^{13}\text{C}$ values in acidic H_2O_2 solution may include: (1) isotopic fractionation during the partial dissolution of original carbonate; (2) dissolution of isotopic distinct carbonate compositions in the heterogeneous minerals; (3) successfully removal of organic contaminants which may produce isotopically distinct CO_2 ; (4) isotopic exchange with the dissolved atmospheric CO_2 in the $\text{CO}_2\text{-HCO}_3^- \text{-CO}_3^{2-}$ system. To avoid any carbonate $\delta^{13}\text{C}$ alteration during pretreatment, the H_2O_2 solution is suggested to be buffered and isolated from air.

4.2. Oxygen isotope

Most interpretations of $\delta^{18}\text{O}$ changes in the literature were focused on the partial dissolution of carbonate (Boiseau and Juillet-Leclerc, 1997; Wierzbowski, 2007; Serrano et al., 2008; Lebeau et al., 2014; Schone et al., 2017). However, altered $\delta^{18}\text{O}$ values in the literature (Table 1) are different from the apparently positive changes in biogenic and authigenic carbonates observed in this study (Fig. 3b) in terms of magnitude and direction. The discrepancy suggests that there might be additional mechanisms in this study, which may have implications to other relevant studies.

Similar to $\delta^{13}\text{C}$ values, the CO_2 released from organic matter can produce negative bias in $\delta^{18}\text{O}$ values (Oehlerich et al., 2013; Lebeau et al., 2014; Falster et al., 2018). Successfully removal of organic contamination using H_2O_2 , therefore, should lead to positive and accurate

Table 3Oxygen isotope values of H₂O₂ solution and carbonate, before and after treatment. Synthetic and travertine samples were treated by 10% H₂O₂ for 18 h.

Sample	$\delta^{18}\text{O}$ of H ₂ O ₂ solution (SMOW, ‰) ^a		$\delta^{18}\text{O}$ of carbonate (PDB, ‰) ^a		
	before treatment	after treatment	before treatment	after treatment	$\Delta(\delta^{18}\text{O})$
Synthetic	-7.8 ± 0.0	undone	-6.9 ± 0.0	-6.6 ± 0.0	0.3 ± 0.0
	240.5 ± 0.1	undone	-6.9 ± 0.0	-1.4 ± 0.2	5.4 ± 0.2
Travertine	-7.8 ± 0.0	6.9 ± 5.0	-12.8 ± 0.0	-11.8 ± 0.1	1.0 ± 0.1
	240.5 ± 0.1	199.5 ± 8.1	-12.8 ± 0.0	-10.1 ± 0.1	2.7 ± 0.1

^a Errors are presented in one standard error.

$\delta^{18}\text{O}$ values. This mechanism can explain our observed enriched $\delta^{18}\text{O}$ values in biogenic carbonate, but it should not be the case in synthetic calcite which is supposed to be pure and without any organic matter. Because of limited amounts of CO₂ liberated from organic compounds in MDAC and travertine samples as discussed in Section 4.1, this explanation might not be the reason causing dramatic $\delta^{18}\text{O}$ changes (> 1‰) in some MDAC and travertine samples either.

Some previous studies (Grauel et al., 2013; Falster et al., 2018) have observed recrystallization of carbonate in acidic H₂O₂ solution via SEM images. According to Fig. 2, the surface of authigenic carbonate used in this study obviously changed after being treated by acidic H₂O₂ solution. Although it is hard to tell whether there is any new carbonate phases re-precipitated from our SEM images, the oxygen isotope exchange via CaCO₃-HCO₃⁻/CO₃²⁻-H₂O can be tested by isotopically labeled H₂O. Here, synthetic calcite and travertine samples were treated by 10% H₂O₂ solution made by ¹⁸O-enriched H₂O ($\delta^{18}\text{O}_{\text{H}_2\text{O}} = +240.5 \pm 0.1\text{‰}$, VSMOW) for 18 h. Both samples present apparently larger $\delta^{18}\text{O}$ changes than those treated by regular 10% H₂O₂ solution ($\delta^{18}\text{O}_{\text{H}_2\text{O}} = -7.8 \pm 0.0\text{‰}$, VSMOW, Table 3), demonstrating that the $\delta^{18}\text{O}$ value of carbonate mineral in acidic H₂O₂ solution can be influenced by isotopic exchanges with H₂O.

Additionally, another interesting phenomenon is that the magnitude of $\Delta(\delta^{18}\text{O})$ differences between regular and ¹⁸O-enriched H₂O₂ solution treatments in travertine aragonite is smaller than synthetic calcite (Table 3). The $\Delta(\delta^{18}\text{O})$ value after treatment of ¹⁸O-enriched H₂O₂ is +5.4‰ in synthetic calcite, while it is +2.7‰ in travertine aragonite. Over the course of H₂O₂ pretreatment, we observed continuous and violent bubbling in the reaction vessel for travertine and some of MDAC samples (e.g. MDAC-C1). In contrast, only a few bubbles slowly appeared in the H₂O₂ solution reacted with marble, synthetic and biogenic carbonates. It is well known that travertine and MDACs are rich in transition-metal-bearing compounds (Cody et al., 2004), which can catalyze the decomposition of H₂O₂ via the Fenton reaction (Lousada et al., 2012; Enami et al., 2014). Therefore, these isotopically distinct phenomena probably indicated H₂O₂ auto-decomposition in solution with travertine and MDAC samples during treatment. The $\delta^{18}\text{O}$ value in our H₂O₂ reagent is not measured but should be close to atmospheric oxygen (~24‰) because the manufacture of H₂O₂ around the world is almost exclusively via the catalyzed reaction between H₂ and atmospheric O₂ (Campos-Martin et al., 2006), and $\delta^{18}\text{O}$ values of various commercially available H₂O₂ (45 unique brands) exhibit a narrow range of $\delta^{18}\text{O}$ values (21–26‰) (Barnette et al., 2011). H₂O produced from H₂O₂ auto-decomposition thus possess isotopic composition notably different from that of original H₂O₂ solution, though the kinetic fractionation process remains unclear and deserve further investigation. Qualitatively, the newly produced H₂O increased (or decreased) $\delta^{18}\text{O}$ values of H₂O in regular (or ¹⁸O-enriched) H₂O₂ solution, and subsequently altered isotopic compositions of travertine in a way different from synthetic calcite as observed in this study (Table 3).

Similar to $\delta^{13}\text{C}$, the mechanisms of changes in $\delta^{18}\text{O}$ values after acidic H₂O₂ treatment may include: (1) isotopic fractionation during the partial dissolution of original carbonate; (2) dissolution of isotopic distinct carbonate compositions in the heterogeneous minerals; (3)

successfully removal of organic contaminants which may produce isotopically distinct CO₂; (4) isotopic exchange with surrounding solvent via CaCO₃-HCO₃⁻/CO₃²⁻-H₂O system. Therefore, pretreatment on $\delta^{18}\text{O}$ analysis is suggested to use the buffered H₂O₂ solution to avoid any oxygen isotope exchange during dissolution-reprecipitation process in the weak acidic solution.

4.3. Clumped isotope

In theory, the measured clumped isotope value may be altered after H₂O₂ treatment due to the partial dissolution of carbonate materials and/or successfully removing of the organic matter. Most of our observed changes in Δ_{47} values, expect for several MDAC samples, however, are less than our 2-SD analytical uncertainty ($\pm 0.032\text{‰}$). Biogenic samples (coral, land snail, and bivalvia) present identical Δ_{47} values before and after H₂O₂ treatment (Fig. 3c), although some organic compounds were removed successfully as discussed in Sections 4.1 and 4.2. The results indicate that the concentration of organic contaminants in these samples is not high enough to produce statistically significant analytical artifacts in clumped isotope measurements.

In contrast, some MDAC samples show remarkable positive Δ_{47} changes, beyond the analytical uncertainty (e.g. MDAC-C1, Fig. 3c). As discussed in previous sections, both carbon and oxygen isotopic exchange occurred in acidic H₂O₂ solution via carbonate dissolution-reprecipitation process, leading to the non-linear mixing effect on Δ_{47} values. According to Defliese and Lohmann (2015), the magnitude and direction of Δ_{47} mixing effect are controlled by the difference of isotopic compositions between endmembers. The larger difference in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values leads to larger Δ_{47} offset. Based on our observations, positive offsets in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of MDAC samples are significant after 10% H₂O₂ treatment, yielding the positive Δ_{47} offset in MDACs as calculated by Defliese and Lohmann (2015). We present this relationship qualitatively in Fig. 5, where Δ_{47} offsets are plotted against the sum

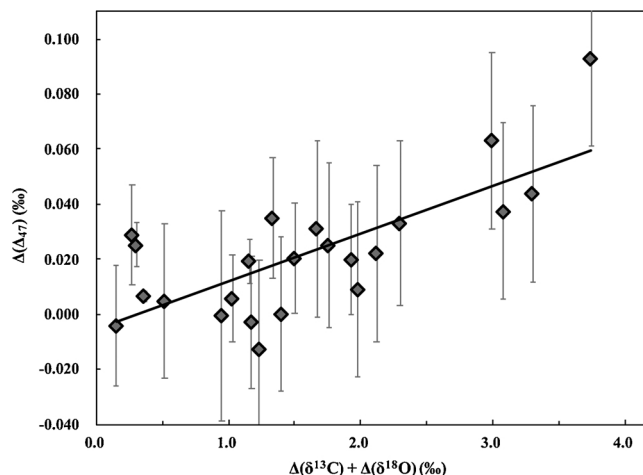


Fig. 5. Changes in Δ_{47} values plotted against the combined changes in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. Error bars present 2 standard errors.

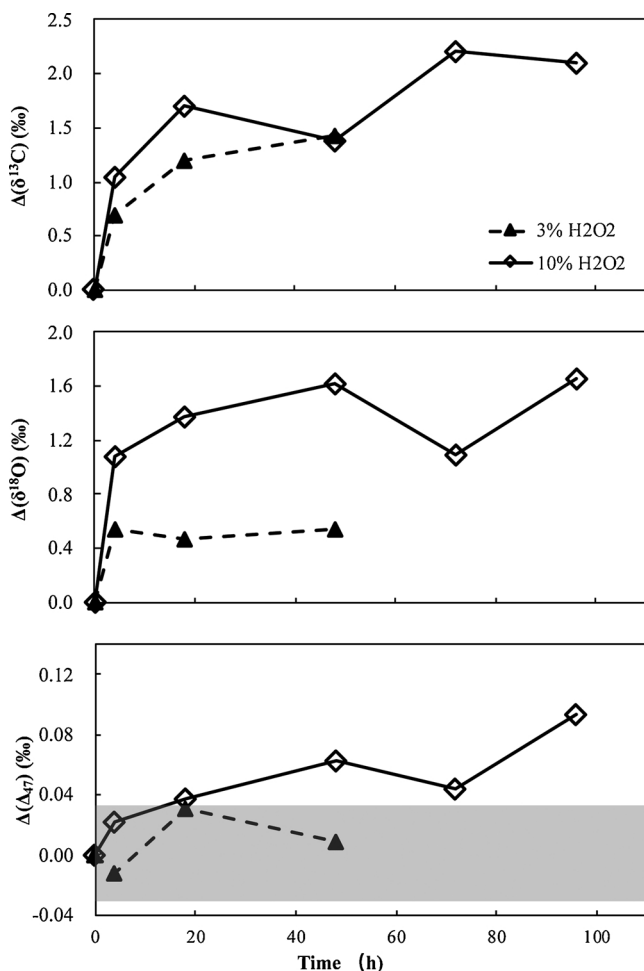


Fig. 6. Changes in isotopic values of MDAC-C1 along with the treatment time at two different H₂O₂ concentrations. Grey shaded area presents the 2-SD uncertainty of our clumped isotope analysis.

of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ offsets. A clear positive correlation supports that the mixing effects should be considered as the most important reason altering original Δ_{47} values during H₂O₂ treatment.

We note that the changes in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of synthetic calcite are relative small, while the Δ_{47} offset is larger than 1-SD systematic uncertainty ($\pm 0.016\%$). This change, if not an analytical error, can also be produced by the mixing effect because the Δ_{47} value of the original synthetic calcite sample ($\sim 0.4\%$) is notably differently from isotopically altered carbonates ($\sim 0.7\%$ at room temperature), which enlarges the mixing effect suggested by Defliese and Lohmann (2015).

4.4. An application to MDACs

Because large shifts of isotopic signatures were found in MDACs, cautions should be taken into isotopic analysis of MDACs in the future. Based on mechanisms discussed above, we investigate the isotopic shift in MDACs as a function of H₂O₂ concentration and reaction time (Fig. 6) with an aim to determine the ideal H₂O₂ treatment strategy.

For carbon isotope, both 3% and 10% H₂O₂ treatments show similar trends due to a strong influence of atmospheric CO₂. This process led to formation of atmospheric-CO₂-relevant-carbonates, of which $\delta^{13}\text{C}$ values are ca. 45‰ heavier than MDAC-C1. The trend in 3% H₂O₂ treatment displays a smaller magnitude, suggesting that a higher pH may minimize dissolution-precipitation processes in the solution because of Le Chatelier's principle. The $\delta^{18}\text{O}$ changes in both 3% and 10%

H₂O₂ treatments approach steady states after 20 h, and the magnitude of 3% H₂O₂ treatment is three times smaller than 10% H₂O₂ solution. The difference may be due to the amount of H₂O₂ decomposed under the catalysis of transition metal compounds, which produce different $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ changes in H₂O₂ solution. Changes in Δ_{47} values of MDAC samples are controlled by differences in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, and therefore the sample after 96 h 10% H₂O₂ treatment yields the largest Δ_{47} bias.

In summary, for MDAC samples, H₂O₂ treatment is not recommended since the organic contamination only produce negligible CO₂ gas in the acid digestion as shown in this study. However, if the samples are suspected to contain high amount of organic matter and have to be treated before isotopic analysis, decreasing the H₂O₂ concentration, shortening the reaction time, leaving the solution in a CO₂-free environment, and adjusting the H₂O₂ solution to a basic condition (Falster et al., 2018) may solve the analytical problem. This optimized protocol has been used in our recent study (Zhang et al., 2019): the authors treated their MDAC samples with 1% H₂O₂ for 4 h, and yielded isotopic alteration within their analytical error, i.e. $+0.19 \pm 0.24\%$, $+0.08 \pm 0.21\%$ and $-0.003 \pm 0.016\%$, for $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47} , respectively.

5. Conclusion

The effect of H₂O₂ treatment on stable isotope analysis of 7 types of carbonate minerals were examined and discussed in this study. We found that $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47} values were altered after the H₂O₂ treatment and corresponding mechanisms vary.

The positive $\delta^{13}\text{C}$ changes are attributed to (1) isotopic fractionation during the partial dissolution of original carbonate; (2) dissolution of isotopic distinct carbonate compositions in the heterogeneous minerals; (3) successfully removal of organic contaminants which may produce isotopically distinct CO₂; (4) isotopic exchange with the dissolved atmospheric CO₂ via the CO₂-HCO₃⁻-CO₃²⁻ system. Similarly, mechanisms of changes in $\delta^{18}\text{O}$ values may include: (1) isotopic fractionation during the partial dissolution of original carbonate; (2) dissolution of isotopic distinct carbonate compositions in the heterogeneous minerals; (3) successfully removal of organic contaminants; (4) isotopic exchange with surrounding solvent via the CaCO₃-HCO₃⁻/CO₃²⁻-H₂O system, and transition metals in some carbonate minerals such as travertine can enlarge this effect by catalyzing the decomposition of H₂O₂ and subsequently changing $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of H₂O₂ solution. Finally, the magnitude of changes in Δ_{47} values are controlled by the non-linear mixing effect of two types of carbonates with different $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values: original carbonate minerals and isotopically altered ones. Cautions should be taken for samples presenting large changes in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values after H₂O₂ treatment, which may yield a large shift of Δ_{47} from the true value.

For the carbonate materials which may suffer the high risk of organic contamination, such as biogenic carbonate, the H₂O₂ treatment before isotopic analysis is suggested. To prevent the isotopic alterations during the dissolution-precipitation process in the H₂O₂ solution, a buffered solution isolated from the atmospheric CO₂ is recommended. On the other hand, for authigenic carbonates which has less chance to be contaminated by organic matter, the H₂O₂ treatment is unnecessary. If authigenic samples suspected to contain high amount of organic matter have to be treated before isotopic analysis, following measures should be taken: decreasing the H₂O₂ concentration, shortening the reaction time, leaving the solution in the CO₂-free environment, and adjusting the H₂O₂ solution to a basic condition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.chemgeo.2019.119352>.

References

- Agoha, E.E.C., Mazi, E.A., 2009. Biopolymers from african giant snail shells waste: isolation and characterization. *World Congress on Medical Physics and Biomedical Engineering* 25, 249–251.
- Asami, K., Yamaguchi, T., 1997. Distribution of living and fossil coral barnacles (Cirripedia; Pyrgomatidae) in Japan. *Sess. Org.* 14 (1), 9–16.
- Barnette, J.E., Lott, M.J., Howa, J.D., Podlesak, D.W., Ehleringer, J.R., 2011. Hydrogen and oxygen isotope values in hydrogen peroxide. *Rapid Commun. Mass Spectrom.* 25 (10), 1422–1428.
- Bemis, B.E., Spero, H.J., Bijma, J., Lea, D.W., 1998. Reevaluation of the oxygen isotopic composition of planktonic foraminifera: experimental results and revised paleo-temperature equations. *Paleoceanography* 13 (2), 150–160.
- Boiseau, M., Juillet-Leclerc, A., 1997. H₂O₂ treatment of recent coral aragonite: oxygen and carbon isotopic implications. *Chem. Geol.* 143, 171–180.
- Brand, W.A., Assonov, S.S., Coplen, T.B., 2010. Correction for the O-17 interference in delta(C-13) measurements when analyzing CO₂ with stable isotope mass spectrometry (IUPAC Technical Report). *Pure Appl. Chem.* 82 (8), 1719–1733.
- Campos-Martin, J.M., Blanco-Brieva, G., Fierro, J.L.G., 2006. Hydrogen peroxide synthesis: an outlook beyond the anthraquinone process. *Angewandte Chemie-International Edition* 45 (42), 6962–6984.
- Charef, A., Sheppard, S.M.F., 1984. Carbon and oxygen isotope analysis of calcite or dolomite associated with organic-matter. *Isot. Geosci.* 2 (4), 325–333.
- Cody, G.D., et al., 2004. Assaying the catalytic potential of transition metal sulfides for abiotic carbon fixation. *Geochim. Cosmochim. Acta* 68 (10), 2185–2196.
- Daeron, M., Blamart, D., Peral, M., Affek, H.P., 2016. Absolute isotopic abundance ratios and the accuracy of Delta(47) measurements. *Chem. Geol.* 442, 83–96.
- Defliese, W.F., Lohmann, K.C., 2015. Non-linear mixing effects on mass-47 CO₂ clumped isotope thermometry: patterns and implications. *Rapid Commun. Mass Spectrom.* 29 (9), 901–909.
- Dennis, K.J., Affek, H.P., Passey, B.H., Schrag, D.P., Eiler, J.M., 2011. Defining an absolute reference frame for 'clumped' isotope studies of CO₂. *Geochim. Cosmochim. Acta* 75 (22), 7117–7131.
- Dunbar, R.B., Wellington, G.M., Colgan, M.W., Glynn, P.W., 1994. Eastern pacific sea surface temperature since 1600 A.D.: The $\delta^{18}\text{O}$ record of climate variability in Galapagos Corals. *Paleoceanogr. Paleoclimatology* 9 (2), 291–315.
- Eiler, J.M., 2011. Paleoclimate reconstruction using carbonate clumped isotope thermometry. *Quat. Sci. Rev.* 30, 3575–3588.
- Enami, S., Sakamoto, Y., Colussi, A.J., 2014. Fenton chemistry at aqueous interfaces. *Proc. Natl. Acad. Sci. U.S.A.* 111 (2), 623–628.
- Epstein, S., Buchsbaum, R., Lowenstam, H., Urey, H.C., 1951. Carbonate-water isotopic temperature scale. *Geol. Soc. Am. Bull.* 62 (4), 417–426.
- Epstein, S., Buchsbaum, R., Lowenstam, H.A., Urey, H.C., 1953. Revised carbonate-water isotopic temperature scale. *Geol. Soc. Am. Bull.* 64 (11), 1315–1325.
- Falster, G., Delean, S., Tyler, J., 2018. Hydrogen peroxide treatment of natural lake sediment prior to carbon and oxygen stable isotope analysis of calcium carbonate. *Geochim. Geophys. Geosystems* 19 (9), 3583–3595.
- Feldmeijer, W., Metcalfe, B., Scussolini, P., Arthur, K., 2013. The effect of chemical pretreatment of sediment upon foraminiferal-based proxies. *Geochim. Geophys. Geosystems* 14 (10), 3996–4014.
- Fernandez, M.S., Valenzuela, F., Arias, J.I., Neira-Carrillo, A., Arias, J.L., 2016. Is the snail shell repair process really influenced by eggshell membrane as a template of foreign scaffold? *J. Struct. Biol.* 196 (2), 187–196.
- Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W., Schauble, E.A., Schrag, D., Eiler, J., 2006. ^{13}C - ^{18}O bonds in carbonate minerals: a new kind of paleothermometer. *Geochim. Cosmochim. Acta* 70, 1439–1456.
- Goodfriend, G.A., 1992. The use of land snail shells in paleoenvironmental reconstruction. *Quat. Sci. Rev.* 11 (6), 665–685.
- Grauel, A.L., Schmid, T.W., Hu, B., Bergami, C., Capotondi, L., Zhou, L., Bernasconi, S.M., 2013. Calibration and application of the 'clumped isotope' thermometer to foraminifera for high-resolution climate reconstructions. *Geochim. Cosmochim. Acta* 108, 125–140.
- Grottoli, A.G., Rodrigues, L.J., Matthews, K.A., Palardy, J.E., Gibb, O.T., 2005. Pre-treatment effects on coral skeletal $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. *Chem. Geol.* 221, 225–242.
- Guo, Y., Deng, W., Wei, G., Lo, L., Wang, N., 2019. Clumped isotopic signatures in land-snail shells revisited: possible palaeoenvironmental implications. *Chem. Geol.* 519, 83–94.
- He, B., Olack, G.A., Colman, A.S., 2012. Pressure baseline correction and high-precision CO₂ clumped-isotope (Δ_{47}) measurements in bellows and micro-volume modes. *Rapid Commun. Mass Spectrom.* 26 (24), 2837–2853.
- Keatings, K.W., Holmes, J.A., Heaton, T.H.E., 2006. Effects of pre-treatment on ostracod valve chemistry. *Chem. Geol.* 235, 250–261.
- Kim, S.T., Coplen, T.B., Horita, J., 2015. Normalization of stable isotope data for carbonate minerals: implementation of IUPAC guidelines. *Geochim. Cosmochim. Acta* 158, 276–289.
- Kim, S.T., Mucci, A., Taylor, B.E., 2007. Phosphoric acid fractionation factors for calcite and aragonite between 25 and 75 degrees C: revisited. *Chem. Geol.* 246, 135–146.
- Lebeau, O., Busigny, V., Chaduteau, C., Ader, M., 2014. Organic matter removal for the analysis of carbon and oxygen isotope compositions of siderite. *Chem. Geol.* 372, 54–61.
- Lousada, C.M., Johansson, A.J., Brinck, T., Jonsson, M., 2012. Mechanism of H₂O₂ decomposition on transition metal oxide surfaces. *J. Phys. Chem. C* 116 (17), 9533–9543.
- Mcconnaughey, T., 1989. ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: I. Patterns. *Geochim. Cosmochim. Acta* 53 (1), 151–162.
- Miyajima, Y., Ijiri, A., Miyake, A., Hasegawa, T., 2018. Origin of methane and heavier hydrocarbons entrapped within Miocene methane-seep carbonates from central Japan. *Chem. Geol.* 498, 83–95.
- Muscattine, L., Goiran, C., Land, L., Jaubert, J., Cuif, J.P., Allemand, D., 2005. Stable isotopes ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of organic matrix from coral skeleton. *Proc. Natl. Acad. Sci. U.S.A.* 102 (5), 1525–1530.
- Oehlerich, M., Baumer, M., Lucke, A., Mayr, C., 2013. Effects of organic matter on carbonate stable isotope ratios ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values) implications for analyses of bulk sediments. *Rapid Commun. Mass Spectrom.* 27 (6), 707–712.
- Okumura, T., Takashima, C., Shiraiishi, F., Akmaluddin, Kano, A., 2012. Textural transition in an aragonite travertine formed under various flow conditions at Pancuran Pitu, Central Java, Indonesia. *Sedimentary Geology* 265, 195–209.
- Peral, M., et al., 2018. Updated calibration of the clumped isotope thermometer in planktonic and benthic foraminifera. *Geochim. Cosmochim. Acta* 239, 1–16.
- Roberts, L.R., Holmes, J.A., Leng, M.J., Sloane, H.J., Horne, D.J., 2018. Effects of cleaning methods upon preservation of stable isotopes and trace elements in shells of Cyprideis torosa (Crustacea, Ostracoda): implications for palaeoenvironmental reconstruction. *Quat. Sci. Rev.* 189, 197–209.
- Rubinson, M., Clayton, R.N., 1969. Carbon-13 fractionation between aragonite and calcite. *Geochim. Cosmochim. Acta* 33 (8) 997–8.
- Schone, B.R., Schmitt, K., Maus, M., 2017. Effects of sample pretreatment and external contamination on bivalve shell and Carrara marble $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 484, 22–32.
- Serrano, O., Serrano, L., Mateo, M.A., 2008. Effects of sample pre-treatment on the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of living benthic foraminifera. *Chem. Geol.* 257, 221–223.
- Suess, E., 1970. Interaction of organic compounds with calcium carbonate—I. Association phenomena and geochemical implications. *Geochimica Et Cosmochimica Acta* 34 (2) 157–8.
- Suess, E., 1973. Interaction of organic compounds with calcium-carbonate—II. Organocarbonate association in recent sediments. *Geochimica Et Cosmochimica Acta* 37 (11), 2435–2447.
- Walton, W.R., 1952. Techniques for recognition of living foraminifera. *Cushman Found. Forum. Res. Contr.* 3 (2), 56–60.
- Weidman, C.R., Jones, G.A., 1994. The long-lived mollusc *Arctica islandica*: a new paleoceanographic tool for the reconstruction of bottom temperatures for the continental shelves of the northern North Atlantic Ocean. *J. Geophys. Res. Oceans* 99 (C9), 18305–18314.
- Wierzbowski, H., 2007. Effects of pre-treatments and organic matter on oxygen and carbon isotope analyses of skeletal and inorganic calcium carbonate. *Int. J. Mass Spectrom.* 268 (1), 16–29.
- Woodruff, F., Savin, S.M., Douglas, R.G., 1981. Miocene stable isotope record - a detailed deep pacific-ocean study and its paleoclimatic implications. *Science* 212 (4495), 665–668.
- Zhang, J., Quay, P.D., Wilbur, D.O., 1995. Carbon-isotope fractionation during gas-water exchange and dissolution of Co₂. *Geochimica Et Cosmochimica Acta* 59 (1), 107–114.
- Zhang, N., Yamada, K., Suzuki, N., Yoshida, N., 2014. Factors controlling shell carbon isotopic composition of land snail *Acusta despecta sieboldiana* estimated from laboratory culturing experiment. *Biogeosciences* 11 (19), 5335–5348.
- Zhang, N.Z., Yamada, K., Kano, A., Matsumoto, R., Yoshida, N., 2018. Equilibrated clumped isotope signatures of land-snail shells observed from laboratory culturing experiments and its environmental implications. *Chem. Geol.* 488, 189–199.
- Zhang, N., Lin, M., Snyder, G.T., Kakizaki, Y., Yamada, K., Yoshida, N., Matsumoto, R., 2019. Clumped isotope signatures of methane-derived authigenic carbonate representing equilibrium values of their formation temperatures. *Earth Planet. Sci. Lett.* 512, 207–213.