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The Effect of Extraction Techniques on Ca Concentrations and Isotope Ratios of Marine Pore Water

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Abstract

Comparing two different techniques applied for the extraction of marine pore water samples from sediments, the well-established Whole Round (WR) method and the more recent Rhizon method, in terms of their effects on stable calcium isotope ratios in extracted pore waters, we recognize a systematic offset between the two sampling methods. Higher $\delta^{44/40}$Ca values are associated with lower Ca concentrations for the Rhizon sampling technique and lower $\delta^{44/40}$Ca values are associated with higher Ca concentrations for the corresponding WR-derived pore water samples. Models involving Rayleigh fractionation and mixing calculation suggest that the observed offset is most likely caused by a combined process of $CaCO_3$ precipitation and ion exchange taking place during Rhizon sampling-induced CO_2 degassing. Changing pressure, extraction time or extraction yield during WR pressing does not lead to a variation in $\delta^{44/40}$Ca, indicating that no Ca isotope fractionation takes place during the sampling of pore water. On the basis of analytical and modelling results, WR samples appear to provide $\delta^{44/40}$Ca values that are more representative of the 'true' pore water isotopic composition. While the difference between the sampling techniques is close to the present-day analytical precision of Ca isotope analysis, it may become more relevant with increasing analytical precision in the future.

Keywords

Pore water, Rhizon, Whole Round, IODP, isotope fractionation, Ca isotopes

1. Introduction

Marine sedimentary pore waters are dynamic reservoirs that exhibit characteristic fluctuations in their chemical and isotopic composition in spatial and temporal dimensions. These changes in the pore water composition are important indicators of early diagenetic processes and fluid flow. For example, iron, manganese, nitrate and sulphate are used to trace various redox processes, while chlorine and $\delta^{18}O$ are used for determining dewatering reactions, reconstruction of past ocean chemistry or formation and dissolution of gas hydrates [e.g. 1-9]. An element of special interest in marine pore waters is Ca, as it is involved in the diagenesis of carbonate minerals. Furthermore, calcium can also be involved in ion exchange and submarine silicate weathering reactions. These diagenetic reactions not only alter the chemical composition of the pore waters (e.g. Ca concentrations), but also their Ca isotopic composition [8-12]. As such, the calcium isotopic composition of pore fluids has been used to trace diagenetic reactions involving Ca, such as carbonate dissolution [10], precipitation [9], ion exchange [9,12-13], and recrystallization [e.g. 10,14,15]. Owing to the higher amount of calcium in the mineral phase compared to the fluid phase, small changes in dissolution, precipitation or recrystallization are reflected quickly in the calcium in the pore waters.

To retrieve marine pore water samples for Ca isotope analyses from more or less consolidated sediments, there are several main approaches: The Whole Round (WR) squeezing method [16-18] which has served DSDP, ODP and IODP for decades as the standard pore water sampling method and alternative sampling methods, including the comparatively new but increasingly popular Rhizon sampling technique [19-23]. For the WR squeezing method, pore water is extracted from the sediment by applying a hydraulic pressure with titanium and stainless-steel cylinders, collecting samples after filtration (typically 0.45 µm pore size) in a syringe [24-25]. With the Rhizon sampling technique, the pore water is extracted from the sediment in a radius of one to three cm (depending on porosity and sampling duration) by applying a gentle vacuum through a micro-porous filter section (typically 0.15 µm pore size), which prevents microbial and colloidal contamination [26]. The pore water is gathered in small containers, such as syringes or vacutainers. For more information, see the appendix.

Dickens et al. [27] showed that Rhizon- and WR-extracted pore water samples have identical Mn and NH_4 concentrations. Although Rhizons have been applied to marine sediments for more than ten years, there is no conclusive evidence on whether the Rhizon and WR techniques generate compatible elemental and isotopic compositions of sedimentary pore water samples [28]. The first comparison of isotopic measurements of WR- and Rhizon-derived pore water samples by Miller et al. [28] revealed a difference in oxygen and hydrogen isotope ratios between the two sampling techniques. The offsets were explained by a combined effect of fractionation by diffusion through, and absorption by, the Rhizons [28]. In addition, fine-grained sediments such as mudstones could fractionate isotopes of passing fluids by the so-called ultrafiltration effect, owing to their ability to act as a semi-permeable membrane that only passes water and not dissolved ions [29,30]. In contrast, Schrum et al. [21] reported that there are significant variations in alkalinity and dissolved inorganic carbon (DIC) between Rhizon and WR samples. These observations may be related to the sediment composition and the CO_2-H_2CO_3 system in the pore water, because CO_2 degassing induced by pressure relief during Rhizon sampling can cause $CaCO_3$ precipitation and thus alteration of alkalinity and DIC concentration [31], while the concentrations of NH_4, sulphate and chloride seem to be unaffected by this depressurization.

To systematically compare the effects of WR and Rhizon sampling on pore water Ca^{2+} and similar cations, both techniques were applied during IODP Expedition 320 at Site U1332 at two parallel cores from Hole A and C [20]. This revealed offsets in element concentrations such as Ba^{2+}, Ca^{2+}, Li^{+} and Mg^{2+} between pore water samples derived from the two methods (Fig. 1) [20]. The origin of this difference is not yet understood but may relate to either the sampling of different reservoirs such as dissolved and adsorbed species, or dissolution-precipitation reactions. Different stable isotope fractionations might be involved leading to different isotope ratios for the two sampling methods. [Fig. 1 near here]

To further elucidate the processes taking place during pore water sampling, we present the Ca concentration and $\delta^{44/40}$Ca of corresponding WR- and Rhizon-derived samples to determine whether the concentration difference correlates with changes in the $\delta^{44/40}$Ca. In addition, we investigate if the Ca isotopic composition of the pore fluid released during WR squeezing changes with increasing squeezing duration and pressure.

2. Sample Material

2.1 Pore Waters and Sediments from Deep-Sea Drill Cores

During IODP Expeditions 320 and 321 of the PEAT project (Paleo Equatorial Age Transect), pore waters were sampled at eight sites [20]. At Site U1332 (11°54.722′N, 141°02.743′W; 4924 meters below sea level), systematic tests for the comparison of Rhizon and WR sampling were conducted at parallel holes with similar lithological record with an offset between corresponding layers of approximately 1-5 m [20]. Pore water was collected at Hole U1332A by WR squeezing, and with Rhizons at Hole U1332C, 50 m apart [20]. Samples were taken from depths between approximately 25 and 57 m CSF-A (core depth below sea floor) from each core (Table 1). In addition, reference sediment samples were taken from Hole U1332A. The respective segments that were sampled for pore water consist of alternating clayey radiolarian ooze, nannofossil ooze with radiolarians, and nannofossil ooze with 20 to 90 wt% $CaCO_3$ [20]. [Table 1 near here]

2.1.1 Pore Water from Whole Round Squeezing

The cores from Hole U1332A were cut into 5-10 cm WR sections and capped immediately after core retrieval on deck. Before the samples were squeezed, they were extracted from the core liner and the outer surfaces were carefully scraped off using spatulas to minimize potential contamination by drill fluids due to the coring process. The sediment samples were inserted into a steel and titanium whole round squeezing device and the pore water was squeezed out at ambient temperature with a hydraulic press. Primarily pressures of around 20 MPa have been used. Pore water samples were filtered through 0.45 µm Whatman polyether sulfone disposable filters, collected in acid-cleaned plastic syringes, and stored in pre-cleaned 4 ml Zinsser PE screw-top vials. For further details, see Pälike et al. [20].

2.1.2 Pore Water from Rhizon Samplers

The approximately 5 cm long Rhizons were moistened with ultra-pure water prior to sampling to increase the flow rate and to prevent air from being sucked into the sample [27]. Rhizons were inserted into the sediment through drilled holes to the core liner of a segment from 27 to 57 m CSF-A of Hole U1332C, at an angle of approximately 55° because the Rhizons were longer than the sediment core diameter. They cannot be shortened and must be inserted completely into the sediment to avoid uptake of air, as otherwise no vacuum can build up. The Rhizons were connected to pre-evacuated 10 ml syringes collecting the pore water with a gentle vacuum. Within 30 minutes, about 12 ml of pore water was gathered with no significant relation between sampling time and sediment depth [20]. The sediment composition is comparable to the samples used for the WR sampling of U1332A.

2.1.3 Sediments

Three sediment samples taken at a depth of approximately 20 to 65 m CSF-A at Hole U1332A have been chosen as reference for the calcium isotopic composition of the sediment. The sediments of this section of Hole U1332A mainly consist of clayey radiolarian and nannofossil ooze with a $CaCO_3$ content between 25 and 81 wt% [20]. The sediment samples are the residues of the WR squeezing technique, the so-called squeeze cakes [20].

2.2 Progressive Pore Water Extraction Experiment

During IODP Expedition 341 (Gulf of Alaska), a time series experiment was conducted by squeezing a 15 cm long Whole Round sediment sample for 45 minutes and subsampling for pore water at different time intervals (Table 1). The sediment sample is derived from Site U1417C (56°57.5888′N, 147°6.5769′W; 4187.7 meters below sea level) at 148.9 m core depth below seafloor and was characterized as mud with a $CaCO_3$ content of 0 to 1.5 wt% [32]. Three different pressures were applied (55 MPa, 70 MPa, 75 MPa) and 2-3 ml of pore water was sampled in seven time steps from 1 minute to 45 minutes and stored in 20 ml Zinsser PE polyvials.

3. Methods

3.1 Element Concentrations

Elemental concentrations of the progressive pore water extraction experiment were made on approximately 0.1 ml of the pore fluid, which were diluted and measured in 2 % HNO_3 using a Thermo Scientific X-Series II ICP-MS at standard quadrupole methods at the Institut für Planetologie at Münster, Germany. The analytical uncertainties are approximately 5-10 %.

3.2 Calcium purification and isotope analysis

3.2.1 Pore Water Preparation

To purify the Ca from the pore water matrix, in particular to remove K, the ion chromatographic method described by Ockert et al. [12] was applied, using pre-cleaned MCI Gel CK08P resin and a 1.8 N HCl chemistry. A defined amount of pore water, corresponding to ~1.5 µg Ca, was mixed with a ^{42}Ca/^{43}Ca double spike [33], dried down, recovered in 20 µl of 1.8 N HCl and loaded on the conditioned columns. The purified Ca was then evaporated and recovered in about 1 µl of 6 N HCl.

3.2.2 Sediment Preparation

For sediment Ca isotope analyses, aliquots of the squeeze cakes were ground in an agate mortar. An amount of 1 mg of the sample powder was transferred to a PCR Eppendorf tube and leached for 0.5 hours with 1 ml of 2.5 N acetic acid. When the carbonate had completely reacted with the acetic acid, the sample was centrifuged and the fluid phase was separated from the solid silicate phase. Both were dried down and weighed to determine the $CaCO_3$ content of the sediment. Afterwards, the carbonate phase was re-dissolved in 2.5 N HCl and an aliquot of about 1 µg of this leachate was mixed with a ^{42}Ca/^{43}Ca double spike and dried down.

3.2.3 Calcium Isotope Analysis

Calcium isotope analyses were carried out by thermal ionization mass spectrometry on a Triton from Thermo Fisher Scientific at the Institut für Mineralogie (Westfälische Wilhelms-Universität Münster), following the method described in [33]. Calcium (500 ng) was loaded with a TaF_5 activator solution in sandwich technique on Re single-filaments. Samples were analyzed at least in duplicate. Calcium isotope variations are reported as $\delta^{44/40}$Ca normalized to the NIST SRM 915a standard (Eq.1). Average 2 SE of the sample measurements was about

0.04 ‰ (2 SE; n=10). Ten analyses of seawater standard (IAPSO) had a $\delta^{44/40}$Ca of 1.84 ± 0.03 (2 SE; n=10), in agreement with literature values [34,35].

$$\delta^{44/40}Ca\ (‰) = \left(\frac{\left(\frac{^{44}Ca}{^{40}Ca}\right)_{sample}}{\left(\frac{^{44}Ca}{^{40}Ca}\right)_{standard}} - 1 \right) * 1000 \qquad 1)$$

4. Results

4.1 Comparison of WR and Rhizon Sampling

The $\delta^{44/40}$Ca values of the pore waters retrieved by WR sampling from IODP Hole U1332A range from 1.58 to 1.66 ‰ (n=7), while the Rhizon samples from IODP Hole U1332C show values between 1.67 and 1.73 ‰ (n=7; Table 1 and Fig. 2). Although most WR and Rhizon samples overlap within analytical uncertainty, it is noteworthy that all $\delta^{44/40}Ca_{WR}$ values are below the compared $\delta^{44/40}Ca_{rhizon}$ values. In addition, both depth profiles reveal identical patterns with an offset of 0.05 – 0.13 ‰ between the two sampling techniques. The averages of the WR and Rhizon samples differ significantly from each other, with $\delta^{44/40}$Ca values of 1.62 (± 0.02, 2 SE) ‰ and 1.71 (± 0.02, 2 SE) ‰, respectively. Sediment $\delta^{44/40}$Ca values (Table 1 and Fig. 2) of three segments show values ranging between 0.57 and 0.83 ‰ with an average value of 0.66 ‰ (± 0.14, 2 SE; n=3). [Fig. 2 near here]

4.2 Progressive Pore Water Extraction Experiment

The $\delta^{44/40}$Ca values of the samples obtained from the extraction experiment range from 1.49 to 1.58 ‰ with an average value of 1.53 ‰ (± 0.01, 2 SE; Fig. 3). After three and five minutes, values are slightly higher than average, but this is not statistically significant as they overlap within error with the average value. After eight minutes, the $\delta^{44/40}$Ca starts to decrease to a value of 1.51 ‰ and remains in this range for the rest of the experiment. Li^+, Mg^{2+} and Ca^{2+} show comparable evolutions of their elemental concentrations (Table 2 and Fig. 4) decreasing after five minutes, followed by an increase after eight minutes. The elemental concentrations of iron and cobalt (Fig. 4, Table 2) show a strong increase at three minutes corresponding to the $\delta^{44/40}$Ca value, indicating a potential contamination during pressing. [Table 2, Fig. 3 and Fig. 4 near here]

5. Discussion

5.1 Processes affecting the Calcium Concentration and its Isotopic Composition in the Pore Water

Different sampling techniques are used to obtain pore water samples from marine sediments. Currently, WR squeezing is one of the most common methods, especially within the scientific drilling program IODP. Rhizon samplers, however, have become an increasingly employed method not only for shorter cores (tens of meters), but also for deep cores drilled to hundreds of meters depth. During IODP Expeditions 320/321, a systematic test for Ca concentration and isotopic composition was conducted for the first time to evaluate possible influences of the applied sampling technique on the geochemical composition of pore water samples [20]. At Site U1332, samples were taken by both the WR and the Rhizon technique from parallel holes. The results for the element concentrations of Ba^+, Ca^{2+} and Mg^{2+} show a distinct offset between the two extraction techniques, while for Li^+ the differences were not as pronounced [20] (Fig. 1). The calcium and magnesium concentrations derived from the WR squeezing method are up to 6 % and 4 % higher, respectively, than those obtained from the Rhizons. For barium, the offset is even more pronounced, with concentrations from the WR method being more than three times higher than those from the Rhizon method.

In the following, we discuss which processes during sampling may be responsible for these offsets, and which sampling technique is more representative of the pristine pore water. This discussion also considers other geochemical tracers for which differences between Rhizon and WR sampling have been reported, as well as potential mechanisms that have been previously suggested to contribute to the offsets observed in the concentrations and isotope ratios of alkaline earth elements.

Potential processes that may alter the concentration and isotope ratios of alkaline earth elements in the pore water during sampling include precipitation or dissolution of carbonate minerals and ion exchange reactions with clay mineral surfaces. Owing to the different conditions during sampling (over-pressure during WR squeezing and under-pressure during Rhizon sampling), different processes may affect the pore water composition depending on which technique is applied. There are two main hypotheses which may explain the observed differences: a) The Ca chemistry in the pore water during sampling with the Rhizons is affected by carbonate precipitation, and b) during WR squeezing, desorption of clay-bound Ca or carbonate dissolution may take place.

A recent study by Schrum et al. [21] found that the reduced alkalinity and DIC concentrations during Rhizon sampling compared to WR samples are indicative of $CaCO_3$ precipitation, which may be induced by degassing of CO_2. The pH is altered during the Rhizon sampling [21]. This would be consistent with lower Ca concentrations in the pore water when using Rhizon samplers, as found in the samples of the present study. Another important conclusion drawn by Schrum et al. [21] is that the influence of CO_2 degassing during Rhizon sampling owing to pressure reduction is dependent on the sediment composition and pore water concentration of CO_3^{2-}. In carbonate-bearing sediments, the effect of CO_2 degassing is much more important than in clastic, detrital sediments [21]. Since the sediments studied at Site U1332 have overall high carbonate contents (Fig. 2), it is likely that calcium carbonate is precipitating during Rhizon sampling. This would lead to reduced pore water Ca concentrations and higher pore water $\delta^{44/40}$Ca values, as ^{40}Ca is preferentially incorporated into the solid $CaCO_3$ during precipitation [11] at relatively fast rates of carbonate precipitation [36]. In fact, this systematic is demonstrated by our samples, as the Rhizon-derived samples have systematically about 0.1 ‰ higher $\delta^{44/40}$Ca and lower calcium concentration compared to the WR-derived samples (Fig. 1 and 2).

5.2 Modelling the Influence of CO_2 Degassing and Desorption during Pore Water Sampling

To evaluate the influence of CO_2 degassing on the pore water Ca concentration and isotopy, and to test if the analyzed Ca concentrations and isotope ratios can quantitatively be explained by carbonate precipitation, the evolution of the pore water composition during $CaCO_3$ precipitation was modeled with a Rayleigh fractionation calculation (Eq. 2, Fig. 5 I).

$$\frac{\delta^{44/40}Ca}{\delta^{44/40}Ca_{initial}} = f^{(\alpha-1)} \qquad 2)$$

For this model, the average WR $\delta^{44/40}$Ca and calcium concentration values were used as starting point, assuming that the WR values approximate the pristine and unaffected pore water. Carbonate precipitation was modeled for three different fractionation factors, (1000 lnα) -0.6 ‰, -1.2 ‰ and -2.0 ‰, representing the range of Ca isotope fractionation found in $CaCO_3$ precipitation experiments [e.g. 36-39]. The model shows that carbonate precipitation during Rhizon sampling leads to higher $\delta^{44/40}$Ca and lower Ca concentration, but applying reasonable fractionation factors, the majority of the Rhizon-derived pore water sample compositions cannot be explained. Only a 1000 lnα factor of -2 ‰ covers two of the calcium isotope composition measured during Rhizon extraction. Explaining the Rhizon-derived data only by precipitation of $CaCO_3$ during sampling would therefore require unrealistically large Ca isotope fractionation factors. This reasoning strongly indicates that carbonate precipitation during Rhizon sampling alone cannot explain the offset between both sampling methods.

On the other hand, extracting pore water from the sediment using the piston cylinder press, adsorbed Ca may be desorbed from particle surfaces into solution, leading to an increase in Ca concentration. Because the lighter Ca isotopes are preferentially adsorbed to clays [12,40], the Ca concentration increase should be accompanied by lower $\delta^{44/40}$Ca. To test this hypothesis, we apply a mixing calculation, assuming the average $\delta^{44/40}$Ca value and Ca concentration of the Rhizons-derived pore waters as the "real", unaffected pore water value (Fig. 5 II). For the mixing calculation, we used the formula:

$$\delta^{44}Ca_{mix} = a * \delta^{44}Ca_{x} + \delta^{44}Ca_{y} * (1 - a) \qquad 3)$$

with x and y for two different components and (1-a) as a proportion of the component y.

To the average Rhizon calcium concentration and calcium isotopic values, the model adds three different endmember compositions to the pore water. The applied $\delta^{44/40}$Ca values of the added components (A: 1.2 ‰, B: 0.7 ‰ and C: -0.8 ‰) are representative of Ca desorbed from deep-sea clay minerals and marine biogenic carbonates. The $\delta^{44/40}$Ca endmember values are derived from the "real" pore fluid and the experimentally determined Ca isotope fractionation for the adsorption of Ca on the respective clay minerals (A: $1000 \ln\alpha = -0.5$ ‰ ≙ Montmorillonite; B: $1000 \ln\alpha = -1$ ‰ ≙ Illite and C: $1000 \ln\alpha = -2.5$ ‰ ≙ Kaolinite [12]). The $\delta^{44/40}$Ca of endmember B (0.7 ‰) agrees not only with Ca desorption from Illite, but also resembles the $\delta^{44/40}$Ca of marine biogenic and cement carbonate. Mixing calculation B is therefore also representative for carbonate mineral dissolution, a further potential source of Ca during WR sampling. Desorption of Ca from clay minerals or carbonate mineral dissolution would increase the Ca concentration and reduce the $\delta^{44/40}$Ca of the pore fluid compared to those samples with Rhizons. The model shows that endmember values of 0.7 to -0.8 ‰ calculated from analyzed pore water and experimental determined fractionation factor is the most likely to explain the offset between Rhizon and WR methods. Consequently, dissolution of calcium carbonate during WR pressing would be also in general agreement with the pore water Ca concentration and $\delta^{44/40}$Ca systematic, showing lower $\delta^{44/40}$Ca and higher Ca concentrations in the porewater samples derived from WR pressing compared to those sampled with Rhizons. The magnitude of this effect could be related to the lithology of the sediments, as $CaCO_3$ dissolution depends on the $CaCO_3$ content in the solid phase [e.g. 41]. However, the model demonstrates that an endmember composition in the range of natural clay mineral desorption cannot explain most of the analyzed data.

While neither calcium carbonate precipitation during Rhizon sampling nor Ca desorption during WR pressing alone can fully reproduce the analyzed data, a combination of both processes, calcium sourced from dissolution or removed through precipitation, may reconcile the observations. The noteworthy differences between the WR and Rhizon sampling technique in the pore water concentrations of other metal elements, the difference in the $\delta^{44/40}Ca$, and the Rayleigh calculation suggest the following concept: pressure release in the sediment by the gentle vacuum of the Rhizon sampling technique leads to precipitation of $CaCO_3$ and, subsequently, to desorption of Ca^{2+} from the clay mineral surfaces caused by the loss of Ca^{2+} in the pore waters following carbonate precipitation. The establishment of a new equilibrium between dissolved and adsorbed ions in the pore water system [12,42], elements such as Mg and Ba that compete for adsorption sites can also be adsorbed to or desorbed from mineral surfaces as the Ca concentration in the pore water increases or decreases. Given the fact that not only Ca but also Mg, Ba and Li are affected in the analyzed pore water samples, the reason for the differences between Rhizons and WR sampling techniques is most likely a coupled process of $CaCO_3$ precipitation and mineral surface desorption, since Mg and Ba are not as strongly affected by $CaCO_3$ precipitation as Ca. Calcium carbonate precipitation leads to increasing $\delta^{44/40}Ca_{PW}$ and to a reduction in Ca concentration in the pore water, which further causes a disequilibrium between dissolved and adsorbed Ca, leading to a desorption of Ca from clay mineral surfaces (Fig. 5 III). This effect causes a partial compensation of the precipitation related pore water Ca^{2+} concentration decrease and a potential lowering of the $\delta^{44/40}Ca_{PW}$, as the adsorbed Ca should be lighter than the dissolved pore water Ca. [Fig. 5 near here]

The amount and isotope composition of released Ca depends on the cation exchange capacity and isotope fractionation of the available clay minerals [12,42]. The calculated average amount of Ca^{2+} precipitated during the Rayleigh fractionation, thus the difference between the modelled Rayleigh value and the average of the WR is about 1.05 mM and after the assumed desorption of Ca^{2+} from the clay mineral surfaces, the difference between the two sampling techniques is about 0.37 mM. Average concentration differences of Mg and Ba between Rhizons and WR in the pore water is about 1.18 mM for Mg and 0.0015 mM for Ba (Fig. 6). This decrease of Mg and Ba in the pore water during Rhizon sampling is caused by Mg and Ba occupying the Ca places on the clay mineral surfaces that are vacant after its desorption. Especially Mg exhibits a high adsorption affinity to clay minerals [43,44]. These observations are in accordance with the model and the measured data. In addition, the equivalents of Mg newly adsorbed to the clay (difference between Mg_{WR} and Mg_{Rh}) agree well with the equivalent of desorbed Ca. Assuming that all surface sites are occupied, this ion exchange reaction would lead to a desorption of other cations, for example Mg, Ba and Li, as observed in the increase of these elements in the pore water samples, leading to higher concentrations in the WR samples. [Fig. 6 near here]

From the geochemical results alone, it cannot be unambiguously decided, which of the two scenarios are correct, either $CaCO_3$ dissolution and subsequent ion exchange during WR pressing or carbonate precipitation and ion exchange during Rhizon sampling, since both match the relative differences in $\delta^{44/40}Ca$ and Ca concentration of WR and Rhizon samples. However, taking into account the observation of Schrum et al. [21] it is more likely that rather $CaCO_3$ precipitation and Ca desorption occurs during Rhizon sampling than $CaCO_3$ dissolution and Ca adsorption during WR pressing. The impact of this precipitation-induced desorption on the pore water is therefore dependent on the clay mineral content and composition of the respective sediment. The effect of precipitation-induced desorption cannot be directly observed in our data because the effects of $CaCO_3$ precipitation and clay mineral desorption have a combined influence on the Ca concentration and $\delta^{44/40}Ca$ in the pore water system. The measured Rhizon samples have higher Ca isotope values than the WR samples, indicating that $CaCO_3$ precipitation is the dominant process, but the deviations from the Rayleigh fractionation trends indicate that the precipitation-induced desorption process is also taking place (Fig. 5 III). From the studied sediments, which are relatively rich in carbonate (16-90 wt% $CaCO_3$) no relation between lithology and carbonate precipitation-ion exchange behavior during Rhizon sampling was apparent. However, because the WR-Rhizon comparison experiment was restricted to relatively carbonate-rich sediments, a different systematic in carbonate poor lithologies cannot be completely ruled out and is pending further verification. However, in sediments with different mineralogical compositions, such as a higher content of clay minerals and thus higher amounts of adsorbed Ca^{2+}, the effect of Ca desorption may be larger.

To independently test, if precipitation-ion exchange during Rhizon sampling or rather carbonate dissolution or ion exchange during WR filter pressing takes place, we conducted a progressive pore water extraction experiment, which revealed a constant $\delta^{44/40}$Ca over the time (Table 2, Fig. 3). We can show with the time series experiment of the WR squeezing method on sediments of the Alaska margin that neither sampling duration nor pressure changes affect the $\delta^{44/40}$Ca isotope ratio, at least in the studied sediment type with low $CaCO_3$ contents (approximately 0.6 wt% $CaCO_3$ [32]). This indicates that there is either no Ca desorbed from clay minerals or $CaCO_3$ dissolved during the WR pore water squeezing, or the contributions of desorbed or dissolved and free pore water Ca stay constant throughout the sampling period, while preliminary experiments indicate that the calcium concentration sampled by Rhizons does not depend on sampling time [45].

6. Conclusion

During this study, a systematic difference in $\delta^{44/40}Ca_{PW}$ and Ca concentration between WR and Rhizon sampling technique was determined, with WR-derived samples showing higher Ca concentration and lower $\delta^{44/40}Ca_{PW}$ compared to the Rhizon-derived ones. No significant change in the Ca isotopic composition during progressive extraction of pore water in the piston cylinder press could be identified, indicating that no carbonate dissolution or Ca desorption under pressure takes place, or at least does not change with increasing pressure or sampling duration. Modelling $CaCO_3$ precipitation and Ca desorption suggests that the Rhizon samples are affected by a coupled process of $CaCO_3$ precipitation and Ca ion exchange from mineral surfaces, and that WR samples are probably more representative of the pristine pore water compared to the Rhizons. These observations point towards a systematic sampling bias between both methods. Following the Rayleigh model and mixing calculations, Rhizons could be used for sediments with low $CaCO_3$ content, while WR should perform better in carbonate rich sediments. However, the differences observed in our samples are small compared to the $\delta^{44/40}$Ca variability in natural pore waters and close to the present-day analytical precision. The observations for the Ca isotope system may also apply to other stable isotope systems, such as Mg, Ba and Li, as for these elements different element concentrations between WR and Rhizons were observed as well. While for most geochemical questions, pore water Ca isotope data obtained from both techniques appear to be compatible, the potential sampling bias may vary for different types of sediments and may become more significant as the analytical precision of Ca isotope analysis will increase.

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Declaration of Interest Statement

This study has no competing interests.

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Appendix

Porewater Sampling Techniques

For using the WR squeezing method, sample throughput is limited by the need of careful cleaning of the hydraulic press after every sample to prevent cross-contamination. During this pore water sampling method, the WR section of the sediment core is compressed by squeezing [27] with a pressure of up to 300 MPa, which is higher than any water pressure affecting sediments even in the deep ocean [28]. As a result, microbial cells may be destroyed, which may result in a contamination of the pore water by the release of cytoplasm [46]. Gieskes [2] studied some possible influences on pore water sample quality and considered them to be minimal, with only insignificant influence on geochemical measurements. The reaction with atmospheric oxygen was suggested to potentially alter the pore water chemistry [47] during sample preparation, but newer studies concluded that the WR method may even reduce the probability of reactions of the pore water with air during sampling, since there is almost no exposure of the sediment to the atmosphere within the press [21]. Rhizons were primarily developed to collect terrestrial soil water [26,27], but first applications to marine sediment cores by Seeberg-Elverfeldt et al. [22] on a gravity core and by Dickens et al. [27] to deep sea drill cores demonstrated the potential of this sampling technique for marine pore water and led to their increasing usage. The main advantage of the Rhizon sampling technique is that it is easily applicable in the field and does not require the use of large, heavy hydraulic presses. Further, it is possible to obtain high spatial resolution, and in addition numerous samples can be simultaneously collected using multiple Rhizon samplers, making the sampling much faster than with the hydraulic press. Another advantage is that the sedimentary record remains largely undisturbed, as the Rhizon sampler has a small diameter of 2.4 mm and uses a gentle vacuum to collect the interstitial water instead of applying pressure [22,27]. Rhizons make use of the natural permeability of the sediments to extract pore waters with their gentle vacuum, and therefore yield less pore water from clay-rich, consolidated sediments than the WR squeezing technique. In addition, the Rhizon samplers can bend or break when inserted into consolidated sediments of greater sediment depth [45], but this can be remediated by poking a hole into the sediment with a stick (see [20]). Further, the core liner can remain closed and Rhizon samplers can be inserted through drilled holes in the liner, thus the O_2 exposure remains minimal.

#	Sample Type	Time [minutes]	Volume [ml]	Pressure [MPa]	CSF-A [m]	$\delta^{44/40}$Ca [‰]	2 SE	n
U1417C								
17H-5	*WR*	1	3	55	148.9	1.51	0.06	8
17H-5	*WR*	3	2	55	148.9	1.58	0.01	2
17H-5	*WR*	5	2	55	148.9	1.58	0.04	2
17H-5	*WR*	8	2	55	148.9	1.51	0.01	2
17H-5	*WR*	25	2	70	148.9	1.51	0.01	2
17H-5	*WR*	30	3	70	148.9	1.49	0.05	4
17H-5	*WR*	45	2	75	148.9	1.51	0.02	4

#	Sample Type	$CaCO_3$ [wt %]*	Ca [mmol*l^{-1}]*	CSF [m]	$\delta^{44/40}$Ca [‰]	2 SE	n
U1332A							
3H-5	*Sed.*	25.2		20.85	0.59	0.02	2
4H-2	*WR*		10.8	25.85	1.58	0.02	4
4H-5	*WR*		10.7	30.35	1.65	0.05	4
5H-2	*WR*		10.6	35.35	1.59	0.02	4
5H-5	*WR*		10.4	39.85	1.62	0.03	3
5H-5	*Sed.*	81.8		39.85	0.83	0.04	2
6H-3	*WR*		10.4	46.35	1.63	0.06	4
6H-5	*WR*		10.2	49.35	1.62	0.04	4
7H-3	*WR*		10.7	55.85	1.66	0.12	4
8H-2	*Sed.*	70.9		65.35	0.57	0.02	2
U1332C							
4H-1	*RZ*		10.4	27.05	1.71	<0.01	2
4H-3	*RZ*		10.6	30.8	1.74	0.04	2
5H-1	*RZ*		10.3	36.55	1.69	0.04	3
5H-4	*RZ*		10.2	41.05	1.67	0.05	5
6H-2	*RZ*		10.2	48.3	1.71	0.02	2
6H-5	*RZ*		9.9	52.05	1.72	0.05	2
7H-5	*RZ*		10.3	56.8	1.73	0.02	2

Table 1: $\delta^{44/40}$Ca of the Whole Round (WR) time series experiment (U1417C) and of the Whole Round (U1332A) and Rhizon (RZ) samples (U1332C) and corresponding sediment samples (Sed.) of U1332A. *: Ca^{2+} concentration and $CaCO_3$ content of Site U1332 taken from Pälike et al. [20]. Depth is given as CSF or CSF-A (Core depth below Sea Floor).

#	Time [minutes]	Ca [mmol*l^{-1}]	Ba [µmol*l^{-1}]	Fe [µmol*l^{-1}]	Co [µmol*l^{-1}]
U1417C					
17H-5	1	23.06	2.46	44.56	0.03
17H-5	3	20.61	2.57	87.16	0.06
17H-5	5	17.84	1.95	41.48	0.03
17H-5	8	19.54	1.96	43.72	0.02
17H-5	25	21.28	1.92	41.05	0.02
17H-5	30	19.04	2.08	51.01	0.03
17H-5	45	20.85	2.22	53.52	0.03

Table 2: Elemental concentrations of the time series experiment of Ca, Ba, Fe and Co.

Analytical uncertainties are approximately 5-10 %.

Fig. 1: Comparison of Ca^{2+}, Ba^{2+}, Li^{+} and Mg^{2+} in pore waters retrieved by WR squeezing (diamonds) and Rhizon sampling (circles) of marine sediments of IODP Hole U1332 A and C, respectively [20]. The Ca^{2+}, Li^{+} and Mg^{2+} measured on WR derived samples show slightly higher concentrations and distinctly higher concentration for Ba^{2+}.

Fig. 2: Comparison of $\delta^{44/40}Ca$ of pore water (PW) retrieved by WR (Hole U1332A, diamonds) and Rhizon (Hole U1332C, circles) sampling with $\delta^{44/40}Ca$ values (this work) of the sediment (Hole U1332A, squares) and corresponding $CaCO_3$ contents (stippled line [20]). Calcium isotope measurements of WR and Rhizon samples show the same overall patterns, but Rhizon samples have slightly higher $\delta^{44/40}Ca$ values. The $CaCO_3$ content ranges for most sediments between 20 and 90 wt% [20].

Fig. 3: $\delta^{44/40}Ca$ as a function of elapsed time during WR pore water pressing during IODP Exp. 341. Increased pressure is indicated from 55 – 75 MPa. Stippled line shows average $\delta^{44/40}Ca$ value of all measurements. The second and third sample is slightly enriched in heavy isotopes. After three minutes, the $\delta^{44/40}Ca$ is levelling to the average value towards the end of the experiment. No release of Ca by ion exchange or carbonate dissolution due to pressure increase is recognizable. The $CaCO_3$ content of the squeezed sediment ranges between 0 and 1.5 wt% [32].

Fig. 4 Element concentration measurements of the time series experiment. The measurement after three minutes of Fe and Co reveal a potential contamination from the steel cylinders of the WR-press during sampling. The evolution of the Ba and Ca concentration remain comparable during the whole experiment.

Fig. 5: Pore water evolution calculations for $CaCO_3$ precipitation, dissolution, and ion exchange during WR (diamonds) and Rhizon sampling (triangles).

I: Rayleigh fractionation calculation of carbonate precipitation during Rhizon sampling (triangles). Assuming the average WR value is the "real" value. Pore water evolution during $CaCO_3$ precipitation calculated for 1000lnα of -0.6 ‰ (A), -1.2 ‰ (B) and -2.0 ‰ (C). The Rayleigh fractionation during carbonate precipitation cannot reproduce most of the measured values and is out of range of the error of the average Rhizon values (black triangle).

II: Mixing calculations of desorbed Ca from clay minerals with different fractionation factors and Ca from dissolved $CaCO_3$. Desorption and dissolution are not distinguishable since both processes release light Ca into the solution and may result in similar signatures as biogenic carbonate solutions. Taking the average Rhizon value (triangles) as "real" value, Ca is released due to the applied pressure of the WR method (diamonds). As light Ca isotopes are preferentially adsorbed on clay mineral surfaces, the more Ca is desorbed the lighter the pore waters will become [12]. Calculated for the endmembers 1.2 ‰ (M ≙ Montmorillonite), 0.7 ‰ (I ≙ Illite or carbonate dissolution) and -0.8 ‰ (K ≙ Kaolinite) and their fractionation factors (1000lnα of -0.5 ‰ (A), -1.0 ‰ (B) and -2.5 ‰ (C), respectively (fractionation factors from [12]).

III: Combined $CaCO_3$ precipitation and ion exchange during Rhizon sampling. While neither $CaCO_3$ precipitation nor desorption of light Ca alone can explain the offset between WR and Rhizons, we suggest coupled $CaCO_3$ precipitation and (secondary) desorption, indicated by the three arrows indicating Ca desorbed from the different clay mineral endmembers Montmorillonite (dashed arrow), Illite (solid arrow) and Kaolinite (dotted arrow).

Fig. 6: $\delta^{44/40}Ca_{PW}$ against the 1/Mg element concentrations from [20]. The dashed line represents the Rayleigh fractionation of Ca as shown in Fig. 5 III. It is noteworthy that the concentration of Mg decreases during Rhizon sampling more significantly than Ca. This can be explained by adsorption of Mg to the free clay mineral surfaces after the desorption of Ca from these. Error bar indicates an uncertainty of about 1 % (1 SD).