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Article

Online Acid Extraction Coupled with ICP–MS for Iodine-to-Calcium Ratio Measurements in Marine Carbonate Rock

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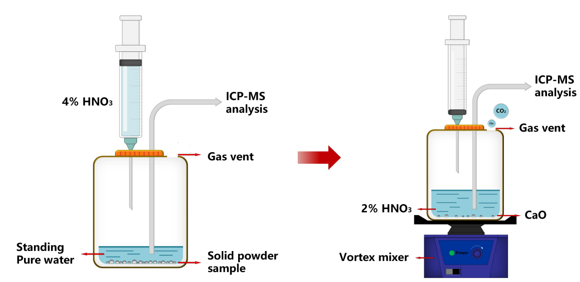
ABSTRACT: The iodine-to-calcium (I/Ca) ratio in marine carbonates can indicate changes in seawater redox. The use of inductively coupled plasma mass spectrometry (ICP–MS) to determine the I/Ca ratio in carbonates is challenging owing to low iodine content, volatility, and significant Ca matrix effects. In this study, an online extraction device was designed to evaluate the influence of extraction time on the detection of iodine signals. The intensity of I signal increased from 0 to 3 min after the addition of 2% HNO_3, and a stable I signal was obtained from 3 to 8 min. After 8 min, the analytical signal decreased owing to the volatilization of iodine. Experimental results revealed a linear relationship between the intensity of I/Ca ratio and the concentration of I/Ca ratio, indicating that Ca can serve as an excellent internal standard (I/Ca ratio) to correct the attenuation of the I signal caused by Ca matrix effects. Therefore, a novel online acid extraction method coupled with ICP–MS was developed by strictly controlling extraction time (3–5 min) and using the I/Ca ratio for direct correction to obtain the final I/Ca ratio, with a detection limit of 0.02 μmol/mol and relative standard deviation ranging from 1.5% to 10.3%. The proposed method was applied to determine the I/Ca ratio in carbonate reference materials. The measured I/Ca ratios were consistent with the reference values.



INTRODUCTION

As a new redox proxy, the iodine-to-calcium ratio (I/Ca) in marine carbonates can indicate changes in the redox state of seawater.[1–5] The potential principle is that the oxygen content of seawater is positively correlated with IO_3^-. During carbonate precipitation, IO_3^- (oxidation state I) is preferentially incorporated, whereas I^- (reduction state I) is not.[1,6–9] Therefore, the I content in marine carbonates indicates the oxygen content of ancient seawater, providing insights into the redox evolution of the ocean through geological time.[10–13] Thus, the accurate determination of iodine in marine carbonates is essential.

Currently, two main methods are used to measure I in marine carbonates: neutron activation analysis (NAA) and weak-acid extraction coupled with inductively coupled plasma mass spectrometry (ICP–MS). The NAA method has a low detection limit, low analytical efficiency, requires sample irradiation, and is limited by the availability of the instrument.[14–16] Therefore, ICP–MS has been adopted as the primary method in most laboratories. The dilute-acid dissolution method coupled with ICP–MS proposed by Lu *et al.*[1] involves weighing approximately 4 mg of a powdered sample and adding 3% nitric acid (HNO_3) to completely dissolve the carbonate sample. During ICP–MS analysis, indium and cesium (5 ng/mL) were used as internal standards. The final test solution was diluted to contain 50 ng/mL Ca and 0.5% tertiary amine (pH = approximately 3) to stabilize iodate and the internal standards in the solution. Loope *et al.*[17] employed the weak-dilute-acid dissolution method coupled with ICP–MS to determine iodine in marine carbonate samples from Turkey and South China across the Permian–Triassic boundary, aiming to constrain shallow marine redox conditions during the end-Permian mass extinction. Sun *et al.*[18] employed ICP–MS to measure the I/Ca ratios in modern deep-sea scleractinian and bamboo corals collected from oceans globally to investigate the mechanisms of incorporation of iodate into coral skeletons and to assess the potential of the I/Ca ratio of corals as a proxy for seawater oxygenation.

Although the ICP–MS method has been widely used, significant variations in the I/Ca values have been reported by different research groups for the same carbonate reference material (*e.g.*, JCp-1 coral powder). For example, Chai and Muramatsu[19] reported an I/Ca value of 4.33 ± 0.36 μmol/mol (n = 5), and Lu *et al.*[1] reported a value of 4.27 ± 0.06 μmol/mol (n = 8). More studies have reported lower values, such as that by Glock *et al.*,[20] which reported 3.82 ± 0.39 μmol/mol (n = 60), and that by Hardisty *et al.,*[3] which reported similar values. Recently, slightly higher I/Ca ratios have been reported, such as in the study by Winkelbauer *et al.*,[21] which reported a value of 4.53 ± 0.11 μmol/mol, and that by He *et al.*,[22] which reported a value of 4.52 ± 0.14 μmol/mol (n = 14). Long-term measurements at Syracuse University yielded an average I/Ca value of 3.70 ± 0.27 μmol/mol (1σ, n = 2280).[23] The main reasons could be as follows: 1) Loss of iodine owing to volatilization continues to affect the measured values. Glock *et al.* used the stabilizer tetramethylammoniumhydroxide (TMAH) and conducted ICP–MS detection within 2 h after sample preparation to minimize loss due to volatilization.[20] However, the addition of the organic reagent TMAH can introduce complex matrix effects during the detection of I by ICP–MS, including sensitization effects that lead to positive errors in I measurements.[24–26] In addition, I impurities in TMAH may also lead to inaccurate measurement of low I content. 2) The Ca matrix effect causes low I sensitivity during ICP–MS analysis,[27,28] usually requiring higher dilution factors (*e.g.*, >2000) for marine carbonates before ICP–MS analysis. Ca concentrations can remain as high as 200 ppm (*e.g.*, 2000 dilution) in the analytical solution, and the coexisting Ca ions generate space-charge effects during ion transport, which repel the target iodine ions and ultimately reduce the number of I ions reaching the detector of the ICP–MS. Although excessive dilution (*e.g.*, >2000) can reduce the Ca matrix effect, it also reduces iodine concentration (<0.5 ppb) in the analytical solution, making accurate measurement impossible (I content in marine carbonates is 0.05–0.5 ppm). Further research is required to address these issues.

The aim of this study was to systematically evaluate 1) the effect of extraction time on I volatility using a specially designed online extraction device and 2) the influence of a coexisting calcium matrix and its correction. A reliable online acid extraction method coupled with ICP–MS was developed for the accurate determination of the I/Ca ratio in marine carbonate rock based on the strict control of reaction time and the proposed I/Ca-based signal self-correction strategy.

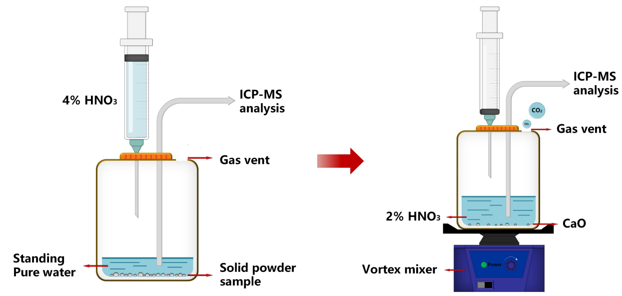


Fig. 1 Schematic of the real-time online monitoring device.

EXPERIMENTAL

Instrumentation. A simple reaction device was designed and coupled with ICP–MS for the online monitoring of the I signal to investigate the dissolution time required for complete iodine release with minimal volatilization loss in carbonate rocks. As shown in Fig. 1, this device consists of a syringe, a Savillex PFA reagent bottle with a gas vent drilled in its upper part to allow the escape of gases generated during the reaction (Eden Prairie, MN, USA), and a PFA sample tubing (ID: 0.5 mm, OD: 1.6 mm, Agilent Technologies, USA). The samples were thoroughly mixed with HNO_3 in the bottle using a vortex mixer (MX-S; Dragonlab, Shanghai). This setup enabled the real-time detection of short-term variations in iodine signals during the reaction between HNO_3 and carbonate rocks. Elemental analyses were performed using an inductively coupled plasma mass spectrometer (Agilent 7700x, Agilent Technologies, USA). Instrumental parameters were optimized using a 1 μg/L tuning solution to achieve maximum signal intensity and stability. Under the optimized ICP–MS conditions (Table S1), the intensity of the ^{127}I signal was >10000 cps ng^{-1} mL^{-1}. The background signal in 2% HNO_3 was less than 2000 cps.

Experimental procedures

(1) Approximately 100 mg of the powdered solid sample was placed in a PFA vial, followed by the addition of approximately 60 mL of ultrapure water. A syringe was preloaded with 50 mL of 4% HNO_3 for later use. The ICP–MS was operated in time-resolved analysis mode to monitor the background iodine signal in pure water.

(2) After the background signal stabilized, the 4% HNO_3 in the syringe was slowly introduced into the vial. The acid addition rate was carefully controlled to prevent the solid particles from being displaced or splashed by the rapid liquid flow.

(3) Once the reaction began, the mixture was gently vortexed for approximately 30 s to ensure completion. During this process, care was taken to prevent unreacted coarse particles from entering

the sample introduction line.

(4) The I signal was continuously recorded by the ICP–MS for 20 min.

Reagents. High-purity argon gas (99.999%) was supplied by Wuhan Heyuan Qingsheng Gas Co., Ltd. TMAH (25% aqueous solution) was purchased from Macklin Biochemical Co., Ltd. High-purity HNO_3 was prepared by single sub-boiling distillation using a Savillex PFA sub-boiling system (Eden Prairie, MN, USA). The standard solutions of Ca and Te (1000 µg/mL each) were obtained from the National Analysis Center for Iron and Steel, China. Potassium iodate (KIO_3, GR, 99.8% purity) was purchased from Macklin Biochemical Co., Ltd.

Reference materials. Four certified reference materials (CRMs) of carbonate rock—GSR-21, GSR-22, GSR-23, and GSR-27—and one reference material of coral— JCp-1—were purchased from the China National Institute of Metrology (NIM) and National Metrology Institute of Japan (NMIJ), respectively, to evaluate the accuracy of the developed method. A sediment CRM GSD-5a purchased from NIM was used to evaluate the effect of time on I extraction from noncarbonate components.

RESULTS AND DISCUSSION

Validation of the conventional method. During the initial experiments, we validated commonly used methods (*e.g.*, dissolution in HNO_3 with or without the TMAH stabilizer, followed by ICP–MS measurement within 2 h[19,20]) using carbonate CRMs. Isotope ^{126}Te was used as an internal standard to correct for potential signal drift caused by instrumental instability or matrix effects. External calibrations were performed using an I standard solution for quantification.

As listed in Table 1, the recoveries of iodine from the four CRMs, calculated as (measured/reference value) x 100%, ranged from 54% to 72% when the conventional HNO_3 dissolution method was used. Even when 0.5% TMAH was added as a stabilizer, iodine volatilization was only partially prevented, and the recoveries remained low (68%–80%). Such iodine losses are mainly attributed to the formation of highly volatile species (*e.g.*, HI) owing to reactions occurring in the acidic media. In addition, the large amount of CO_2 released during the decomposition reaction between carbonate materials and HNO_3 may facilitate the escape of volatile I_2, thereby intensifying iodine loss.[29, 30]

Therefore, the accurate analysis of I in carbonate rocks at low levels is challenging and requires careful consideration of the temporal variation in iodine volatilization and the effect of the coexisting Ca matrix on iodine measurements.

Table 1. Results of I determination in carbonate materials using two conventional ICP–MS methods (N = 3)

Carbonate rock CRMs		Dissolution by 2% HNO_3		Dissolution by 2% HNO_3 + 0.5%TMAH	
No.	Reference value (µg/g)	Measured value (µg/g)	Recovery (%)	Measured value (µg/g)	Recovery (%)
GSR-21	0.5	0.36±0.05	72	0.38±0.06	76
GSR-22	0.3	0.20±0.06	67	0.24±0.02	80
GSR-23	0.5	0.27±0.02	54	0.34±0.04	68
GSR-27	0.5	0.03±0.01	60	0.38±0.05	76

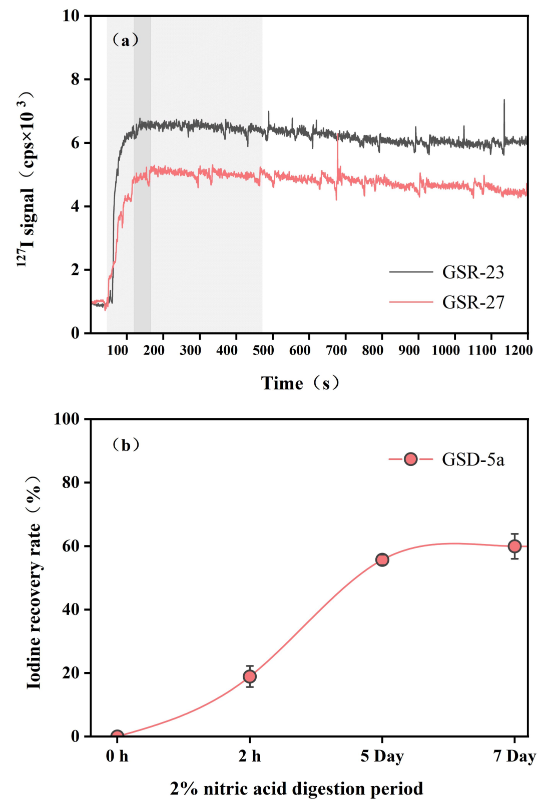


Fig. 2 (a) Variation in iodine signal intensity during the dissolution of carbonate rocks (GSR-23 and GSR-27) in 2% HNO_3. (b) Recovery of I during the dissolution of silicate material (GSD-5a) in 2% HNO_3.

Effect of extraction time on iodine release behavior. Fig. 2a shows the time-resolved iodine signals obtained during the dissolution of the CRMs (GSR-23 and GSR-27) in 2% HNO_3. The intensity of the iodine signal increased rapidly within 50–120 s, followed by a gradual increase and stabilization between 120 and 180 s. A steady-state condition was reached at approximately 180 s and was maintained between 180 and 480 s, after which the intensity of the signal gradually decreased. The overall changes in the intensity of iodine signal can be divided into three stages: (1) rapid-release stage: iodine was quickly liberated from the carbonate rock into the solution; (2) steady-state stage: the iodine signal remained relatively stable after the reaction between HNO_3 and the carbonate lattices; and (3) volatilization stage: volatile iodine species were formed under acidic conditions, leading to a gradual decrease in the intensity of the iodine signal by 700–1000 cps (approximately 15% iodine loss) within 20 min. After 2 h of dissolution, the total loss of iodine exceeded 20% (Table 1).

The effect of reaction time on the iodine release behavior was also investigated using a sediment reference material (GSD-5a), which is mainly the product of silicate weathering with a certified iodine content of 2.4 μg/g. As shown in Fig. 2b, 20% of the iodine (approximately 0.48 μg/g) was extracted after soaking GSD-5a in HNO_3 for 2 h, and up to 60% of the iodine was released after seven days. Because silicate lattices cannot dissolve in HNO_3,[31, 32] the extracted iodine could be inferred to originate mainly from the iodine adsorbed on the surface of GSD-5a. This observation supports previous findings that coexisting noncarbonate components (*e.g.*, organic matter) may cause a positive bias in iodine measurements.[33–35] Interestingly, only 2% of the iodine (approximately 0.048 μg/g) was extracted between 180 and 480 s (Fig. 2b), indicating that, to a certain extent, the contribution of iodine released from coexisting silicate components can be neglected when it is extracted from carbonate lattices. Therefore, rapid dissolution (3–8 min) in 2% HNO_3 coupled with online ICP–MS analysis is theoretically feasible. Considering the complete release of iodine from the carbonate lattice and the stability of the iodine signal, the ICP–MS data collection time can be controlled to within 3–5 min of acid addition (Fig. 2a). At this time, minimal iodine release from noncarbonate phases (*e.g.*, organic matter) can be ensured (Fig. 2b).

Ca matrix effect and I/Ca calibration. Fig. 3a shows that when the Ca concentration in the solution is below 100 μg/g, the ^{127}I signal is only slightly affected by matrix effects and instrumental drift. Therefore, conventional internal standards used for iodine determination, such as ^{126}Te, can still be used for correcting instrumental fluctuations and matrix-induced deviations caused by carbonate samples. However, when the Ca concentration exceeds 100 μg/g, partial Ca deposition occurs on the sampling cone surface, reducing ion transmission efficiency and compromising signal stability. This effect becomes particularly significant in high-Ca matrices and is one of the primary causes of ICP–MS signal attenuation and poor reproducibility.[27,28,29] In the extract solution of real carbonate rocks, which are characterized by high Ca content (approximately 40%) and low I content (<0.5 μg/g), even after 1000-fold dilution, the Ca concentration often exceeds 300 μg/g, leading to significant deviations of the measured iodine values from their true concentrations.

Interestingly, the synchronous variations in ^{127}I and ^{43}Ca signals shown in Fig. 3a indicate that ^{43}Ca serves as an ideal internal standard for iodine analysis in carbonate rocks. Compared with the exogenous internal standard (*e.g.*, ^{126}Te), using an intrinsic component (^{43}Ca) in carbonates could provide superior matrix compatibility and consistent signal response (Fig. 3a), thereby

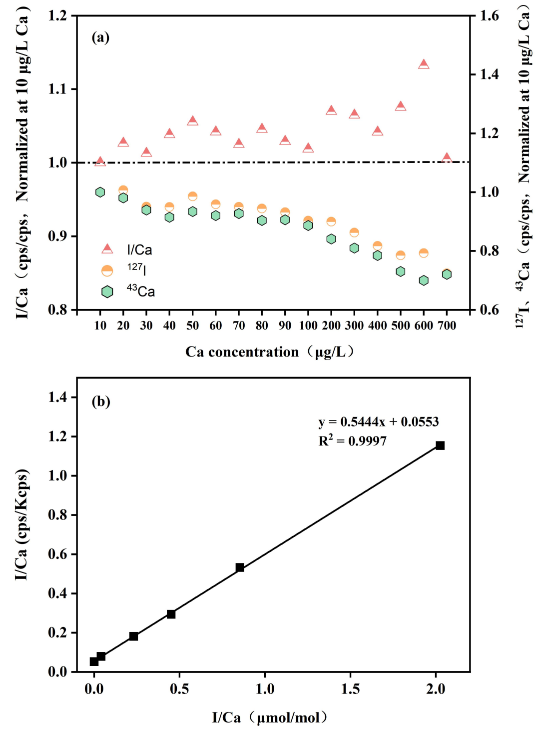


Fig. 3 (a) Effect of Ca matrix on iodine signal intensity (normalized to 10 μmol/mol Ca). (b) External standard curve of I/Ca (cps/Kcps) versus I/Ca (μmol/mol).

effectively minimizing measurement bias caused by compositional variations or dissolution conditions. As shown in Fig. 3b, excellent linearity ($R^2 = 0.9997$) was observed between the I/Ca signal ratios and I/Ca molar concentration ratios (0, 0.039, 0.20, 0.39, 0.79, and 1.97 μmol/mol). Thus, the final I/Ca molar concentration ratio for each carbonate sample can be obtained directly from the external calibration curve (Fig. 3b) by directly converting the measured intensity ratio (I/Ca, cps/Kcps) into the corresponding molar ratio (I/Ca, μmol/mol).

Analytical performance. The calculated detection limit of I/Ca for the proposed method is 0.02 μmol/mol, which is lower than that reported in previous studies (0.025-0.1 μmol/mol). [12,15,20,21] The detection capability of this method adequately covers the range of I/Ca ratios previously reported for marine carbonate rocks (0.1–2.5 μmol/mol).[2,9,13,36] The precision, expressed as the relative standard deviation from five replicate determinations, ranged from 1.5% to 10.3%.

Carbonate RM analysis. The proposed method was used to analyze three representative marine carbonate CRMs: marbles (GSR-21 and GSR-22), limestones (GSR-23 and GSR-27), and corals (JCp-1), originating from Southwest China and Japan. The $CaCO_3$ content of these samples ranged from 86.8% to 98.6% (Table 2). As listed in Table 2, the iodine concentrations in the four

Table 2. Measured I/Ca ratios in five carbonate CRMs (μmol/mol)

Carbonate CRMs No.	CaCO₃ %	Measured I/Ca (N=3)	Reported values	Reference values
GSR-21	92.28	0.47±0.05	0.47±0.03 [37] 0.51±0.05 [29]	0.46
GSR-22	86.84	0.29±0.06	0.30±0.08 [29]	0.32
GSR-23	98.59	0.36±0.08	0.40±0.02 [37] 0.53±0.07 [29]	0.40
GSR-27	96.41	0.38±0.08	0.28±0.02 [29]	0.41
JCp-1	95.54	3.64±0.11	4.27±0.06 [1] 4.67–5.31 [15] 4.33±0.36 [19] 3.82±0.39 [20] 4.53±0.11 [21] 4.52±0.14 [22]	3.70±0.27 [23]

GSR samples measured using the proposed method agreed well with the reference values (recoveries ranging from 91.3% to 104%), indicating the reliability of the developed method. For the coral JCp-1, although our measured value (3.64±0.11 μmol/mol) was slightly lower than those reported in previous studies (3.82–5.31 μmol/mol),[1,15,19-22] it agreed well with the long-term monitoring result (3.70 ± 0.27 μmol/mol) obtained by Lu's laboratory from 2012 to 2018,[23] further confirming the reliability of the method.

Potential limits. This method can be used for relatively pure marine carbonates or those containing small amounts of silicate phases. However, it cannot be employed for samples with complex compositions such as marine carbonates rich in organic matter, clay, or phosphates. In addition, I adsorbed on the surface of pure or slightly silicate-bearing marine carbonates may also be extracted, potentially leading to overestimated results. Therefore, in practical applications, careful sample selection is essential, and sedimentary carbonate samples with fewer coexisting components should be chosen.

CONCLUSION

This study demonstrates that the use of an online extraction device is an effective approach for evaluating the effect of extraction time on iodine analysis in marine carbonates. The coexisting Ca in the carbonate-extracted solution can serve as an excellent internal standard for I measurement by ICP–MS analysis, enabling the direct quantification of the I/Ca ratio or molar concentration ratios in marine carbonates. However, this method is mainly applicable to relatively pure carbonates (*e.g.*, >90% $CaCO_3$), and caution should be exercised when samples containing a high proportion of other complex phases (*e.g.*, marine carbonates rich in organic matter, clay, or phosphates) are analyzed.

AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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