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# Micropowder collecting technique for stable isotope analysis of carbonates

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**Micromilling is a conventional technique used in the analysis of the isotopic composition of geological materials, which improves the spatial resolution of sample collection for analysis. However, a problem still remains concerning the recovery ratio of the milled sample. We constructed a simple apparatus consisting of a vacuum pump, a sintered metal filter, electrically conductive rubber stopper and a stainless steel tube for transferring the milled powder into a reaction vial. In our preliminary experiments on carbonate powder, we achieved a rapid recovery of 5 to 100 µg of carbonate with a high recovery ratio (>90%). This technique shortens the sample preparation time, improves the recovery ratio, and homogenizes the sample quantity, which, in turn, improves the analytical reproducibility. Copyright © 2011 John Wiley & Sons, Ltd.**

The oxygen and carbon isotopes ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) of carbonate minerals provide an environmental record of the geological past. A recent trend in this research area is high-resolution analysis, and diversified tools have been developed to extract microgram-size sub-specimens from appropriate sites in rock and skeletal material. Micromills are currently the most commonly used tools in the intra-annual high-resolution sampling of diagenetic calcite cements,<sup>[1,2]</sup> stalagmites,<sup>[3]</sup> reef corals,<sup>[4,5]</sup> bivalves,<sup>[1]</sup> and fish otoliths.<sup>[6,7]</sup>

The sample quantity required for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  measurement has recently been significantly reduced with the technological advancement of mass spectrometers, which allows further increase in analytical resolution. Ishimura *et al.* have developed a continuous-flow system that only requires 0.2 µg of carbonate.<sup>[8]</sup>

However, one of the main problems regarding high-resolution analysis concerns the recovery ratio of the milled sample.<sup>[9]</sup> Until now, sample recovery has been mostly performed with a pointed scalpel blade,<sup>[1,7]</sup> and a substantial proportion of the milled material has been lost during transfer to a reaction vial. A higher recovery ratio has been demonstrated using a method developed by Charlier *et al.*, which was applied to single crystals in magmatic rocks.<sup>[10]</sup> In their method, milling was performed for a test sample covered with a droplet of ultrapure water, and the sample was then recovered as a slurry from the sample surface into a vessel using a micropipette. The obtained recovery ratio was 80–85%.<sup>[10]</sup> However, this is a time-consuming procedure,

and it is unsuitable for carbonate minerals that need to be completely dried before isotopic measurement. Here, we introduce a new recovery technique for carbonate specimens, and demonstrate experimental results showing that our technique improves recovery rate and handling time.

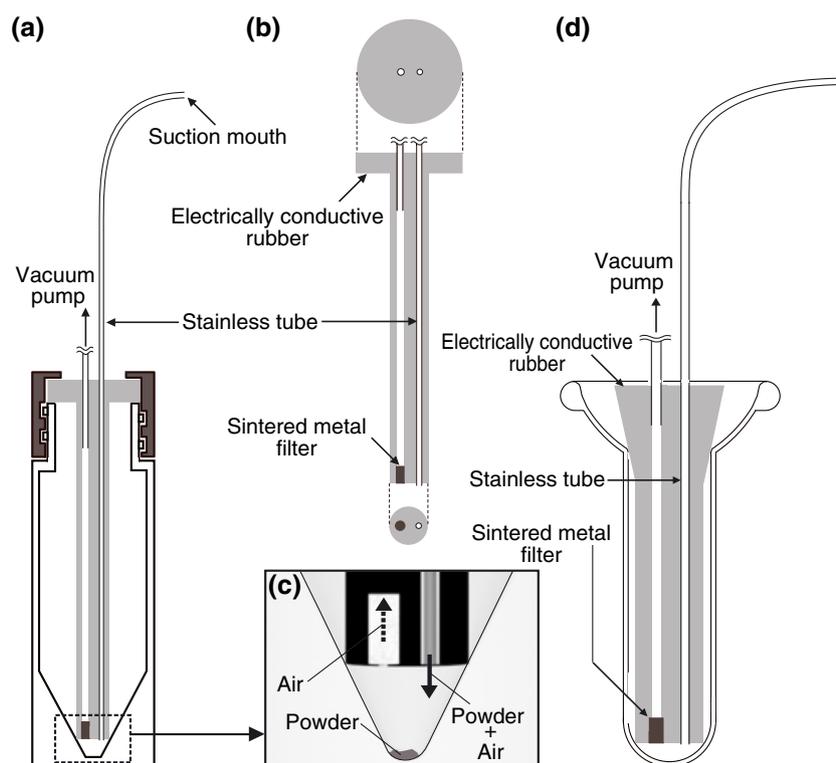
## APPARATUS

Our technique uses equipment having the same structure as a vacuum cleaner. The apparatus shown in this paper was designed to be used with glass vials from Isoprime Ltd. (Cheadle Hulme UK) and Thermo Fisher Scientific Inc. (Bremen, Germany) for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  analyses.

The apparatus consists of an electrically conductive rubber stopper, a stainless steel suction tube (0.6 mm o.d., 0.3 mm i.d.) for collecting powder, a sintered metal filter, and an evacuation tube connected to a vacuum pump (Fig. 1). A vinyl evacuation tube on the pump side and a stainless steel tube on the rubber stopper side are each connected to a sintered metal filter (1.0 mm o.d., 2 mm thickness) with a 1.0 µm opening. All these parts have an antistatic coating in order to prevent electrostatic adhesion of the powder to the inside of the suction tube and to the rubber surface.

The operation of this apparatus is quite simple. First, the cap of the glass vial is screwed down until the vial is sealed. At the same time, the circumference of the rubber end touches the inner surface of the glass vial (Figs. 1(a) and 1(b)). Thereby, a small airtight space is formed at the bottom of the vial (Fig. 1(c)). We used a diaphragm-type dry vacuum pump (oil-free: ULVAC Inc., Kanagawa, Japan) with an actual pumping rate of 12–14 L/min and an ultimate pressure of  $24.0 \times 10^3$  Pa. Next, the vacuum pump is turned on, and milled powder is collected using the tip of the suction tube (suction mouth; Fig. 1(a)). The powder is then sucked into the airtight space together with air, and only the

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**Figure 1.** Structure and operation procedure of apparatus for recovering powder sample for isotope analysis. The cap of the glass vial is screwed down (a) until the bottom of the electrically conductive rubber (b) touches the inside of the vial. Thereby, an airtight space is formed at the bottom of the vial (a, c). Powder from the suction mouth is transported to the airtight space with air, and the sintered metal filter (c) prevents sample loss through the evacuation tube. (d) Apparatus designed for vial used with the Kiel device manufactured by Thermo Fisher Scientific Inc.

air goes through the sintered metal filter and the evacuation tube. The powder remains at the bottom of the airtight space (Fig. 1(c)). After the vacuum pump has sucked up the powder, it remains switched on for a few seconds to remove any residual powder from the inside of the suction tube. Finally, the cap is unscrewed to remove the apparatus. The amount of powder remaining in the suction tube is usually negligible, but to err on the side of caution, the suction tube is cleaned with compressed air from the rubber end to avoid contamination.

## EXPERIMENTS

### Powder of known weight

In order to assess the powder recovery rate of the apparatus, a recovery test was performed using powder of known weights. Various amounts of calcite powder ranging from 5 to 100  $\mu\text{g}$  were weighed on paper using a microbalance. The weighed powders were transferred to the vial using the apparatus. We also measured 5–100  $\mu\text{g}$  of powder directly transferred to the vial, in order to obtain the relationship (for 100% recovery ratio) between the powder weight and the  $\text{CO}_2$ -gas volume emitted by reaction with purified phosphoric acid. The gas volume was quantified using the mass 44 ( $\text{CO}_2$ ) signal intensity on the mass spectrometer coupled with

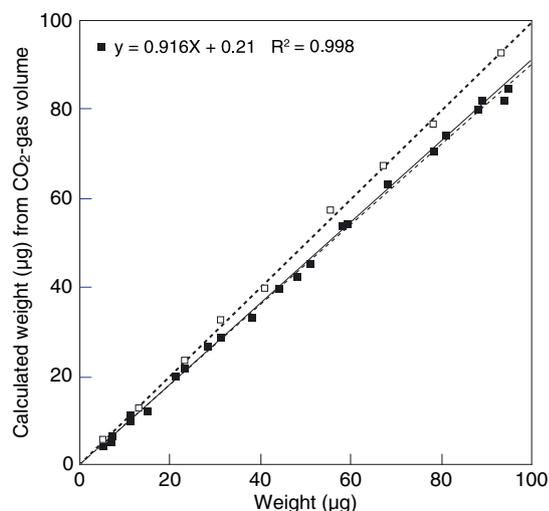
an automated carbonate preparation system (IsoPrime Ltd.) at the Japan Agency for Marine-Earth Science and Technology (JAMSTEC, Kangawa, Japan). The amount of powder recovered by the apparatus was then calculated based on the intensity of the mass 44 signal.

### Milled powder obtained using micromill system

In order to use the apparatus with biogenic carbonates, powder samples were taken from cold-water coral *Lophelia pertusa*, which was collected by the Integrated Ocean Drilling Program (IODP Expedition 307) in the northeast Atlantic, using a computer-controlled micromill system (Geomill 326; Izumo-Web Co., Ltd., Shimane, Japan). Twenty samples were taken across 700  $\mu\text{m}$  of accretionary growth. The milled trench was set to be 50  $\mu\text{m}$  wide and 200  $\mu\text{m}$  deep. The polished specimen and two-dimensional plots of coordinates along growth features are shown in Fig. 3(a). The volume of milled carbonate was calculated from the length, width, and depth of each trench, and the mass was calculated by assuming that the sample consists of solid aragonite (horizontal axis of Fig. 3(b)). The powder was transferred from each trench to the reaction vial using the apparatus and measured using the mass spectrometer (IsoPrime Ltd.). The amount of powder recovered was quantified from the volume of the  $\text{CO}_2$  gas (mass 44 signal intensity).

## RESULTS AND DISCUSSION

Figure 2 shows the results of the recovery rates in the first experiment; the transfer of the weighed powder using the apparatus. The sample weights, ranging from 5 to 100  $\mu\text{g}$ , are highly correlated with the  $\text{CO}_2$ -gas volume ( $R^2 > 0.99$ ). The dashed line in Fig. 2 indicates 100% recovery, and most of the results indicate recovery ratios of greater than 90%. The



**Figure 2.** Sample recovery of carbonate powder of known weight (5–100  $\mu\text{g}$ ). Solid squares indicate the results obtained with the apparatus. Recovery ratios greater than 90% (thin-dashed line indicates theoretical 90% recovery) were obtained with the apparatus, in contrast to the procedure without the apparatus (thick-dashed line with white squares indicates 100% recovery;  $R^2 = 0.995$ ).

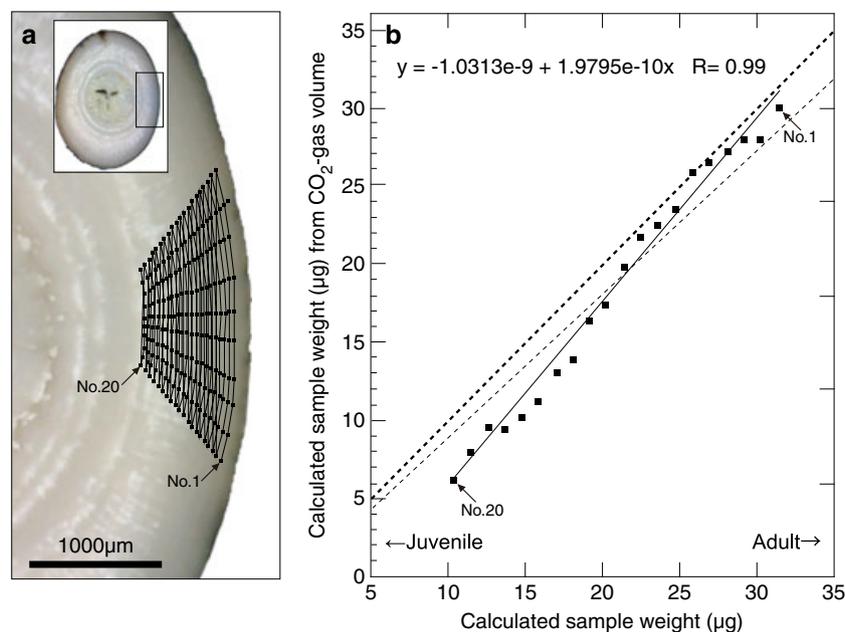
regression line of the results almost intersects the origin (Fig. 2), indicating that our apparatus can obtain a high recovery ratio even for a small amount of powder. The loss of up to 10% of the powder may be due to the electrostatic adhesion of the powder to the inside of the stainless steel tube and electrically conductive rubber stopper.

Figure 3 shows the results of the second experiment of micromilling a coral (*Lophelia pertusa*) skeleton. The measured sample weights ranging from 10 to 30  $\mu\text{g}$  are highly correlated with calculated weights ( $R = 0.99$ ), which means that there is effective sample recovery as well as accurate mount control of the micromilling system. The regression line has a larger x-intercept (2.0  $\mu\text{g}$ ; Fig. 3) than the line of the first experiment (Fig. 2). This probably means that there is some adhesion of the powder in the milled trench.

The apparatus presented in this study could be used to improve the efficiency of serial microsampling for high-resolution isotope analysis. The apparatus can be modified to accommodate various types of reaction vials that have a tapered structure by adjusting the length and width of the rubber component. For example, an apparatus for use with a Kiel device manufactured by Thermo Fisher Scientific Inc. is shown in Fig. 1(d).

## CONCLUSIONS

By combining the apparatus described with a computer-controlled micromill, we can easily and directly collect a complete time-series transect in a carbonate sample. Therefore, this technique can be a powerful tool for high-resolution analyses of the growth banding of biogenic carbonates and it is applicable to the microsampling of other geological materials.



**Figure 3.** Results of micromilling of a coral skeleton (*Lophelia pertusa*). (a) Lines on the skeleton are milled trenches, which follow the growth bands, (b) Calculated weight by micromill system vs. calculated weight from  $\text{CO}_2$ -gas volume for each sampling trench.

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