速 報

SHORT NOTE**Separation of CO₂ from SO₂ with Frozen *n*-Pentane
as a Technique for the Precision Analysis of ¹⁸O in Sulfates**

YOSHIHIKO MIZUTANI* AND SHINYA OANA*

(Received 5 July 1973)

A technique for the extraction of oxygen as carbon dioxide from sulfates has been recently developed for studying oxygen isotopic variations in sulfates occurring in nature¹⁾. The principle of the technique involves the recovery of sulfates as barium sulfate by normal chemical procedure, the reduction of barium sulfate with pure graphite at temperatures of 1000–1100°C in a vacuum system to extract oxygen as carbon dioxide and carbon monoxide, and the conversion of carbon monoxide into carbon dioxide by electric discharge at the liquid nitrogen temperature. The carbon dioxide obtained is analyzed for ¹⁸O by a McKinney-type mass spectrometer.

It has been, however, known for some time that the reduction of impure barium sulfate results in the presence of sulfur dioxide in the carbon dioxide, and that the sulfur dioxide content in carbon dioxide appears dependent upon the amount of impurity in the barium sulfate. The sulfur dioxide gives unfavourable effects upon the precision of the oxygen isotope measurements of the carbon dioxide. The carbon dioxide, if it contains

more than a few per cent of sulfur dioxide, presumably differs in oxygen isotopic ratio from the barium sulfate from which the carbon dioxide is prepared, because of the oxygen isotopic fractionation between carbon dioxide and sulfur dioxide during the carbon reduction. In addition, if the carbon dioxide contains more than 3 % of sulfur dioxide, the recorder trace of the oxygen isotope measurement of carbon dioxide is disturbed by the sulfur dioxide, as shown in Fig. 1. Although the reason why the sulfur dioxide gives such a zigzag variation to the recorder trace is unknown, the effect apparently heightens with increasing sulfur dioxide content of carbon dioxide.

The HF-HCl treatment can be used to remove impurities, such as silicates and carbonates, from the barium sulfate without any appreciable oxygen isotopic change, as described by Rafter and Mizutani²⁾. However, in the case of rather clean barium sulfates, from which the carbon dioxide containing only less than a few per cent of sulfur dioxide can be obtained, the removal of sulfur dioxide from the carbon dioxide may be more helpful for

* Department of Earth Sciences, Faculty of Science, Nagoya University, Chikusa, Nagoya, Japan

Fig. 1. Typical recorder trace of mass spectrometric ^{18}O analysis of carbon dioxide, showing the effect of coexisting sulfur dioxide.

Trace 1: $\text{SO}_2 = 0.80\%$, and Trace 2: $\text{SO}_2 = 0.18\%$.

the oxygen isotopic analysis than the purification of the barium sulfate. Thus, the *n*-pentane technique described by Oana and Ishikawa³¹, with some modifications, has been examined to remove sulfur dioxide from the carbon dioxide extracted from barium sulfates by the carbon reduction.

The apparatus used is shown in Fig. 2. After the system is evacuated, tap B is closed and the carbon dioxide extracted from the

Fig. 2. Apparatus for the separation of carbon dioxide from sulfur dioxide.

A, B, C, and D: tap, E: Pirani gauge, F: gas sample bottle, G: trap, H: *n*-pentane bath, and I: Dewar flask containing liquid nitrogen.

barium sulfate is transferred into the system through tap D by cooling trap G with liquid nitrogen. After tap D is closed, trap G is immersed in a *n*-pentane bath and then a Dewar flask containing liquid nitrogen is placed around the *n*-pentane bath until *n*-pentane is completely frozen. The carbon dioxide is condensed again into trap G, and a residuum, if any, is pumped off. The liquid nitrogen is removed from trap G and is placed around the gas sample bottle. As the temperature of trap G rises from the liquid nitrogen temperature to the melting point of *n*-pentane, -130.8°C , carbon dioxide evolves slowly from trap G and condenses into the gas sample bottle, leaving sulfur dioxide in trap G. The evolution of carbon dioxide is easily followed by measuring the pressure change by a Pirani gauge attached to the system. When the Pirani gauge reading decreases to less than 5×10^{-3} mmHg, tap A is closed. Fig. 3 shows two examples of the pressure change in the Pirani gauge reading during this separation process.

In order to see whether this separation process gives any isotopic change to the carbon dioxide, the procedure has been tested on the mixtures of sulfur dioxide and carbon dioxide of a known oxygen isotopic composition. The

**Separation of CO₂ from SO₂ with Frozen *n*-Pentane
as a Technique for the Precision Analysis of ¹⁸O in Sulfates**

Fig. 3. Separation of carbon dioxide from sulfur dioxide with frozen *n*-pentane.

Run 1: the sample is a mixture of 2 cm³ of CO₂ and 2 cm³ of SO₂ (STP), Run 2: the sample is a mixture of 3.9 cm³ of CO₂ and 0.1 cm³ of SO₂ (STP). Arrows (1) and (2) indicate the time at which tap A was closed on Runs 1 and 2, respectively. Time: from the removal of liquid nitrogen from the *n*-pentane bath, and pressure: Priani gauge reading.

results obtained are quite satisfactory in the purity and isotopic recovery of carbon dioxide, as shown in Table 1.

The test has been also done to see the isotopic reproducibility of the over-all analytical procedure for the oxygen isotopic analysis of sulfates. Four barium sulfate samples have been analyzed by the carbon reduction method of Mizutani⁴⁾ followed by the above-mentioned *n*-pentane treatment.

Table 2 shows the results obtained. It is

found that the sulfur dioxide content of carbon dioxide can be always reduced to less than 0.2 % by the *n*-pentane treatment, and that the oxygen isotopic analysis of sulfates seems to be reproducible within the error of the order of 0.1 ‰ by help of the *n*-pentane treatment.

In summary, it can be said that the *n*-pentane technique developed is simple and rapid, and that it affords more reliability to the oxygen isotopic analysis of sulfates by the carbon reduction method.

Table 1. Oxygen isotopic composition and the sulfur dioxide content of carbon dioxide before and after the *n*-pentane treatment to remove sulfur dioxide.

Sample No.	Before treatment		After treatment	
	SO ₂ , %	δ ¹⁸ O, ‰ SMOW	SO ₂ , %	δ ¹⁸ O, ‰ SMOW
M-190	50	n. d.*	0.2	n. d.*
M-191-1	4.5	+8.7	0.2	+8.7
M-191-2	1.9	+8.7	0.3	+8.7
M-191-3	1.4	+8.7	0.2	+8.5
M-191-4	0.6	+8.7	0.2	+8.6

* Not determined.

Y. Mizutani and S. Oana

Table 2. Oxygen isotopic composition and the sulfur dioxide content of the carbon dioxide extracted from barium sulfates by the carbon reduction method.

Sample No./Run No.	Before the <i>n</i> -pentane treatment		After the <i>n</i> -pentane treatment	
	SO ₂ , %	δ ¹⁸ O, ‰ SMOW	SO ₂ , %	δ ¹⁸ O, ‰ SMOW
A-24/1	2.6	—*	0.21	+3.0
A-24/2	2.2	—*	0.15	+3.3
M-125/1	0.72	—*	0.16	+1.9
M-125/2	0.80	—*	0.18	+1.9
A-7/1	n. d.	+3.2	n. d.	n. d.
A-7/2	n. d.	+2.7	n. d.	n. d.
A-7/3	0.40	+2.9	0.14	+2.8
A-7/4	0.48	+3.2	0.15	+2.8
A-7/5	0.36	+3.4	0.17	+3.0
M-200/1	0.14	+9.8	0.10	+9.7
M-200/2	0.11	+9.9	0.07	+9.8
M-200/3	0.06	+9.9	0.04	+9.9

* Could not determined because of the zigzag variation of the recorder trace.

References

- 1) e. g.; T. A. Rafter, *N. Z. J. Sci.*, **10**, 493 (1967), and Y. Mizutani, *Geochem. J.*, **5**, 69 (1971).
- 2) T. A. Rafter and Y. Mizutani, *N. Z. J. Sci.*, **10**, 816 (1967).
- 3) S. Oana and H. Ishikawa, *Geochem. J.*, **1**, 45 (1966).
- 4) Y. Mizutani, *Geochem. J.*, **5**, 69 (1971).