

Rapid Commun. Mass Spectrom. 2014, 28, 1321–1328
(wileyonlinelibrary.com) DOI: 10.1002/rcm.6898

Oxygen isotopic fractionation of O₂ during adsorption and desorption processes using molecular sieve at low temperatures

Insu Ahn^{1,2*}, Minoru Kusakabe³ and Jong Ik Lee¹

¹Korea Polar Research Institute, Incheon 406-840, Korea

²Department of Earth and Planetary Material Science, Tohoku University, Aramaki, Aoba, Sendai, Miyagi 980-8578, Japan

³Department of Environmental Biology and Chemistry, The University of Toyama, Toyama 930-8555, Japan

RATIONALE: Cryogenic trapping using molecular sieves is commonly used to collect O₂ extracted from silicates for ¹⁷O/¹⁶O and ¹⁸O/¹⁶O analyses. However, gases which interfere with ¹⁷O/¹⁶O analysis, notably NF₃, are also trapped and their removal is essential for accurate direct measurement of the ¹⁷O/¹⁶O ratio. It is also necessary to identify and quantify any isotopic fractionation associated with the use of cryogenic trapping using molecular sieves.

METHODS: The oxygen isotopic compositions of O₂ before and after desorption from, and adsorption onto, 13X and 5A molecular sieves (MS13X and MS5A) at 0°C, -78°C, -114°C, and -130°C were measured in order to determine the oxygen isotopic fractionation at these temperatures. We also investigated whether isotopic fractionation occurred when O₂ gas was transferred sequentially into a second cold finger, also containing molecular sieve.

RESULTS: It was confirmed that significant oxygen isotopic fractionation occurs between the gaseous O₂ and that adsorbed onto molecular sieve, if desorption and adsorption are incomplete. As the fraction of released or untrapped O₂ becomes smaller with decreasing trapping temperature (from 0 to -130°C), the isotopic fractionation becomes larger. Approximately half of the total adsorbed O₂ is released from the molecular sieve during desorption at -114°C, which is the temperature recommended for separation from NF₃ (retained on the molecular sieve), and this will interfere with ¹⁷O/¹⁶O measurements.

CONCLUSIONS: The use of a single cold finger should be avoided, because partial desorption is accompanied by oxygen isotopic fractionation, thereby resulting in inaccurate isotopic data. The use of a dual cold finger arrangement is recommended because, as we have confirmed, the transfer of O₂ from the first trap to the second is almost 100%. However, even under these conditions, a small isotopic fractionation (0.18 ± 0.05‰ in δ¹⁷O values and 0.26 ± 0.06‰ in δ¹⁸O values) occurred, with O₂ in the second trap being isotopically enriched in the heavier isotopes. Copyright © 2014 John Wiley & Sons, Ltd.

Oxygen has three stable isotopes (¹⁶O, ¹⁷O and ¹⁸O), with natural abundance of approximately 99.76%, 0.04% and 0.20%, respectively. Oxygen triple-isotopic variations are important diagnostic tracers of extra-terrestrial materials, and, in recent years, they have been applied to studies of terrestrial silicates. The oxygen isotopic ratios of silicate or oxide rocks and minerals are usually measured using O₂ as the analyte gas. Fluorination of the silicate or oxide is followed by purification of the resulting O₂, for isotope ratio measurements using a gas source isotope ratio mass spectrometer. Alternatively, secondary ion mass spectrometry measurements may be employed. In the fluorination technique, a strong oxidizing agent such as F₂ (e.g. Wiechert and Hoefs^[1]) or BrF₅ (e.g. Clayton and Mayeda^[2]) is used to decompose silicates and oxides at high temperature. In recent years, an IR (or UV) laser has been used to promote reaction, at high temperature, between the fluorinating

agent and the silicates or oxides.^[3–11] Extracted oxygen gas from the sample is then purified through several liquid nitrogen traps in a vacuum line before being collected in a cryogenic trap containing molecular sieve, prior to being admitted to the mass spectrometer for isotope ratio measurements.

When cooled to liquid nitrogen temperature, molecular sieves adsorb most gases that would otherwise still be in the vapour phase at that temperature. In the case of silicates that contain nitrogen-bearing compounds (carbonaceous chondrite meteorite samples, for example), traces of NF₃ may be produced together with the principal reaction products O₂ and SiF₄ during the fluorination process. NF₃ is decomposed by electron ionization in the mass spectrometer ion source to form NF⁺ and NF₂⁺. The ¹⁴N¹⁹F⁺ ion has an *m/z* value of 33 and it therefore interferes with the mass 33/32 ratio measurement of O₂ (as required for δ¹⁷O determination). Two methods have been proposed to overcome the NF₃ problem. (1) As advocated by Pack *et al.*,^[13] O₂ is admitted into the mass spectrometer without any cryogenic removal of NF₃. The 'excess' *m/z* 33 signal contributed by NF⁺ is then evaluated and corrected for, from the correlation between the measured 33/32 ratio and the intensity of the *m/z* 52 peak (NF₂⁺). More

* Correspondence to: I. Ahn, Korea Polar Research Institute, Incheon 406-840, Korea.
E-mail: 1128@snu.ac.kr

usually, (2) NF_3 is cryogenically removed from the analyte O_2 , by transfer between two cold fingers containing molecular sieve, before admission of the purified O_2 into the mass spectrometer.^[8,11,12] In this process, O_2 that may have been contaminated by NF_3 is adsorbed onto molecular sieve in the first cold finger at liquid nitrogen temperature (-196°C). The trapped O_2 is subsequently released at -114°C (the melting point of ethanol), while NF_3 is retained by the molecular sieve. The released O_2 is then transferred into a second cold finger containing molecular sieve cooled to liquid nitrogen temperature. After complete transfer of the O_2 , the first trap is isolated by closure of a valve. If only a single cold finger is used, a significant amount of O_2 may still remain on the molecular sieve at -114°C , thereby causing isotopic fractionation. We also found that a trapping temperature of -130°C is not low enough to trap all the gas onto the molecular sieve. Thus, isotopic fractionation may be unavoidable when NF_3 is separated using a single cold finger.

Abe^[14] reported evidence of oxygen isotopic fractionation during adsorption of O_2 onto, and desorption of O_2 from, molecular sieves. He also confirmed isotopic fractionation by incomplete desorption related to the amount of molecular sieves, and estimated that the maximum oxygen isotopic fractionation, reported in terms of the $^{18}\text{O}/^{16}\text{O}$ enrichment factor, and representative of kinetic isotope fractionation during O_2 desorption, could be as large as -4% . However, details of the relative proportion of O_2 that was adsorbed or desorbed at low temperature and the isotopic fractionation during adsorption of O_2 onto, and desorption from, molecular sieves are still not fully understood. In this paper, we present detailed experimental data from an investigation of oxygen isotopic fractionation during desorption and adsorption of O_2 using a single cold finger at different cryogenic temperatures. We also report data obtained from

the use of a dual cold finger arrangement for purification of the O_2 in order to check the oxygen isotopic fractionation that could be accompanied during the transfer of O_2 .

EXPERIMENTAL

For the extraction of O_2 from rocks and minerals, we used the CO_2 laser fluorination system at the Korea Polar Research Institute (KOPRI), Incheon, Korea.^[10] After fluorination, O_2 from any sample is purified and finally recovered in a cold finger made of Pyrex[®] glass tube that contains a pellet of molecular sieve cooled to liquid nitrogen temperature. Synthetic zeolite molecular sieves have a pore size varying from approximately 3 \AA to 10 \AA .^[15,18] In the fluorination technique, purified O_2 is collected onto either MS13X^[2,8-11] or MS5A^[6,7] molecular sieves. In our study, a single MS13X or MS5A pellet, of diameter $1/8''$, was placed in a cold finger; the pellets weighed 96.7 mg for MS13X and 88.6 mg for MS5A. All the pellets were heated to 350°C for 2 h under vacuum at pressure of less than $1.0 \times 10^{-4} \text{ mbar}$, and evacuated overnight at room temperature. Prior to the pellets being used, they were heated again at 350°C for 2 h, in order to remove any gas from the pellets.

Desorption experiments using a single cold finger were conducted as shown in Fig. 1. KOPRI's laboratory reference O_2 gas (referred to as 'KO' hereafter) was introduced into the cold finger and adsorbed at liquid nitrogen temperature. After all the KO was adsorbed (monitored by a micro pressure-transducer), the liquid nitrogen was replaced by a cryogenic bath that was kept at the melting temperature of n-pentane (-130°C), ethanol (-114°C), dry ice (-78°C), or ice (0°C). As the temperature of the cold finger rose from -196°C to the selected cryogenic temperatures, O_2 gas was released from the molecular sieve. This gas was expanded into

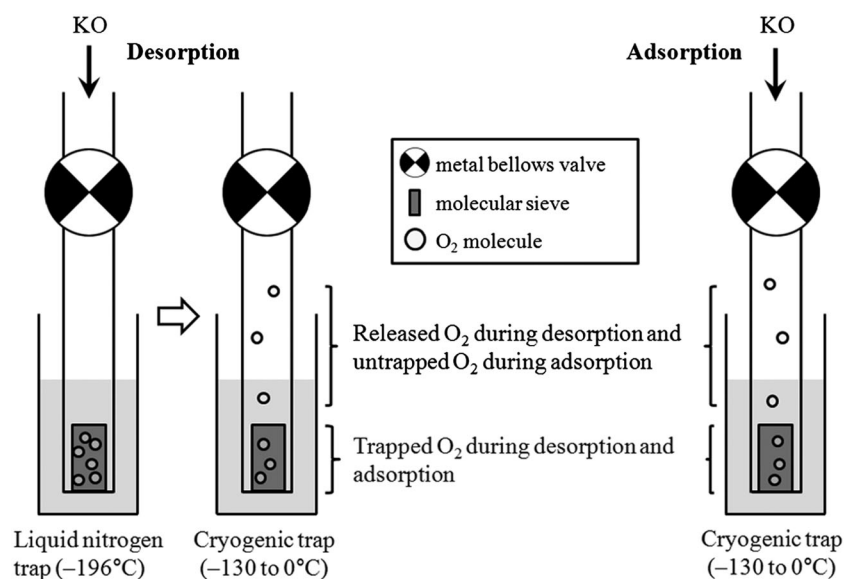


Figure 1. Desorption and adsorption experiments. After all the KO had been adsorbed at liquid nitrogen temperature, the liquid nitrogen trap was replaced by other cryogenic slushes, and desorption experiments were then conducted. For adsorption experiments, KO was directly adsorbed onto the molecular sieve at different cryogenic temperatures.

the sample bellows of the mass spectrometer, for subsequent measurement of the oxygen isotopic composition. For the adsorption experiments, KO was directly adsorbed onto MS13X or MS5A in a cold finger at the respective slush bath temperatures without any prior step (Fig. 1). Both trapped and untrapped O₂ were admitted into the mass spectrometer for isotopic measurements.

We also examined whether isotopic fractionation occurred when the O₂ gas was transferred to, and released from, an arrangement of two cold fingers connected to the vacuum line (Fig. 2). Approximately 90 mg of MS13X was placed in each cold finger. The analytical steps will be described later in more detail.

The variation of the three oxygen isotopes is generally reported using the delta notation, i.e., $\delta^x\text{O} (\text{‰}) = \left[\frac{(\text{}^x\text{O}/\text{}^{16}\text{O})_{\text{sample}}}{(\text{}^x\text{O}/\text{}^{16}\text{O})_{\text{reference}}} - 1 \right]$, where x is either 17 or 18. The oxygen isotopic compositions of most terrestrial samples fall along a linear array on a $\delta^{17}\text{O}$ vs $\delta^{18}\text{O}$ plot; this is the so-called 'terrestrial fractionation' (TF) line and is approximated by $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$ (e.g., Matsuhisa *et al.*^[16]). However, this relationship deviates considerably from linearity when the delta values are far from the point of origin (e.g., the deviation becomes $>1.2\text{‰}$ when $\delta^{18}\text{O} = \pm 50\text{‰}$; see Fig. 7 in Ahn *et al.*^[10]), since the linear expression is an approximation of a power law. Thus, we report our results using a delta prime notation, $\delta^x\text{O} = 1000 \times \ln(1 + \delta^x\text{O})$, as proposed by Miller.^[17] The deviation from the TF line is then defined as $\Delta^{17}\text{O} = \delta^{17}\text{O} - \lambda \times \delta^{18}\text{O}$, where λ is the slope of the TF line. In this study we use a value of 0.5248 for λ .^[10] The data in our tables, figures and text are reported as delta prime values

relative to KO (e.g., as the respective $\epsilon^{17}\text{O}$ and $\epsilon^{18}\text{O}$ factor, as described below). The errors are given as 1σ (standard deviation) unless otherwise stated. The $\Delta^{17}\text{O}$ values are presented as delta prime values calculated after the respective $\epsilon^{17}\text{O}$ and $\epsilon^{18}\text{O}$ results have been converted into the corresponding $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values relative to VSMOW (Vienna Standard Mean Ocean Water).

The oxygen isotopic compositions of O₂ were determined with high precision using an isotope ratio mass spectrometer of high abundance sensitivity (PRISM III, VG Isotech, Manchester, UK). The typical analytical precision was better than $\pm 0.05\text{‰}$ for both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values.^[10] The laboratory working standard gas, KO, used for the experiments, was high purity (99.999%) O₂. The reproducibility of the KO gas measurements ($n=98$) was $\pm 0.06\text{‰}$, $\pm 0.08\text{‰}$ and $\pm 0.05\text{‰}$ for $\delta^{17}\text{O}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values, respectively. Samples smaller than about 9 μmol of O₂ were not measured.

RESULTS AND DISCUSSION

Proportion of released O₂ during desorption and proportion of trapped O₂ during adsorption

The amount of O₂ released during desorption from the molecular sieves (MS13X and MS5A) was measured manometrically using a micro pressure transducer. The proportion of released O₂ decreased with decreasing temperature of desorption, as shown in Table 1. The proportion of O₂ released from MS13X and MS5A

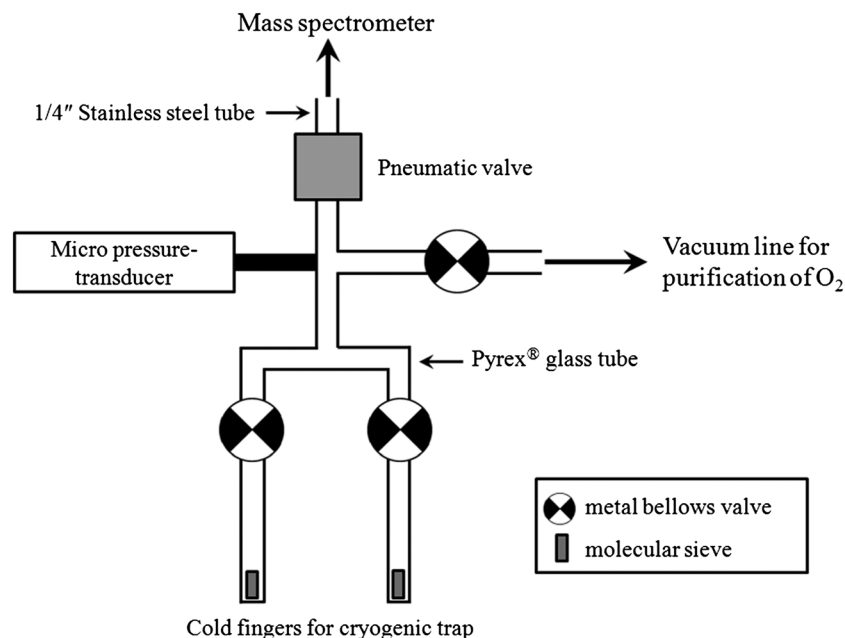


Figure 2. Schematic diagram of the dual cold finger arrangement, which is similar to that reported in previous studies.^[8,11,12] O₂ gas that may have been contaminated by NF₃ is adsorbed onto the molecular sieve in the first cold finger at liquid nitrogen temperature (-196°C). The trapped O₂ gas is then released at -114°C (ethanol slush temperature) while NF₃ is retained by the first molecular sieve. The released O₂ released is then transferred into the second cold finger, which contains molecular sieve cooled to liquid nitrogen temperature.

Table 1. Results of desorption experiments

Cryogenic trap	Released O ₂ (%)	Isotopic enrichment factor (‰)		Δ ¹⁷ O (‰)	
		ε ¹⁷ O _{sample-KO}	ε ¹⁸ O _{sample-KO}		
MS13X	n-pentane	41.4	-1.43	-3.18	0.20
		41.4	-1.61	-3.49	0.19
	ethanol	41.0	-1.55	-3.33	0.16
		67.4	-1.32	-2.83	0.14
		66.9	-1.24	-2.68	0.14
		67.2	-1.32	-2.81	0.12
	dry ice	92.5	-0.08	-0.27	0.03
		92.5	-0.14	-0.38	0.03
		92.0	-0.14	-0.35	0.01
	ice	99.6	0.06	0.06	0.00
		99.6	0.00	-0.01	-0.02
		99.6	0.07	0.05	0.02
		99.6	0.07	0.05	0.02
	MS5A	n-pentane	20.4 ± 0.5 (n = 6)		
ethanol		46.0	-2.65	-5.32	0.14
		46.2	-2.71	-5.51	0.18
		45.5	-2.42	-4.90	0.15
		46.6	-2.66	-5.39	0.17
		45.3	-2.70	-5.57	0.22
		47.2	-2.63	-5.46	0.24
dry ice		86.3	-0.95	-1.93	0.07
		84.2	-1.18	-2.39	0.08
		87.1	-1.03	-1.96	0.01
		86.7	-0.99	-1.93	0.03
ice		98.8	-0.01	-0.01	0.01
		97.9	-0.10	-0.10	-0.03

$\epsilon^{17 \text{ or } 18}\text{O}_{\text{sample-KO}} = \alpha^{17 \text{ or } 18}\text{O}_{\text{sample-KO}} - 1$
 n.d. = not determined (< 9 μmol of O₂)

was 98–100% at 0°C, 86–92% at -78°C, 46–67% at -114°C, and 20–41% at -130°C (Fig. 3(a)). During adsorption, the proportion of O₂ trapped on the molecular sieves increased with decreasing trapping temperature. The proportion of trapped O₂ on MS13X and MS5A was 8–13% at -78°C, 32–52% at -114°C, and 58–61% at -130°C (Fig. 3(b)). Under most conditions, the proportion of released and untrapped O₂ from MS13X was greater than that from MS5A, indicating that O₂ molecules are trapped slightly more readily on MS5A than on MS13X at low temperatures. O₂ was completely trapped onto both molecular sieves at -196°C.

Oxygen isotope fractionation during desorption and adsorption

The oxygen isotopic fractionation factors (*α^{17 or 18}) during desorption and adsorption of O₂ from/onto molecular sieves are related to the enrichment factors (*ε^{17 or 18}O) relative to the isotopic composition of the initial KO gas, as:

$$\alpha^{17 \text{ or } 18}\text{O}_{\text{sample-KO}} = 1 + \epsilon^{17 \text{ or } 18}$$

The corresponding, δ^xO values, relative to VSMOW, are obtained from:

$$\delta^{17 \text{ or } 18}\text{O}_{\text{sample-VSMOW}} = \left[\frac{1 + \delta^{17 \text{ or } 18}\text{O}_{\text{KO-VSMOW}}}{1 + \epsilon^{17 \text{ or } 18}\text{O}_{\text{sample-KO}}} \right] - 1$$

The ε values of O₂ released during desorption decreased significantly with decreasing temperature (Table 1), as shown in Fig. 4(a). In the case of MS13X at -130°C, the ε values were calculated as -1.53 ± 0.09‰ for ¹⁷O and -3.33 ± 0.16‰ for ¹⁸O. The ε values obtained when using MS5A were found to be generally more negative than those obtained when using MS13X. The proportion of O₂ released from MS5A also became lower than that from MS13X as the desorption temperature decreased (Fig. 3(a)). Release of a lower O₂ fraction from MS5A may be associated with larger isotopic fractionation.

Similar experiments were conducted for adsorption, in order to calculate the isotopic fractionation associated with partial trapping of O₂. As described above, KO gas was introduced into the cold finger containing molecular sieve and was adsorbed at different temperatures, from 0 to -130°C. The residual (untrapped) O₂ gas was measured for its oxygen isotopic composition. Although most of the untrapped gas was transferred into the inlet bellows, a small fraction still remained in the cold finger. It was technically difficult to separate the remaining O₂ from O₂ trapped by the molecular sieve. To evaluate the fractionation of trapped O₂, we assumed the following: (1) the isotopic composition of O₂ retained on the molecular sieve can be calculated by a simple mass-balance relationship between untrapped O₂ and the total quantity of O₂ initially introduced into the cold finger, and (2) the oxygen isotopic composition of untrapped O₂ admitted into

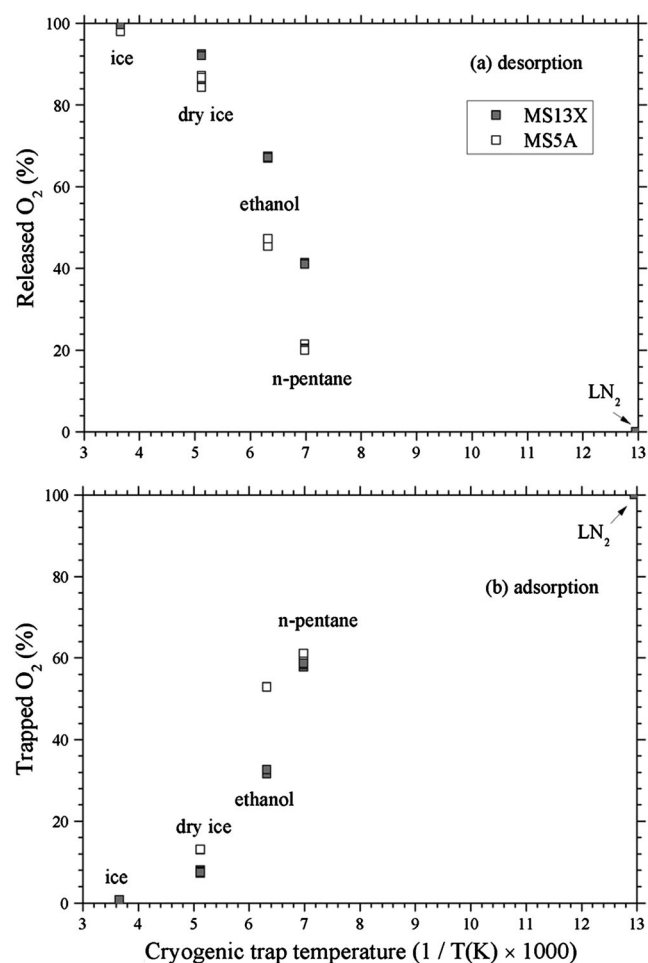


Figure 3. Proportions of released O₂ during desorption (a) and trapped O₂ during adsorption (b) by a cryogenic trap at different temperatures. The proportions of released O₂ decreased with decreasing temperature of desorption. However, those of the trapped O₂ increased with decreasing trapping temperature of the molecular sieve.

the mass spectrometer is the same as that of the O₂ remaining in the cold finger after the admission of the untrapped gas. Under these assumptions, the following relationship holds:

$$X = x_a + x_b + x_c$$

where X indicates the initial amount (μmol) of KO, which is the sum of x_a (untrapped O₂ admitted into the mass spectrometer), x_b (O₂ remaining in the cold finger after the admission of x_a), and x_c (O₂ trapped on the molecular sieve). The amount of X , x_b , and the sum of x_b and x_c were determined manometrically, for x_c is released from the molecular sieve when the cryogenic trap is removed, and mixes with x_b in the cold finger at room temperature. The values of x_a and x_c can then be obtained by simple subtraction.

The oxygen isotopic compositions of the mixture of x_b and x_c were determined by mass spectrometry. The isotopic mass-balance relation is given by:

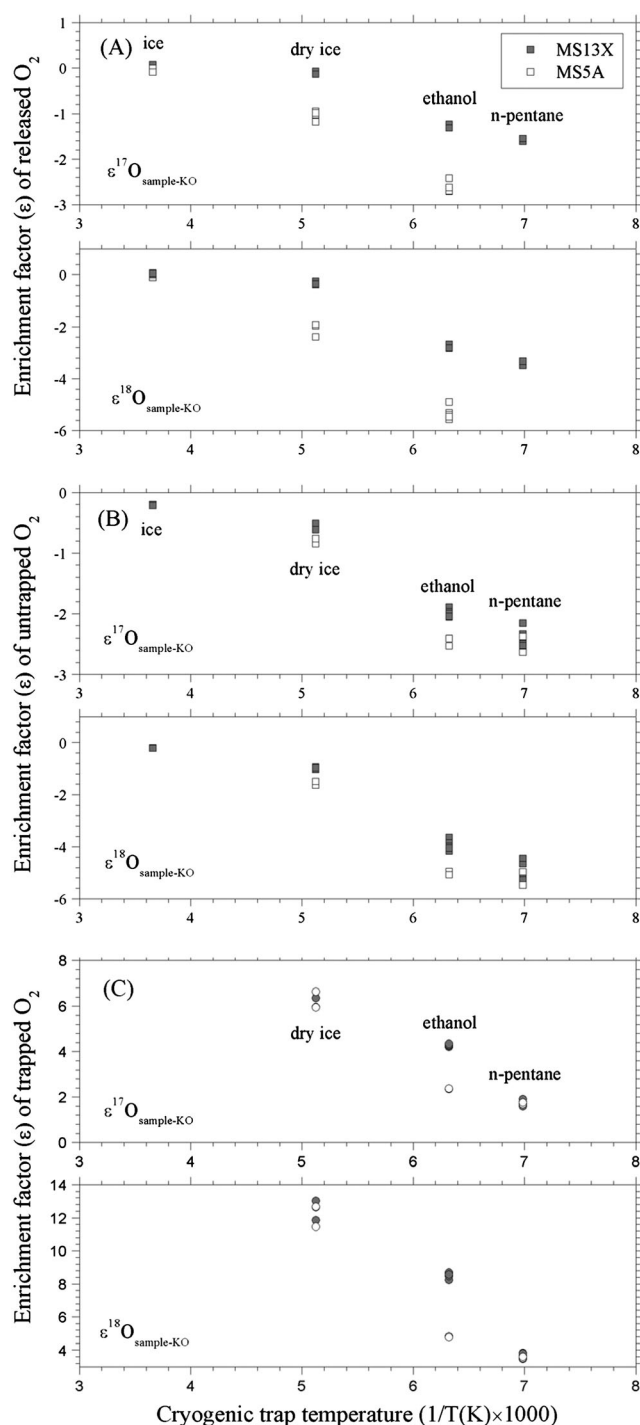


Figure 4. Isotope enrichment factors (ϵ) of O₂ released during desorption (a) and untrapped (b) and trapped (c) O₂ during adsorption at different trapping temperatures. Evaluated ϵ values of released O₂ relative to KO during desorption decreased significantly with decreasing temperature (a). The ϵ values of untrapped O₂ during adsorption were negative, whereas those of trapped O₂ were positive (b and c). The difference between the ϵ values of untrapped and trapped O₂ became smaller with decreasing trapping temperature.

$$(x_b + x_c) \times \delta^i O_{\text{mixture}} = x_b \times \delta^i O_{\text{untrapped}} + x_c \times \delta^i O_{\text{trapped}}$$

where i is 17 or 18. The δ^i values of x_b were assumed to be identical to those of the untrapped O_2 . The δi value of the trapped O_2 can be calculated when the other components are known.

The evaluated enrichment factors (ϵ) of the untrapped O_2 were negative, whereas those of the trapped O_2 were positive (Figs. 4(b) and 4(c)). The difference became smaller with decreasing trapping temperature, e.g., $13.38 \pm 0.53\%$ at -78°C , $12.46 \pm 0.35\%$ at -114°C , and $8.52 \pm 0.53\%$ at -130°C in $\epsilon^{18}\text{O}$ (Table 2). This indicates that the minor isotopes (^{17}O and ^{18}O) are more easily absorbed onto the molecular sieve during incomplete cryogenic trapping. The fractionation when using MS5A seems to be slightly smaller than when MS13X is used. The difference between the two molecular sieves, however, is insignificant except at the ethanol slush temperature (Figs. 4(b) and 4(c)). In all cases, the $\epsilon^{17}\text{O}$ values from desorption and adsorption experiments were $\frac{1}{2}$ of the corresponding $\epsilon^{18}\text{O}$ values, confirming that desorption and adsorption are mass-dependent processes, consistent with the findings by Abe.^[14]

$\Delta^{17}\text{O}$ values of released and untrapped O_2 during desorption and adsorption

The $\Delta^{17}\text{O}$ values during desorption and adsorption showed a clear relationship with the trapping temperature, a finding that has not previously been reported.^[14] The $\Delta^{17}\text{O}$ values

of the O_2 released during desorption changed almost linearly with the proportion of O_2 released from the molecular sieve (Fig. 5(a)). At -130°C , less than 50% of the O_2 was released from MS13X and MS5A. The largest $\Delta^{17}\text{O}$ values were obtained under these conditions. The $\Delta^{17}\text{O}$ values then became smaller as the proportion of released O_2 increased. Almost all the O_2 ($\sim 98\%$) was released from both molecular sieves at 0°C , and the isotopic compositions agreed with those of KO (within 1σ error) standard deviation. Similarly, the $\Delta^{17}\text{O}$ values of the untrapped O_2 became larger as the proportion of trapped O_2 increased (Fig. 5(a)). This trend can be clearly seen in Fig. 5(b), which illustrates the difference between the $\Delta^{17}\text{O}$ values of trapped and untrapped O_2 . As the proportion of trapped O_2 became greater, the $\Delta^{17}\text{O}$ difference became more negative. These results imply that oxygen isotopes are kinetically fractionated by incomplete release and trapping of O_2 from/onto the molecular sieves.

Dual cold finger

We also investigated whether oxygen isotopic fractionation occurred when O_2 was transferred, condensed and released through a dual cold finger arrangement (Fig. 2). In this experiment KO gas was introduced and condensed into the first MS13X trap at liquid nitrogen temperature. After confirming complete trapping, the KO gas was released by increasing the temperature to -114°C using an ethanol

Table 2. Results of adsorption experiments. Oxygen isotopic compositions of untrapped O_2 were measured using mass spectrometry, while those of *trapped O_2 were calculated by isotopic mass-balance relation (see text)

	Cryogenic trap	Trapped volume (%)	Isotopic enrichment factor (‰)					
			untrapped O_2		*trapped O_2		*trapped O_2	untrapped O_2
			$\epsilon^{17}\text{O}_{\text{sample-KO}}$	$\epsilon^{18}\text{O}_{\text{sample-KO}}$	$\epsilon^{17}\text{O}_{\text{sample-KO}}$	$\epsilon^{18}\text{O}_{\text{sample-KO}}$	$\Delta^{17}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)
MS13X	n-pentane	58.2	-2.34	-4.65	1.69	3.62	-0.18	0.10
		57.9	-2.49	-5.03	1.77	3.81	-0.20	0.14
		58.2	-2.16	-4.45	1.59	3.45	-0.20	0.17
		58.7	-2.52	-5.28			n.d.	0.24
	ethanol	32.5	-1.89	-3.64			n.d.	0.02
		32.1	-1.97	-3.86	4.36	8.60	-0.11	0.06
		32.2	-2.03	-3.99	4.26	8.61	-0.22	0.06
		32.2	-2.00	-3.99	4.27	8.47	-0.14	0.09
		31.9	-2.05	-4.16	4.27	8.67	-0.24	0.13
		32.6	-2.05	-4.05	4.33	8.55	-0.12	0.08
	dry ice	7.2	-0.52	-0.93			n.d.	-0.02
		8.0	-0.57	-0.99			n.d.	-0.04
7.9		-0.62	-1.05	6.44	12.67	-0.15	-0.06	
7.4		-0.51	-0.97			n.d.	0.01	
ice	0.6	-0.20	-0.21			n.d.	-0.08	
	0.7	-0.22	-0.22			n.d.	-0.09	
MS5A	n-pentane	60.5	-2.38	-4.97	1.67	3.49	-0.14	0.22
		61.2	-2.64	-5.48	1.75	3.59	-0.11	0.23
	ethanol	53.0	-2.41	-4.96	2.34	4.81	-0.16	0.19
		52.7	-2.53	-5.08	2.37	4.80	-0.12	0.13
	dry ice	12.7	-0.85	-1.63	6.68	12.76	0.03	0.02
		13.0	-0.77	-1.50	5.90	11.37	-0.03	0.03

n.d. = not determined ($< 9 \mu\text{mol}$ of O_2)

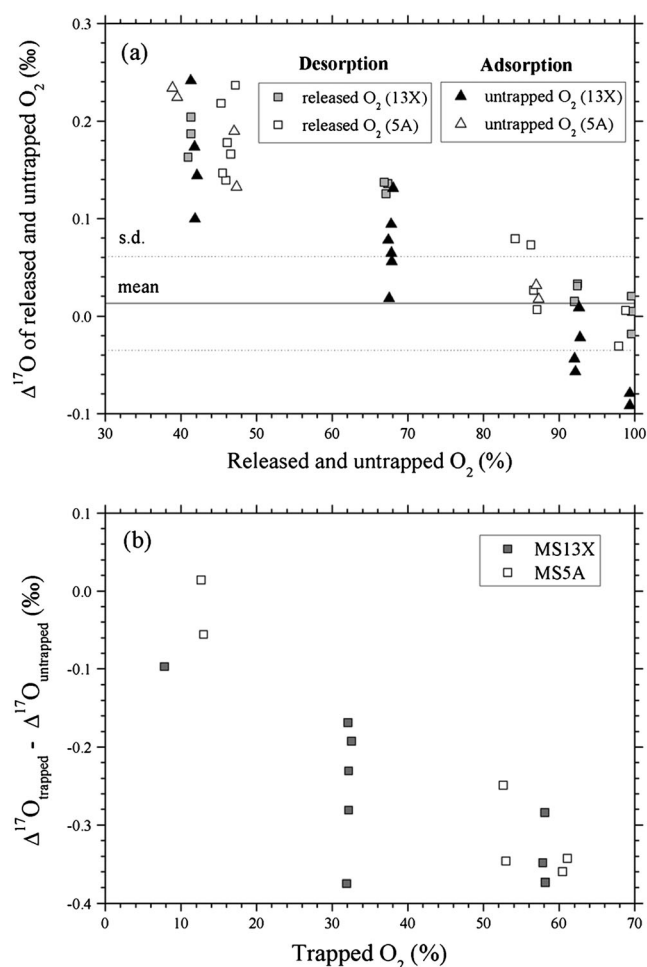


Figure 5. $\Delta^{17}\text{O}$ values of released O_2 during desorption and those of untrapped O_2 during adsorption, showing an almost linear trend with the amount of released O_2 and untrapped O_2 in the molecular sieve (a). The difference between the $\Delta^{17}\text{O}$ results of trapped and untrapped O_2 during adsorption is shown in (b). As the proportion of trapped O_2 becomes greater, the difference becomes larger. Solid and dashed lines refer to mean and 1σ values, respectively, of the $\Delta^{17}\text{O}$ measurements.

slush. At this stage, the released gas was transferred to a second cold finger containing a MS13X pellet at liquid nitrogen temperature. The enrichment factors (ϵ) of released O_2 were slightly positive, by $0.18 \pm 0.05\text{‰}$ in ^{17}O and $0.26 \pm 0.06\text{‰}$ in ^{18}O (Fig. 6). This implies that a small but significant isotopic fractionation is accompanied by O_2 transfer through the dual cold finger filled with MS13X at -114°C . Incomplete desorption from molecular sieve results in isotopic fractionation, as observed by Abe.^[14] He recommended additional mild heating of the molecular sieve after releasing O_2 at room temperature in order to attain complete desorption of O_2 gas. However, additional mild heating may be detrimental if the first trap retains any contaminant gas component, such as NF_3 . We recommend instead that the isotopic compositions be corrected by 0.18‰ in $\delta^{17}\text{O}$ values and 0.26‰ in $\delta^{18}\text{O}$ values if O_2 is released from MS13X at -114°C .

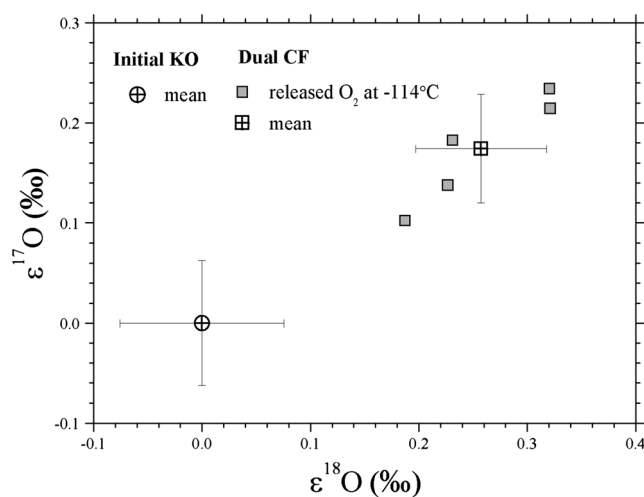


Figure 6. Oxygen isotopic fractionation accompanying the transfer, trapping and subsequent release of O_2 through the dual cold finger arrangement. The isotope enrichment (ϵ) of O_2 released from the dual cold finger was slightly positive, by $0.18 \pm 0.05\text{‰}$ in $\epsilon^{17}\text{O}$ and $0.26 \pm 0.06\text{‰}$ in $\epsilon^{18}\text{O}$.

SUMMARY AND CONCLUSIONS

We have measured the oxygen isotopic composition of O_2 released during desorption from, and adsorption onto, 13X and 5A molecular sieves at 0°C , -78°C , -114°C , and -130°C , in order to determine the associated oxygen isotopic fractionation at these different temperatures. Significant oxygen isotopic fractionation was observed when O_2 was incompletely released from, or incompletely trapped by the molecular sieves. The associated isotopic enrichment factors ($\epsilon^{17}\text{O}$ and $\epsilon^{18}\text{O}$) became closer to unity with increasing temperature during the desorption process. At the melting temperature of n-pentane, the $\Delta^{17}\text{O}$ values were significant ($\sim 0.2\text{‰}$), but the values became smaller and reached zero by 0°C . The reverse trend was obtained during the adsorption process. This reversibility implies that the oxygen isotope fractionation was accompanied by incomplete release (or trapping) of O_2 from/by the molecular sieves. In particular, even at -114°C (ethanol slush temperature), the temperature recommended for separating NF_3 from O_2 , only 40–50% of the O_2 was released during desorption and 40–60% of the O_2 remained untrapped during adsorption experiments. Thus, isotopic fractionation is unavoidable if NF_3 is separated using a single cold finger. It was confirmed that the use of a dual cold finger arrangement guarantees almost 100% transfer of O_2 from the first trap to the second one. However, isotopic fractionation still remains. We checked for separation of NF_3 using a dual cold finger filled with molecular sieve and obtained isotopic fractionation caused by incomplete O_2 transfer in the dual cold finger system. The fractionation was $0.18 \pm 0.05\text{‰}$ in $\delta^{17}\text{O}$ values and $0.26 \pm 0.06\text{‰}$ in $\delta^{18}\text{O}$ values when O_2 was released from the first trap at -114°C and collected at -196°C in the second, if using MS13X.

Acknowledgements

We would like to thank two anonymous reviewers for detailed corrections and constructive comments on our manuscript, which greatly improved its quality. We also thank Mr In-Seong Yoo and Mr Sang Beom Park of KOPRI, and Mr Susumu Takano of the Hiruzen Institute for Geology and Chronology, for their technical support on the maintenance of the mass spectrometer in KOPRI. We are grateful to Prof. Tomoki Nakamura of Tohoku University for his kind advice on this work. This work was supported by KOPRI (Project No. PE14050).

REFERENCES

- [1] U. Wiechert, J. Hoefs. An excimer laser-based micro analytical preparation technique for in-situ oxygen isotope analysis of silicate and oxide minerals. *Geochim. Cosmochim. Acta* **1995**, *59*, 4093.
- [2] R. N. Clayton, T. K. Mayeda. The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim. Cosmochim. Acta* **1963**, *27*, 43.
- [3] Z. D. Sharp. A laser-based microanalytical method for the in situ determination of oxygen isotope ratios of silicates and oxides. *Geochim. Cosmochim. Acta* **1990**, *54*, 1353.
- [4] D. Matthey, C. Macpherson. High-precision oxygen isotope microanalysis of ferromagnesian minerals by laser-fluorination. *Chem. Geol.* **1993**, *105*, 305.
- [5] J. W. Valley, N. Kitchen, M. J. Kohn, C. R. Niendorf, M. J. Spicuzza. UWG-2, a garnet standard for oxygen isotope ratios: Strategies for high precision and accuracy with laser heating. *Geochim. Cosmochim. Acta* **1995**, *59*, 5223.
- [6] D. Rumble, J. Farquhar, E. D. Young, C. P. Christensen. In situ oxygen isotope analysis with an excimer laser using F₂ and BrF₅ reagents and O₂ gas as analyte. *Geochim. Cosmochim. Acta* **1997**, *61*, 4229.
- [7] E. D. Young, D. W. Coutts, D. Kapitan. UV laser ablation and irm-GCMS microanalysis of ¹⁸O/¹⁶O and ¹⁷O/¹⁶O with application to a calcium-aluminium-rich inclusion from the Allende meteorite. *Geochim. Cosmochim. Acta* **1998**, *62*, 3161.
- [8] M. F. Miller, I. A. Franchi, A. S. Sexton, C. T. Pillinger. High precision δ¹⁷O isotope measurements of oxygen from silicates and other oxides: method and applications. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 1211.
- [9] M. Kusakabe, Y. Matsuhisa. Oxygen three-isotope ratios of silicate reference materials determined by direct comparison with VSMOW-oxygen. *Geochim. J.* **2008**, *42*, 309.
- [10] I. Ahn, J. Lee, M. Kusakabe, B.-G. Choi. Oxygen isotope measurements of terrestrial silicates using a CO₂-laser BrF₅ fluorination technique and the slope of terrestrial fractionation line. *Geosci. J.* **2012**, *16*, 7.
- [11] R. Tanaka, E. Nakamura. Determination of ¹⁷O-excess of terrestrial silicate/oxide minerals with respect to Vienna Standard Mean Ocean Water (VSMOW). *Rapid Commun. Mass Spectrom.* **2013**, *27*, 285.
- [12] R. N. Clayton, T. K. Mayeda. Oxygen isotopes in eucrites, shergottites, nakhlites, and chassignites. *Earth Planet. Sci. Lett.* **1983**, *62*, 1.
- [13] A. Pack, C. Toulouse, R. Przybilla. Determination of oxygen triple isotope ratios of silicates without cryogenic separation of NF₃ – technique with application to analyses of technical O₂ gas and meteorite classification. *Rapid Commun. Mass Spectrom.* **2007**, *21*, 3721.
- [14] O. Abe. Isotope fractionation of molecular oxygen during adsorption/desorption by molecular sieve zeolite. *Rapid Commun. Mass Spectrom.* **2008**, *22*, 2510.
- [15] D. W. Breck. *Zeolite Molecular Sieves: Structure, Chemistry, and Use*. John Wiley, Chichester, **1973**.
- [16] Y. Matsuhisa, J. R. Goldsmith, R. N. Clayton. Mechanisms of hydrothermal crystallization of quartz at 250C and 15 kbar. *Geochim. Cosmochim. Acta* **1978**, *42*, 173.
- [17] M. F. Miller. Isotopic fractionation and the quantification of ¹⁷O anomalies in the oxygen three-isotope system: an appraisal and geochemical significance. *Geochim. Cosmochim. Acta* **2002**, *66*, 1881.
- [18] H. R. Karlsson, in *Handbook of Stable Isotope Analytical Techniques*, (Ed: P. A. de Groot), Elsevier, Amsterdam, **2004**.