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EARTH AND ENVIRONMENTAL SCIENCE
NOVEL-RESULT

Oxidized silver cups can skew oxygen isotope results of small samples

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Abstract

One of the commonly used analytical approaches for measuring oxygen isotope ratios $\delta^{18}O$ of solids (organic and inorganic) is to pyrolyze the samples to gaseous phases and then send the gas into an isotope ratio mass spectrometer system. Solid samples for $\delta^{18}O$ measurements are usually stored in silver cups because of its low reactivity towards oxygen and other oxidants. Samples in silver cups can be dropped directly into the carbon column of the pyrolysis furnace. However, the silver cups can tarnish and then be oxidized over a prolonged storage period. We find that while a small amount of silver oxides does not affect measurements with appreciable sample sizes, it can skew isotope results of small samples. We thus recommend careful storage of samples in silver cups to minimize oxidation, such as under an air-isolated condition, and avoiding prolonged storage for accurate $\delta^{18}O$ measurements.

Keywords: Oxygen isotope; mass spectrometer; silver oxidation

Introduction

Solid samples for oxygen isotope $\delta^{18}O$ measurements are commonly stored in silver cups. However, silver cups tarnish (Ag_2S) upon exposure to H_2S in the air even at parts-per-billion concentrations of H_2S (Franey et al., 1985), especially near the opening of the cups where they are pressed to avoid the samples from falling out (Fig. 1). Other than Ag_2S, a small amount of AgO, Ag_2O, Ag_2SO_3, Ag_2SO_4 can also form on the cup (Franey et al., 1985; Sanders et al., 2015), particularly in the presence of ozone in the air (Wiesinger et al., 2013). Some laboratories store the silver cups in ovens to avoid moisture, which can speed up the oxidation process. Even if the silver cups are stored in room conditions, they can still turn yellow after storage for about a year.

Objective

Silver oxides or sulfate on silver cups can potentially affect the $\delta^{18}O$ measurements. In this study, we explore this problem and the circumstance that the oxidized silver cups become a concern. We measure the $\delta^{18}O$ of silver cups that appear pale yellow, in order to identify if oxidation of the cups can skew $\delta^{18}O$ measurements of small solid samples. We use measurements of oxygen isotope ratios from $BaSO_4$ standards to illustrate the effects of the oxidized silver cups.

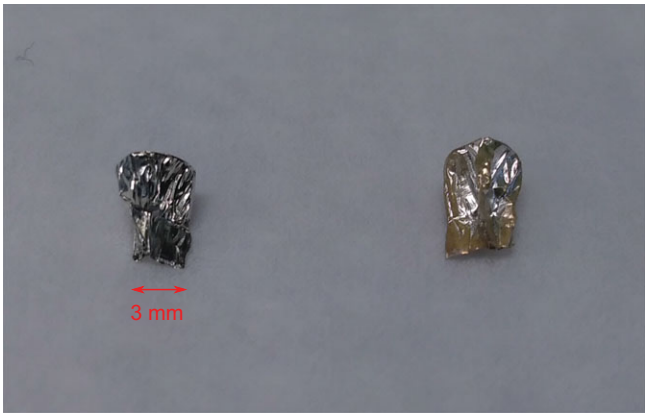

Figure 1. A new silver cup (left) and an old silver cup that has held samples for over a year in room conditions (right). Notice the old cup has turned slightly yellow, especially at its pressed opening.

Methods

We put two silver cups into an 80°C oven to speed up the process of oxidation. The cups turn to pale yellow after a month. We also have a silver cup that has sat in room conditions for over a year and turned pale yellow. We then measure the $\delta^{18}O$ of these three silver cups with a Hekatech high-temperature pyrolysis furnace and a continuous flow isotope ratio mass spectrometer system (CF-IRMS, Finnigan MAT 253 in continuous flow mode using a Conflo III open split interface). Before the measurements, the system passed the linearity test, background test and zero test. In the same run, we measure the $\delta^{18}O$ of IAEA-SO-5 $BaSO_4$ standard to compare the oxygen peak sizes from standard sulfate and the silver cups. $\delta^{18}O$ values (V-SMOW) are calibrated with international standards for oxygen isotopes: IAEA-SO-5, USGS-32, NBS-127 and IAEA-SO-6. The standard deviation of the measurements is 0.18‰.

Results

The three yellow silver cups give small peaks of oxygen in the mass spectrum results (Fig. 2a). The cups stored in an 80°C oven show amplitude-28 of only 141 mV and 112 mV. The amplitude-28 of the cup stored in room conditions for over a year is larger, at 219 mV. $\delta^{18}O$ values (9.4‰, 11.5‰, −4.5‰) from such small amounts of oxygen are not accurate and are only for reference here.

In the same run, ~200 μg of $BaSO_4$ (IAEA-SO-5, about 27% of the mass is from O) produces an amplitude-28 at about 6,500 mV, and 43 μg $BaSO_4$ at about 1,500 mV (Fig. 2b). This means when 200 μg $BaSO_4$ is used for BaSO4-$\delta^{18}O$ measurements, the oxides from the silver cup contribute less than ~3.5% of the oxygen being measured. However, when only 43 μg $BaSO_4$ is measured, the oxides from the silver cup can contribute roughly 13% of the oxygen.

Discussions

Our experiment demonstrates that when using conventional sample sizes (e.g., 200 μg $BaSO_4$), the oxidized silver cups are not a concern for the accurate measurements of $\delta^{18}O$. However, when only a small sample is available, or the sample is impure so the oxygen content is lower than expected, the oxides on the silver cups can skew the $\delta^{18}O$ results.

The scale of the skewness can vary, depending on the time of storage, the quantities of oxygen compounds and the isotope compositions of oxidants. For instance, $\delta^{18}O$ of both atmospheric O_2 and H_2O vary according to environmental conditions (e.g., Craig, 1961; Klots & Benson, 1963; Benson & Krause, 1980). These oxidants on silver cups will skew $\delta^{18}O$ results differently.

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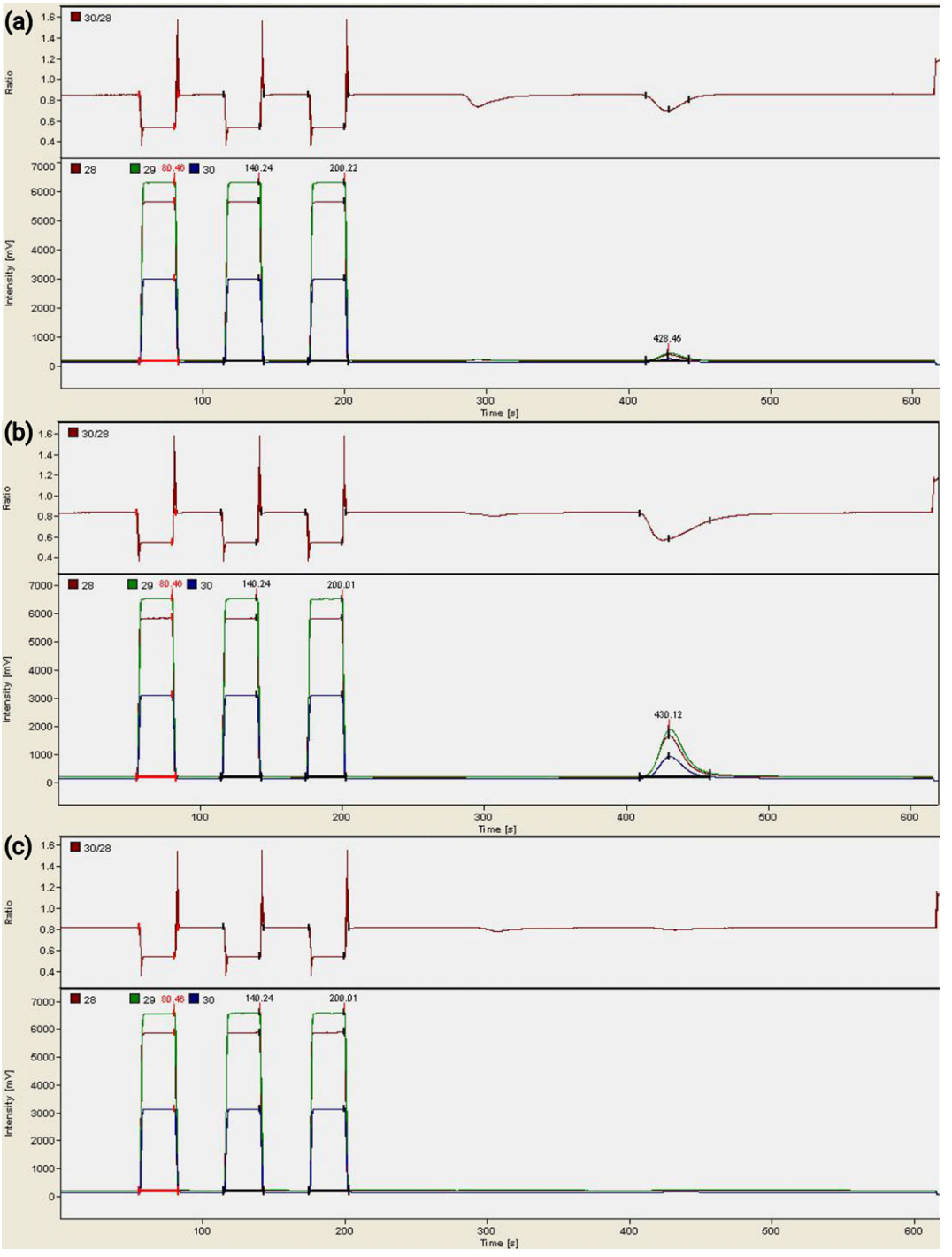

Figure 2. Mass spectrum results from the mass spectrometer. In each mass spectrum, the first three peaks at the left are from the reference gas (tuned for measuring 200 μg of $BaSO_4$) and the fourth peak is the peak of the oxygen from the sample. (a) An old, pale yellow silver cup gives a small oxygen peak. (b) 43 μg of $BaSO_4$ gives an oxygen peak larger than that in (a). (c) In comparison, a new silver cup gives no oxygen peaks in the mass spectrum.

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If prolonged storage of samples in silver cups is unavoidable, simple methods to postpone the oxidation process include vacuum-sealing the sample holders and storing the samples in a desiccator. Storing samples in an argon- or nitrogen-filled environment may be considered for storage over an extensive period. The laboratory condition, e.g., whether natural gas is present, matters as natural gas contains a minor amount of H_2S. An effective and clean heating, ventilation, and air conditioning (HVAC) system of the laboratory should also help lessen the oxidation problem.

Conclusions

Our results demonstrate that if small or impure samples are measured for their oxygen isotope compositions, oxidized silver cups that hold the samples can skew the measurements. Our finding suggests that proper sample storage is also an important step for accurate isotope measurements. When small sample sizes are unavoidable, we recommend shortening the storage period with the silver cups and vacuum-sealing the sample holders to delay the oxidation process.

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Author Contributions. MYT and KT designed the study and performed the experiments. MYT, WY and KT analyzed the data and wrote the article.

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Data Availability Statement. The data that support the findings of this study are available in Supplementary Material.

Conflict of Interest Declaration. MYT, WY and KT declare none.

Supplementary Materials. To view supplementary material for this article, please visit http://dx.doi.org/10.1017/exp.2020.15.

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Peer Reviews

Reviewing editor: Dr. Il-Nam Kim

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This article has been accepted because it is deemed to be scientifically sound, has the correct controls, has appropriate methodology and is statistically valid, and met required revisions.

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Review 1: Oxidized silver cups can skew oxygen isotope results of small samples

Reviewer: Zhengyu Xia

Lehigh University, Earth and Environmental Sciences

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Comment

Comments to the Author: The authors study a well-defined laboratory question and the paper is well-written. A few comments:Line 12 measuring oxygen isotope ratio (d18O) OF THE SOLIDS (ORGANIC AND INORGANIC)Line 27 OTHER THAN Ag2SLine 75-76, can result in THAT … COULD SKEW d18O results differentlyLine 126, MASS spectrumIn some newly built laboratory building, the air is controlled by HVAC system as that I expect H2S and O3 concentrations are monitored and should be even less than a trace value, so in my experience the silver cups do not seem to decay in color. Also, rather than consider the mass balance in d18O, why do not just measure the same standard BaSO4 sample in a separate run in a new silver cup and a tarnished cup and see how much permille of d18O is skewed?

Score Card

Presentation

5.0 /5

Is the article written in clear and proper English? (30%)	5/5
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Context

5.0 /5

Does the title suitably represent the article? (25%)	5/5
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Analysis

Does the discussion adequately interpret the results presented? (40%)	5/5
Is the conclusion consistent with the results and discussion? (40%)	5/5
Are the limitations of the experiment as well as the contributions of the experiment clearly outlined? (20%)	5/5

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