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A Comparison of Sulfur Isotope Standards Used in Different Laboratories

Porównanie wzorców składu izotopowego siarki stosowanych w różnych
laboratoriach

Сравнение изотопных стандартов серы употребляемых в разных лабораториях

INTRODUCTION

A set of 16 sulfur isotope standards, listed in Tab. 1, was analysed
with respect to our laboratory SO_2 standard produced by combustion
of a natural ZnS sample (sphalerite) from the Silesia-Cracovian ore
deposits. The measurements were performed with a modified MI-1305
mass spectrometer [5, 6], its apparent precision being as much as 0.05
per mil. All the samples were converted into SO_2 as described below.
Inasmuch a Nier type collector was used, the following formula was
accepted for $\delta^{34}S$ calculations [3]:

$$\delta^{34}S = 1092.9 \left(\frac{R^{66}_{sample}}{R^{66}_{standard}} - 1 \right),$$

where R^{66} is the ion current ratio I^{66} to I^{64}. In this formula the $\delta^{18}O(SO_2)$-
-depended term is omitted that may cause a small uncertainty dis-
cussed below. Necessary instrumental corrections were introduced in the
delta values [3].

SAMPLE PREPARATION

All Ag_2S samples were oxidized with Cu_2O according to the method established by R o b i n s o n and K u s a k a b e [11]. ZnS samples were also oxidized to SO_2 with Cu_2O at a slightly higher temperature (810°C) for a longer time (45 minutes). Pyrite samples were oxidized at two selected temperatures: 800 and 1000°C. The higher temperature is sug-gested by R o b i n s o n and K u s a k a b e.

All $BaSO_4$ samples were processed directly to SO_2, at 850°C, using $NaPO_3$. This simple method was developed in our laboratory [4]. A native sulfur sample was converted into Ag_2S with Ag powder in an evacuated sealed glass ampoule, at 500°C, and, independently, a portion of it was oxidized to sulfate ion with HNO_3—HCl—Br_2 mixture to be finally precipitated as $BaSO_4$.

RESULTS AND DISCUSSION

The obtained average $\delta^{34}S$ values with their standard error are pre-sented in Tab. 1. Although the apparent precision was about 0.05 per mil, these results show a lower accuracy, mainly due to sample preparation techniques. The best reproducibility is to be attributed to SO_2 produc-tion from $BaSO_4$. However, the use of two independent methods of pre-paration of sulfur dioxide can cause a systematic difference in $\delta^{18}O$ (SO_2). Our recent experience shows that the oxygen isotope composition in SO_2, produced directly from $BaSO_4$, is sufficiently constant although the oxygen isotope ration in $BaSO_4$ samples varies throughout the natural variation range. In order to compare the $\delta^{18}O$ in SO_2, produced by this method with these produced by Cu_2O combustion, the native sulfur sample NBS-120 was prepared by using both methods. The obtained delta values indicate that both kinds of SO_2 contained oxygen with almost identical isotopic composition.

Different oxidation temperatures may also produce differences in oxygen isotopic composition. However, it is difficult to explain somewhat distinct differences in $\delta^{34}S$ for iron sulfides by $\delta^{18}O$ variations in SO_2. Sulfur dioxide produced from these sulfides at 1000°C, as R o b i n s o n and K u s a k a b e suggested, shows generally a better reproducibility in $\delta^{34}S$ than does SO_2 produced at 800°C. Some of SO_2 samples, obtained from Canyon Diablo specimen, contained a considerable admixture of CO_2 which was accurately removed by freezed n-pentane [7].

Taking into account all the above difficulties in sample preparations, we may compare the obtained delta values with those accepted in other laboratories. Assuming that $\delta^{34}S = 0.2^0/_{00}$ for our laboratory standard, we

Tab. 1. The results of δ³⁴S measurements vs. laboratory standard not corrected for δ¹⁸ differences

No.	Standard	δ³⁴S measured	Remarks	δ³⁴S accepted
1	FeS, Canyon Diablo specimen no. SL-236-6	−0.45 ±0.12 −0.20 ±0.09	oxidized at 800°C oxidized at 1000°C	0.00
2	FeS, Sikhote-Alin	−0.42 ±0.08 −0.18 ±0.04	oxidized at 800°C oxidized at 1000°C	0.00 W. A. Grinenko
3	S, NBS-120	1.05 ±0.09	Ag₂S	?
4	SO₄²⁻ Ocean, Atlantic surface, long. 30°W, lat. 16°N	0.98 ±0.05 20.30 ±0.05	BaSO₄ BaSO₄	20.2 Sasaki (1972) 20.99 Rees et al. (1978)
5	Ag₂S, SL-277-1	3.10 ±0.03		2.54 J.M., 2.52 C.E.R.
6	Ag₂S, SL-277-2	−5.30 ±0.12		−5.85 J.M., −6.3 C.E.R.
7	Ag₂S, SL-277-3	11.96 ±0.06		11.06 J.M., 11.8 C.E.R.
8	Ag₂S, SL-277-4	16.69 ±0.16		15.80 J.M., 16.3 C.E.R.
9	Ag₂S, SL-277-5	8.10 ±0.06		7.60 J.M., 8.1 C.E.R.
10	Ag₂S, SL-277-6	22.54 ±0.16		22.30 J.M., 23.1 C.E.R.
11	Ag₂S, SL-277-7	47.83 ±0.15		47.62 J.M., 49.3 C.E.R.
12	Ag₂S, SL-277-12	−37.91 ±0.19		?
13	ZnS synthetic	−4.90 ±0.07	oxidized at 810°C	−5.40 R. O. Rye
14	BaSO₄ synthetic	3.74 ±0.07		3.6 R. O. Rye
15	FeS₂, Park City	3.92 ±0.17 2.65 ±0.07	oxidized at 800°C oxidized at 1000°C	3.2 R. O. Rye
16	FeS₂, Spiro Tunnel	3.21 ±0.24 2.75 ±0.05	oxidized at 800°C oxidized at 1000°C	3.0 M. L. Jensen

obtain a good agreement between the meteorites, on the one hand, and ocean water sulfate and pyrite standards (oxidized at 1000°C), on the other. Also $\delta^{34}S$ for synthetic $BaSO_4$ agrees, within the limits of error, with the accepted value. Such an assumption, however, disagrees with $\delta^{34}S$ values accepted for all the Ag_2S samples and the synthetic ZnS sample derived from McMaster University. From this set of standards follows, for our laboratory standard, $\delta^{34}S = -0.6^0/_{00}$[1].

In order to explain whether this difference was due to oxidation of meteoritic troilite, a portion of Sikhote-Alin specimen was converted into $BaSO_4$. However, in this case we have obtained the $\delta^{34}S$ value almost identical with that obtained for SO_2 prepared at 1000°C.

The conclusion is as follows. We have detected $0.8^0/_{00}$ discrepancy between the two groups of laboratory standards which, we hope, will be explained soon in interlaboratory comparisons already initiated by Dr. C. E. Rees of McMaster University.

ADDENDUM

A satisfactory explanation of the discrepancy mentioned above, of $0.8^0/_{00}$, between Ag_2S and CDT standards has been found in our laboratory during stable isotope measurements intercalibration in September 1980. This intercalibration exercise is a follow-up of the recommendations expressed in 1976 by Consultants' Meeting convened by I.A.E.A. in Vienna, to discuss the problem of stable isotope standard and intercomparison of measurements in natural compounds [2]. Our laboratory has taken part in the measurements of the following sulfur isotope standards:

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[1] If this value is accepted for our laboratory standard, one can see that the results obtained here are convergent rather with the data obtained by Jan Monster (J.M.) than with those of C. Edward Rees (C.E.R.). The deviation of C.E.R. and J.M. scales (established on the use of SF_6 and SO_2, respectively) by factor 1.0368 is probably related to correction factors involved in the use of SO_2 for sulfur isotope analysis [8, 9].

1. OGS: Barium sulfate precipitated from ocean water by Y. Horibe (University of Tokyo, Japan). The sample is aiming at intercalibrating ^{34}S and ^{18}O measurements in sulfates, but later it will also be used for calibrating laboratory standards, when its isotopic composition is well established.

2. Soufre de Lacq: Sample of natural elemental sulfur deriving from Lacq deposit (France), provided by E. Roth (Centre d'Etudes Nucléaries, Saclay, France).

Both standards were measured at the same time as CDT, SL-277-1, NBS-120 and our own Ocean SO_4^{2-}. The Ag_2S sample SL-277-1 was oxidized with Cu_2O at two temperature ranges: 800 and 850—900°C. These temperatures were measured outside of the reactor tube. Details on $\delta^{34}S$ measurements vs. laboratory standards contains Tab. 2. The means of $\delta^{34}S$ values for SO_2 obtained at 800 and 850—900°C were 3.56 ± 0.12 and 2.85 ± 0.05, respectively. Thus they differ exactly by 0.71 ± 0.12 per mil.

Tab. 2. δ ^{34}S measurements in SO_2 produced by oxidation of Ag_2S at 800 and 850—900°C. Numbers in brackets indicate preparation number

$T \approx 800°C$	$850 < T < 900°C$
3.39 (1)	3.04 (1)
3.13 (1)	2.81 (1)
4.01 (2)	2.72 (1)
3.72 (3)	2.88 (2)
3.30 (1)	2.79 (3)
3.99 (2)	
3.29 (1)	
4.16 (3)	
3.10 (4)	
3.54 (4)	

Moreover, the higher oxidation temperature provides SO_2 with much better reproducible isotopic ratios $^{34}S/^{32}S$ and $^{18}O/^{16}O$. Inasmuch as the yield of reaction was similar for both temperature ranges, the oxygen fractionation at lower oxidation temperature seems to be responsible for 0.8 per mil discrepancy in case of all Ag_2S samples. Therefore such correction should be introduced in the results presented in Tab. 1, samples No. 5—12. The corrected values are in excellent agreement with these obtained by J. Monster who used direct burning technique.

An important conclusion which follows from this experiment is that the use of a higher oxidation temperature, of 850—900°C instead of 800°C, as recommended Robinson and Kusakabe [11], greatly increases the reproducibility of sulfur isotope ratios. Actually, the temperature of 850°C was used at the University of California, Los Angeles [1].

The final results of sulfur isotope standards vs. CDT are in Tab. 3. These results are corrected for oxygen isotopic composition in SO_2. We have found that SO_2 produced from Ag_2S and FeS is enriched in ^{18}O by 2.5 ± 0.6 per mil in comparison with SO_2 produced from $BaSO_4$. This difference was determined by preparing a portion of barium sulfate from the Ag_2S sample SL-277-1. It is worthwile to notice that Cu_2O was prepared from CuO which first was roasted in air and then under vacuum at $800°C$ for 8 hours.

Tab. 3. δ ^{34}S values vs. CDT for sulfur isotope standards used in the UMCS laboratory ((own measurements)

Standard	Form analysed	δ ^{34}S $\pm$standard error
SL-277-1	Ag_2S	2.52 $\pm$0.06
Soufre de Lacq elemental S	$BaSO_4$	15.37 $\pm$0.06
NBS-120 elemental S	$BaSO_4$	0.79 $\pm$0.06
OGS-1	$BaSO_4$	20.05 $\pm$0.07
$SO_4{}^{2-}$ Ocean	$BaSO_4$	20.06 $\pm$0.08

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STRESZCZENIE

Praca przedstawia wyniki precyzyjnych pomiarów wartości $\delta^{34}S$ dla następujących wzorców: dwóch próbek troilitu (meteorytów Canyon Diablo i Sichote Alin), siarczanu wody oceanicznej, dwóch pirytów (Park City i Spiro Tunnel) oraz dziesięciu próbek syntetycznych (Ag_2S, ZnS i $BaSO_4$) stosowanych w U. S. Geological

Survey, Denver, Colorado i Katedrze Chemii Uniwersytetu McMaster (Hamilton, Kanada). Stwierdzono przesunięcie skali opartej na wzorcach Ag_2S, SL-277 o $-0,8‰$ względem skali CDT.

Р Е З Ю М Е

В работе представлены результаты прецизионных измерений $\delta^{34}S$ следующих стандартов: двух образцов троилитов (Каньон Дьябло и Сихотэ-Алинского), сульфата океанической воды, двух образцов пиритов (Парк Сити и Спиро Туннел), десяти синтетических образцов (Ag_2S, ZnS и $BaSO_4$) применяемых в U.S. Geological Survey Денвер, Колорадо и Кафедре Химии Университета Мк Мастер, Гамильтон, Канада. Обнаружен сдвиг шкалы основанной на стандартах Ag_2S, SL-277 на $-0,8‰$ относительно шкалы CDT.

Złożono w Redakcji 6 V 1980 roku.