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USE OF NEGATIVE ION MASS SPECTROMETRY  
FOR SIMULTANEOUS DETERMINATION OF SULFUR  
ISOTOPE RATIOS  $\Delta^{33}\text{S}$  AND  $\Delta^{34}\text{S}$

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#### ABSTRACT

We describe a newly constructed dual inlet system and triple collector for precision study of sulfur isotope anomalies,  $\Delta^{33}\text{S}$ , using negative ion mass spectrometry.  $\text{SO}_2$  gas is admitted to the ion source where it is ionized either to  $\text{SO}^-$  or  $\text{S}^-$  by low energy electrons (resonant ionization) and the ion beam is analyzed by a single focusing magnetic analyzer. Another gas which can be used for  $\delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  analysis by negative ion mass spectrometry is  $\text{SF}_6$  on mass spectrum of  $\text{SF}_5^-$  ions.

**Keywords:** isotope anomalies, terrestrial minerals, sulfates, sulfides

#### INTRODUCTION

The isotope anomalies received recently a great attention by a number of investigators (e.g. Thiemens 2006, Thiemens & Shaheen 2013, Eiler et al. 2014 and refs therein), therefore we propose here a novel approach in their study as described below. By isotope anomalies we understand the deviations of  $\delta^{33}\text{S}$  from respective value of  $0.52\delta^{34}\text{S}$  predicted by the mass-dependent theory (Urey 1947, Bigeleisen &

Mayer 1947). These anomalies, denoted as  $\Delta^{33}\text{S}$ , were first encountered in meteorites by Hulston & Thode (1965), but later on also in some billion years old Earth minerals (Farquhar et al. 2000). Large anomalies of  $\Delta^{33}\text{S}$  recorded in Precambrian sulfides and sulfates result most likely due to ionization phenomena of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  in ancient Earth atmosphere. Due to severe analytical difficulties of isotope analysis of  $\delta^{33}\text{S}$  by mass spectrometry, small anomalies were not well recognized at Earth surface level by far, except the oldest sulfur.

The goal of the present study is to overcome the most crucial difficulty by applying negative ion mass spectrometry. With the proposed idea we will attack the problem of the analysis of minor variations of  $\delta^{33}\text{S}$  with negative ion spectrometry. Đông and Tiên (1989) reported that no interfering peaks occur in the mass spectrum of  $\text{S}^-$  using conventional gas  $\text{SO}_2$ . They were able to determine  $\delta^{34}\text{S}$  only with analytical precision 1.5‰ on a single collector mass spectrometer.

Inasmuch as the peak of mass-33 is about five times lower than peak 34, necessary precision of  $\delta^{33}\text{S}$  determination should be enhanced several times in comparison to that attained for  $\delta^{34}\text{S}$ . We will try to enhance maximally the precision of isotope ratios determination by a single focusing ( $R = 15 \text{ cm}$ ) and triple collector isotope ratio mass spectrometer (IRMS).

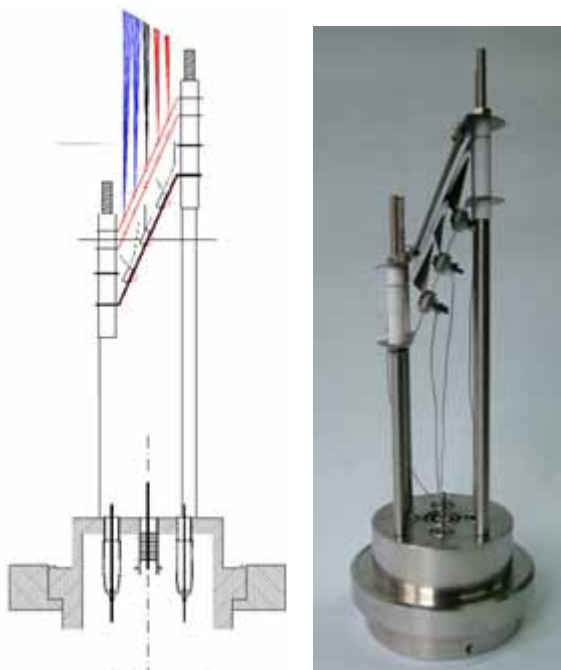
## MASS SPECTROMETER

In our IRMS we have retained the alignment and electromagnet manufactured by Nuclide, Pennsylvania, in the 70's of the XX century, whereas the flight tube, ion source, collector assembly and gas inlet system have been designed for the measurements of isotope ratios. The overall view on the mass spectrometer is shown in Fig. 1. The vacuum system comprises two rotary pumps – one for the inlet system and one is used as backing pump for two turbo pumps of the differential ultra high vacuum (UHV) in the flight tube. The pumping speed of these turbo pumps is 250 L/s which guarantees a dynamic vacuum during analysis at the level  $10^{-8}$  Torr in the flight tube. There is also one small ion sputtering pump (pumping speed 50 L/s) operated all the time, but it is open to the UHV only during breaks in analysis, i.e. when the turbo pumps are turned off. All the three pumps can be isolated from the UHV chamber by 2 manually operated all-metal valves or by a gate valve installed at the ion source.



**Figure 1:** Overall view on the 60° magnetic sector mass spectrometer. The inlet system is installed at the front of this picture. The ion source is on the right side and the collector assembly on the left. The mass spectra and isotope analyses are computer controlled.

In Fig. 2 is shown the triple collector assembly dedicated for simultaneous collection of the 3 isotopes in  $S^-$  spectrum. The same slit system can be used for positive ions of  $O_2^+$ .



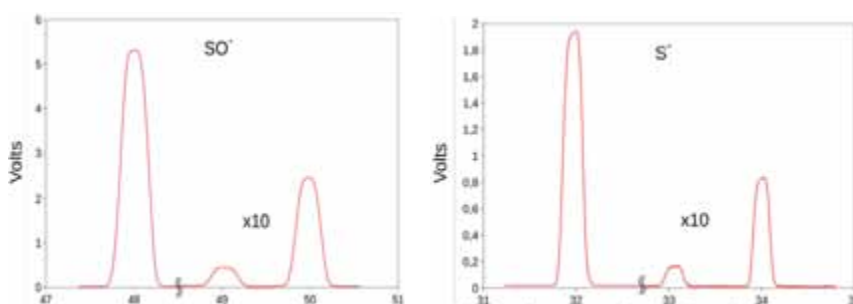
**Figure 2:** Triple collector assembly, the design is on the left and a photo on the right.

Negative ions  $\text{SO}^-$  and  $\text{S}^-$  are produced from being easily prepared  $\text{SO}_2$  gas in the ion source with a hot cathode immersed in external magnetic field. The ions were produced by low energy electrons at so-called resonance (see e.g. Hałas 2002). The construction of this ion source will be described in detail elsewhere.

The inlet system is arranged as it is described in Hałas (1979). The volume of the standard channel is large and constant, whereas that of the sample channel is small and variable. Such arrangement assures nearly constant pressure of the standard over an extended time of analysis. A bellows installed in the sample channel allows to equalize the pressure of sample gas to that of standard gas. Gas is admitted to the ion source through SS 1/8 inch capillaries whose ends are installed in the pneumatically operated changeover valve. A gas pressure  $\sim 20$  Torr is kept in the inlet system during analysis to assure viscous flow condition from both channels (Hałas 1980, 1982).

## RESULTS AND DISCUSSION

The first results obtained on  $\text{SO}_2$  gas with this new instrument look highly promising. The obtained mass spectra of negative ions produced from  $\text{SO}_2$  gas are shown in Fig. 3. Note that peaks of  $\text{SO}^-$  are almost 3 times higher than those for  $\text{S}^-$ , hence they are more suitable for  $\delta^{34}\text{S}$  analysis. However in this case the isotopic peak of  $^{33}\text{S}$  at mass 49 is also contributed by  $^{17}\text{O}$ . This is not the case in the isotopically clean spectrum of  $\text{S}^-$ . Therefore this spectrum will be used for simultaneous  $\delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  analysis using triple collector assembly.



**Figure 3:** Obtained mass spectra of  $\text{SO}^-$  and  $\text{S}^-$  by scanning electric current in the electromagnet coils. The right part of each spectrum is 10-fold magnified. The ion current was recorded as the voltage drop on  $10^{11} \Omega$  resistor.

Our preliminary test confirmed this conclusion. The obtained standard deviations of the average values from ten 60-second runs were 0.5 and 0.1 permil, respectively. Undoubtedly for too low precision of  $\delta^{33}\text{S}$  excessive noise on high-ohm resistor available ( $10^{12}$  ohms) is responsible. This resistor will be replaced by a high quality one from OHMITE.

We have also tested mass spectra of two other gaseous sulfur compounds, namely hydrogen sulfide ( $\text{H}_2\text{S}$ ) and sulfur hexafluoride ( $\text{SF}_6$ ). The first of them has no isotopically clean mass spectrum. The peaks of  $\text{S}^-$  are accompanied with  $\text{HS}^-$  peaks, so  $^{33}\text{S}^-$  is overlapped by  $\text{H}^{32}\text{S}^-$ . On the other hand,  $\text{SF}_6$  is ideal gas for measurements of high ion currents of  $\text{SF}_5^-$ , which has isotopically pure mass spectrum (Fluor has only one stable isotope,  $^{19}\text{F}$ ). Moreover, this gas is practically non-adhesive. For the above reasons it may be recommended as excellent gas for negative IRMS (it is already used since the 60's of the XX century in positive ion IRMS). The preparation method of this gas by fluorination of solids sulfur compounds is, however, more difficult than  $\text{SO}_2$  preparation from sulfides (Robinson and Kusakabe 1975) or sulfates (Halas and Szaran 1999).

## CONCLUSION

We report here about a negative ion IRMS which is suitable for both  $\delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  measurement on the  $\text{S}^-$  spectrum or respective  $\text{SF}_5^-$  spectrum. Initial tests of delta measurements indicate a high possible precision, which may lead to detect minor anomalies in sulfur isotope composition ( $\Delta^{33}\text{S}$ ) which may exist in geologically young minerals, particularly those formed during big  $\delta^{34}\text{S}$  sulfate excursions of ocean in the Phanerozoic (Holser 1977, Claypool et al. 1980).

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## REFERENCES

1. Bigeleisen J., Mayer M.G. 1947. Calculation of equilibrium constants for isotopic exchange reactions. *J. Chem. Phys.* 15, 261–67.
2. Claypool G.C., Holser W.T., Kaplan I.R., Sakai H., Zak I. 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation, *Chem. Geol.* 28, 199–260.
3. Đông P., Tiên P.M. 1989. Isotopic ratios otherwise measured, In: P. Longevialle (editor) *Advances in Mass Spectrometry*. Vol. 11B, 1812–1813, Heyden & Son Ltd, London.
4. Eiler J.M., Bergquist B., Bourg I., Cartigny P., Farquhar J., Gagnon A., Guo W., Hales I., Hofmann A., Larson T.E., Levin N., Schauble E.A. and Stolper D. 2014. *Frontiers of stable isotope geosciences, Chemical Geology* 327, 119–143.
5. Farquhar J., Bao H., Thiemens M. 2000. Atmospheric influence of Earth's earliest sulfur cycle, *Science* 289, 756–758.

6. Hałas S. 1979. An automatic inlet system with pneumatic changeover valves for isotope ratio mass spectrometer. *J. Phys E: Sci. Instrum.* 12, 418–421.
7. Hałas S. 1980, 1982. An automatic inlet system for a mass spectrometer (In Polish). Patent description P.204655 (14.02.1978) and Patent Nr 106, 824.
8. Hałas S. 2002. Źródła jonów ujemnych w spektrometrach mas. *Prace Naukowe Politechniki Warszawskiej z.* 143, 53–63.
9. Hałas S. and Szaran J. 1999. Low temperature thermal decomposition of sulfates to SO<sub>2</sub> for on-line <sup>34</sup>S/<sup>32</sup>S analysis, *Analytical Chemistry* 71, 3254–3257.
10. Holser W.T. 1977. Catastrphic chemical events in the history of ocean, *Nature* 267, 399–403.
11. Hulston J.R., Thode H.G. 1965. Variations in the S33, S34, and S36 contents of meteorites and their relation to chemical and nuclear effects. *J. Geophys. Res.* 70, 3475–84.
12. Thiemens M.H. 2006. History and applications of mass-independent isotope effects. *Ann. Rev. Earth Planet. Sci.* 34, 217–62.
13. Robinson B.W. and Kusakabe M. 1975. Quantitative preparation of sulfur dioxide, for <sup>34</sup>S/<sup>32</sup>S analyses, from sulfides by combustion with cuprous oxide. *Analytical Chemistry* 47, 179–1181.
14. Thiemens M.H., Shaheen R. 2013. Mass-Independent Isotopic Composition of Terrestrial and Extraterrestrial Materials, *Treatise in Geochemistry* 2nd Edition, Elsevier.
15. Urey H.C. 1947. The thermodynamic properties of isotopic substances. *J. Chem. Soc. London.* 1947, 562–581.