ESIR 2011 *Central European Geology, Vol. 54/1–2, pp. 199–206 (2011)*
DOI: 10.1556/CEuGeol.54.2011.1–2.18

Ab initio calculations of sulfur isotope fractionation factor for H_2S in aqua-gas system

Maciej Czarnacki, Stanislaw Halas
Mass Spectrometry Laboratory, Institute of Physics,
Marie Curie-Sklodowska University, Lublin

High level *ab initio* calculations have been performed for hydrogen sulfide in aqua-gas system. Based on B3LYP density functional method with two Pople basis sets, 6–31G(d) and 6–311++G(d,p), we have obtained the minimum energy structures of H_2S molecule and H_2S–nH_2O hydrogen bonded molecular clusters (where n = 1–5). For these structures the internal and intermolecular harmonic vibrational frequencies were calculated. No scaling factor was used.

Using the Bigeleisen-Mayer formula we have evaluated the reduced partition functions ratios for the clusters and respective sulfur equilibrium isotope fractionation factor as a function of temperature. The highest sulfur isotope fractionation of 1.16‰ (at 20 °C) for hydrogen sulfide in aqua-gas system obtained from our calculations is in good agreement with experimental data published so far (0.85‰ and 1.52‰). This is the first theoretical estimation of sulfur isotope fractionation between gaseous and hydrated hydrogen sulfide (dissolved H_2S).

Address of corresponding author: M. Czarnacki: 20-031 Lublin, Poland
e-mail: maciej.czarnacki@gmail.com

Rapid ^2H analysis of small H_2O samples by CF-IRMS

Eric M. Galimov, Vyacheslav S. Sevastyanov
Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow

Nataliya E. Babulevich
NRC Kurchatov Institute, Moscow

Alexander A. Arzhannikov
Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow

In the past few years, an increase in interest in oxygen-conducting solid electrolyte electrochemical devices has been observed. The basic principles of operation of devices based on the solid electrolyte are (1) the oxidation of organic compounds followed by formation of simple gases CO_2, H_2O, NO_x or (2) the reduction of water and organic compounds followed by formation of H_2. These principles we have used for IRMS analysis of water. The present study is devoted to development of the high-temperature solid electrolyte reactor (SER) based on yttria-stabilized zirconia for decomposition of water. The device proposed is coupled on-line to Delta Plus XP stable isotope mass spectrometer (Thermo Fisher Scientific).

A solid electrolyte possesses the oxygen ions related conductivity at high temperatures (800–1000 °C). This reactor is made of tubular, thin-walled zirconia ceramics with inner diameter of 1 mm and of 10 cm total length. The solid-electrolyte reactor is connected in three-electrode circuit supported by the Elins PS8 Potentiostat. The inner electrode of the reactor served as the working electrode. Reference electrode is on the outer side.

The H_2O is decomposed on the triple-phase interface of the SER. Oxygen is turned into ions which under electrical voltage (1.2V) are moved through solid electrolyte wall outward. The flow of a He carrier gas swept hydrogen to isotope ratio mass spectrometer.

During several seconds compounds passed through the SER. To introduce 0.2 μL of water into He flow at $\sim$1 mL/min a split mode (split ratio 500:1) was used. The injector temperature is held at 250 °C. The solid electrolyte reactor was set to a temperature of 950 °C. Full time of analysis was 100-150 sec.

We measured δD values of water standards: VSMOW, SLAP, OH-1, OH-2, OH-3, OH-4 and obtained precision of 1–2‰. Our reduction SER can also be used for rapid ^2H analysis of organic materials.

New reactor has a very small size, provides rapid measurements of small water sample in the wide range of δD values, and has a good reliability.

Address of corresponding author: V. S. Sevastyanov: ul. Kosygin 19, Moscow 119991, Russia
e-mail: vsev@geokhi.ru

Innovations in technical developments of stable isotope analyses

Stanislaw Halas
Mass Spectrometry Laboratory, Institute of Physics,
Maria Curie-Sklodowska University, Lublin

I will start my lecture by recalling the memory of Roy Krouse, the great ESIR member, who passed away in March 2, 2010. I will mention his developments in stable isotope analysis of sulphur, e.g. use of Paar bomb and Kiba reagent for sulphur preparation in early 80's. At that time he already used GC separation of gaseous components in hydrocarbon gas combined with IRMS to study samples for exploration of fuels. His developments have been recalled in a special issue of *Chemical Geology* by Mayer and Hutcheon (2004) starting from Roy's pioneering study of selenium isotopes.

Then I will review briefly the new developments in the Lublin laboratory. Particularly I will present the latest achievements in highly reproductive oxygen extraction method from phosphates. This method enabled us to calibrate 3 new Ag_3PO_4 standards in cooperation with two internationally well-known laboratories abroad. By the application of this new method, we have studied the oxygen isotopes of shark teeth phosphates from Eocene deposits in Mangyshlak peninsula, Kazakhstan, where we estimated seawater paleotemperatures.

Another important development is the start of a new IRMS for precision chlorine isotope measurement. The achieved precision is better than 0.01‰. Details will be presented in the lecture by A. Pelc during this session.

Finally I would present $^7Li/^6Li$ technique and our first results. We have used the TIMS technique with double filaments in the ion source. We have tried to apply lithium isotope data to explain relatively high concentration of Li (17 mg/L) in the most famous mineral water named "Zuber" from Krynica Spa in Polish Carpathians.

Address: S. Halas: PL 20-31 Lublin, Poland, e-mail: stanislaw.halas@umcs.lublin.pl

UV laser ablation microanalysis of $\delta^{34}S$

Aleksandr V. Ignatiev, Tatiana A. Velivetskaya
Far East Geological Institute, FEB RAS, Vladivostok

Sulphur isotopes have been widely used in the study of igneous, sedimentary, hydrothermal, and biologic processes on the Earth. The development of *in situ* IR laser techniques enables high spatial resolution for sulphur isotope analysis. Laser ablation is becoming a dominant technology for direct solid sampling in geochemistry. UV laser ablation refers to the process in which an intense burst of energy delivered by a short laser pulse is used to remove a portion of sample material. The high photon-energy, short UV wavelength penetrates the plasma more efficiently and directly initiates bond breaking in the sample. These two conditions lead to a larger ablation rate and less fractionation.

We have developed a technique for determination of $^{34}S/^{32}S$ isotope ratios ($\delta^{34}S$) in sulphur-bearing minerals using UV laser ablation. A laser microprobe system has been constructed for high-accuracy (0.2‰), high-precision sulphur isotope analysis (0.1‰) with improved spatial resolution (50–100 μm). The system uses laser for *in situ* spot analysis by ultraviolet (UV) photoablation with 213 nm (Laser UP-213, New Wave Research). Our equipment consists of small volume stainless steel chamber, a capillary quartz reactor with quartz wool and six ports Valco valve with a trap for SO_2. Helium (flow 40 cm^2/min) with 5% impurity of oxygen passes through the chamber. At a photoablation of the sample SO_2 and an aerosol are formed.SO_2 and the aerosol pass through the quartz rector in a stream of helium. The aerosol is oxidized by oxygen to SO_2 at temperature 1000 °C. Total SO_2 is condensed to a trap with liquid nitrogen. The trap is slowly defrozen and cryogenically purified SO_2 enters through the open split in the ion source. Measuring the ratios of sulphur isotopes are carried out on a MAT-253 mass spectrometer. Reference SO_2 with known isotopic composition was used for standardization. Additionally, the camera (chamber?) is loaded with standards IAEA-S1, IAEA-S2, and IAEA-S3. In our system to obtain the amplitude of 1 Volt signal (for pyrite) 150 laser pulses is sufficient at a resolution of 100 μm and the radiation power of about 6 J/cm^2. For all othercases 300 pulses are required at the same power. The high precision is documented by comparing in situ laser data with conventional analyses of sulphides. No dependence of $\delta^{34}S_{V\text{-}CDT}$ values on UV laser energy flux has been observed. Mineral-specific fractionation of sulphur isotopes in analysing pyrite, sphalerite, galena, has not been observed with a UV laser (213 nm)

Address of corresponding author: A. V. Ignatev: FEGI, FEB RAS, pr. Stoletiya Vladivostoka 159,
Vladivostok, 690022 Russia, e-mail: inatiev@fegi.ru

Noble gas measurements from 1 μL of water: fluid inclusions of speleothems

László Palcsu, László Papp, Zoltán Major
Institute of Nuclear Research of the Hungarian Academy of Sciences, Debrecen

We show that noble gases from fluid inclusions can be extracted and measured by a noble gas mass spectrometer. The water amount is measured via its vapour pressure in a certain volume. The accuracy of such a water determination is less than 1% in the case of 1 μl of liquid water, which allows us to determine accurate noble gas concentrations. The overall mass spectrometric measurement process is calibrated by means of well-known air aliquots in the range of $2.5*10^{-5}$ to $1.0*10^{-6}$ ccSTP. The reproducibility of ^{40}Ar measurements is better than 0.6%, while those of krypton and xenon isotopes are 0.9–2.2% and 0.8–2.0%, respectively. Theoretically, these precisions for noble gas concentrations obtained from sample measurements allow us to determine noble gas temperatures with an uncertainty of less than 1 °C. To verify the reliability of the measurement, noble gases of air equilibrated water (AEW) samples have been measured. In this measurement run we have performed numerous measurements. Some of these AEW samples show excess noble gases mainly in the heavier ones. Pre-treatment of the capillaries by helium flushing and heating improved the AEW sample preparation: although the measurement of two samples might have failed, the measurements of other two AEW samples gave reasonable noble gas concentrations very close to the expected ones. Noble gas concentrations obtained from soda straw stalactites showed extra excesses mainly for the heavier noble gases that can be attributed to an artefact from sample preparation, although noble gases of few samples sustain the potential of the method based on temperature dependent solubility concentration to be a useful palaeoclimate proxy.

Address of corresponding author: L. Palcsu: H-4026 Debrecen, Bem tér 18/c, Hungary
e-mail: palcsu@atomki.hu

Chlorine stable isotope ratio analysis by the negative surface ionization of chloromethane

Andrzej Pelc, Stanislaw Halas, Maciej Czarnacki
Mass Spectrometry Laboratory, Institute of Physics,
Marie Curie-Sklodowska University, Lublin

The most common method used in chlorine isotope ratio analysis employs the conversion of a chlorine sample to chloromethane (CH_3Cl) prior to the mass spectrometric analysis. Chloromethane is very convenient for mass spectrometry as it has no memory effect in vacuum systems and could be easily obtained from a chlorine sample and transferred from the preparation line to the inlet system of mass spectrometer (MS) since its melting point is –97.7 °C.

In almost all chlorine isotope ratio studies the chloromethane gas is admitted to an electron impact ion source of an MS, where as many as 14 various type of positive ions are formed. Two of the ion species generated at m/z of 50 and 52, attributed to $CH_3{}^{35}Cl^+$ and $CH_3{}^{37}Cl^+$, are used for the isotope ratio measurements. The possible ions interference has got a considerable impact on the measured isotope ratios.

To eliminate disadvantages of the electron impact ionization and to increase the accuracy and efficiency of chlorine isotope ratio studies a new mass spectrometer with the negative ion source has been constructed. The novel part of this MS is the chlorine ion source which involves negative surface ionization of the chloromethane, whilst the remaining constituents are typical of dual inlet and dual collector MS. The negative ions are generated by the electron attachment to the Cl atoms followed by the CH_3Cl molecule dissociation. Using the invented ion source the only Cl^- anions (m/z = 35 and 37) are generated with efficiency dependent on the filament material and its temperature.

Moreover, enormous yield of the ion beam intensities leads to enhanced precision of the measurements. The standard uncertainty of single determination of $\delta^{37}Cl$ as small as 0.005‰ was obtained. In terms of the sample size the new method is more sensitive than IRMS, but less than TIMS and it requires at least 1 mg Cl. The method can also be applied for bromine isotope analysis on CH_3Br gas without instrumental modifications because Br has electron affinity (3.364 eV) close to that of Cl (3.615 eV).

This research was supported by Polish Ministry of Science and High Education (grant No. N N307 062136).

Address of corresponding author: A. Pelc: M. Curie-Sklodowskiej 1, 20-031, Poland,
e-mail: Andrzej.Pelc@poczta.umcs.lublin.pl

Isotope Ratio Mass Spectrometry for tracing the origin of cyanide for forensic investigation

Illa Tea, Ingrid Antheaum, Ben-Li Zhang
Chimie et Interdisciplinarité, Synthese, Analyse, Modélisation (CEISAM)
CNRS-Université de Nantes, Nantes

Cyanide is often the poison of choice in murders because it is easily available at chemical and photographic supply house. In cases of an offender who has used cyanide, forensic investigation could reveal the source of cyanide and identify the supplier. Traditional forensic techniques are based on anionic impurities analysis for matching cyanide salts back to their source. Nevertheless, this analysis technique may be perturbed by sample contamination.

Our objective was to examine the possibility of distinguishing a set of commercial cyanide through $\delta^{13}C$ and $\delta^{15}N$ values and to develop a protocol for the $\delta^{13}C$ and $\delta^{15}N$ analysis of cyanide extracted from several food and medicine matrices.

Thirteen KCN and 9 NaCN stocks originating from different suppliers, batches and purities were analysed by Elemental Analyser coupled to Isotope Ratio Mass Spectrometry (EA-IRMS). In order to evaluate the ^{13}C and ^{15}N isotope fractionation and its influence during the isolation of cyanide from complex matrices, several methods of cyanide derivatization were tested on two different sources of cyanide solutions and in 3 matrices: orange juice, yogurt drinking and medicine.

The isotopic signature of each commercial cyanide varied from –51.96 to –25.77‰ for $\delta^{13}C$ and from –4.51 to +3.81‰ for $\delta^{15}N$, highlighting the potential of EA-IRMS technique to differentiate cyanide collected from different suppliers and batches. The comparison of isotope analysis results with different derivatives, revealed that $Cu_2[Fe(CN)_6]$ was a most appropriate derivative compared to $Fe_4[Fe(CN)_6]_3$ and AgCN derivatives. Indeed, the $\delta^{13}C$ and $\delta^{15}N$ values of $Cu_2[Fe(CN)_6]$ were identical to those obtained from pure cyanide (KCN and NaCN), suggesting there was no isotope fractionation. The isotopic results obtained for the extracted and isolated cyanide from the 3 matrices showed a good reproducibility of the method and a weak matrix effect on isotope values.

These obtained results show that the developed method for determining N and C isotope in cyanide by EA-IRMS is a good tool for forensic investigations to compare cyanide from crime product with it from supplier.

Address of corresponding author: I. Tea: rue de la Houssinere, BP 92208, F-44322 Nantes, France
e-mail: illa.tea@univ-nantes.fr

Simultaneous measurements of carbon and oxygen isotopologues of carbon dioxide using a mid-IR laser based platform

Eric Wapelhorst
Thermo Fisher Scientific, Bremen

Hans-Jürg Jost, James J. Scherer, Joshua B. Paul
Thermo Fisher Scientific, Redwood City, CA

We are leveraging the strong absorption lines in the mid-infrared to simultaneously measure both isotopologues $\delta^{18}O$ and $\delta^{13}C$ of carbon dioxide at atmospheric concentration. For many applications, such as ecosystem fluxes or atmospheric monitoring, precision and accuracy required is less than $<0.1‰$. In the mid-infrared, CO_2 has very strong transitions that are particularly suited to achieve this goal using a robust multi-pass absorption cell. We will present results from laboratory tests of sensitivity and precision of a sensor currently under development.

Address of corresponding author: E. Wapelhorst: Hanna-Kunath Str. 11, D-28199 Bremen,
Germany, e-mail: eric.wapelhorst@thermofisher.com