

ESIR 2011

Central European Geology, Vol. 54/1–2, pp. 95–99 (2011)

DOI: 10.1556/CEuGeol.54.2011.1–2.9

$\delta^2\text{H}$ and $\delta^{13}\text{C}$ of methane in lignite fermentation

Michał Bucha, Łukasz Pleśniak

*Department of Applied Geology and Geochemistry,
Institute of Geological Sciences,
University of Wrocław, Wrocław*

Katarzyna Kubiak, Mieczysław Błaszczuk

*Department of Microbial Biology, Faculty of
Agriculture and Biology, The Warsaw University of
Life Sciences, Warsaw*

Mariusz-Orion Jędrysek

*Department of Applied Geology and Geochemistry,
Institute of Geological Sciences,
University of Wrocław, Wrocław*

The aim of these analyses was to determine isotopic composition of carbon and hydrogen from methane to indicate fermentation pathways of lignite. The lignite samples were collected from the "Kazimierz Północ" Konin Mine deposit. Those with a grain size of <1 mm were placed in 500 ml glass bottles with M9 medium (microbial nutrient) with various mineral additives and bacterial inoculum. The duration of the fermentation experiment was 3 months at 20 °C, with every 2 weeks sampling. Nine experimental variants involving different mineral additives and two control variants without inoculum were carried out. Results of two of them, i.e. inoculated IVA and IXB, are reported here (6 and 8 samples, respectively). The gas samples were analyzed by means of gas chromatography and isotope ratio mass spectrometry.

As a result of lignite fermentation in IVA and IXB variant of experiments, the total volume of gas were 839 ml and 1929 ml, respectively. In both variants methane appeared in the third day of the experiment and was present during each gas collection till the end of observations reported. The $\delta^{13}\text{C}_{\text{CH}_4}$ ranged from -66.34‰ to -25.77‰ in the IVA and from -71.40 to -34.12‰ in the IXB. The $\delta^2\text{H}_{\text{CH}_4}$ ranged from -361.9 to -249.4‰ and from -370.0 to -293.3‰ , respectively. No correlation between $\delta^{13}\text{C}$ and $\delta^2\text{H}$ in the methane has been observed. Likewise both isotopic values show chaotic variation during the experiment. Gas production varied with time, but the higher value was accompanied by higher $\delta^2\text{H}_{\text{CH}_4}$ value ($R^2=0.46$ in the IVA) and lower $\delta^{13}\text{C}_{\text{CH}_4}$ value ($R^2=0.37$ in the IVA and $R^2=0.33$ in the IXB). This may evidence that variation in amount of methane production during lignite fermentation varied with time and probably depended on methanogenic pathways. The thesis on suspected gradual increase of the role of CO_2 reduction and simultaneous decrease of acetic fermentation pathways, will be discussed during presentation. Alternatively, some carbon compounds contained in nutrients might influence the $\delta^{13}\text{C}_{\text{CH}_4}$ value.

Address of corresponding author: M. Bucha: Max Born pl. 9, 50-205 Wrocław, Poland
e-mail: michal.bucha@ing.uni.wroc.pl

Calculation of chlorine and bromine isotope fractionation factors in aqua-gas system

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

We report calculated values of isotope fractionation factors between chlorine and bromine hydrated anions and gaseous compounds HCl, Cl₂, HBr and Br₂, respectively. For calculation of reduced partition function ratios of hydrated Cl⁻ and Br⁻ anions we used simple model of [Cl/Br(H₂O)_n]- cluster (n = 14) based on electrostatic interaction between ion and water molecules treated as electric dipoles. Reduced partition function ratios for hydrogen chloride, hydrogen bromide and molecular chlorine and bromine were already calculated from vibrational frequencies, reported by earlier studies.

At temperatures 50–80 °C the equilibrium isotope fractionation between hydrated chlorine anion and hydrogen chloride attains 1.55–1.68‰ (this work) which is in good agreement with existing experimental data (1.4–1.8‰). The predicted isotope fractionations between HBr and Br₂ gases and hydrated bromine ion are very small, 1000lnα do not exceed 0.8‰, thus the expected natural variations of bromine isotope composition in aqua-gas system will require enhanced precision for their detection.

This research was supported by the Polish Ministry of Science and Higher Education (Grant No. N N307 062136).

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

Dissolving halite for H, C and S isotopic analysis of fluid inclusions

Wojciech Drzewicki
*Laboratory of Isotope Geology and Geoecology,
The University of Wrocław, Wrocław*

Stanisław Burliga
*Department of Structural Geology and Tectonic
The University of Wrocław, Wrocław*

Janusz Krajniak, Łukasz Pleśniak, Mariusz-Orion Jędrysek
*Laboratory of Isotope Geology and Geoecology
The University of Wrocław, Wrocław*

Among large knowledge on salt formation research, little is known on the origin and especially migration of methane and hydrogen sulphide within salt structures. Therefore, we report hereby on stable isotopic composition of these gases contained in fluid inclusions in the salt, what presumably could allow us to conclude on migration (directions), and identify factors controlling variations in concentration of methane and hydrogen sulphide. To obtain isotopic results, first it was necessary to quantitatively release gases enclosed in inclusions in salt – the proposed method allowed us to obtain the material to determine both chemical and isotopic data. Namely we have carried out decrepitation of fluid inclusions due to dissolving of salt samples in aqueous solution using home-made vacuum line. Standard CH₄ oxidation and H₂S precipitation (cadmium sulphide) and oxidation, have been used for further C and S isotopic ratios analyses (CO₂ and SO₂).

All salt samples used for isotopic analyses of methane and hydrogen sulphide from inclusions, came from salt mine Klodawa (central Poland). Preliminary results showed that inclusions contain (neglecting CO₂): CH₄ (from 0.84 to 2.13%), N₂ (from 66.58 to 71.22%), O₂ (from 23.71 to 30.73%) and Ar (from 1.87 to 2.41%), He (from 0.02 to 0.13%) and H₂S (amount H₂S of the inclusions of salt from 0.7 to 11.1 mol.). The $\delta^{13}\text{C}_{\text{CH}_4}$ value varied from -47.1‰ to -29.7‰ , $\delta\text{D}_{\text{CH}_4}$ value varied from -128.6‰ to -147.6‰ and the $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ value varied from -6.28‰ to 3.20‰ . We will discuss on potential factors controlling isotopic ratios during our presentation.

Address of corresponding author: W. Drzewicki: Cybulskiego 30, 50-205 Wrocław, Poland
e-mail: wojciech.drzewicki@ing.uni.wroc.pl

Origin of Precambrian carbonate rocks of the Ukrainian Shield by geological-structural peculiarities and isotopic signatures

Vasyl' Guliy

Ukrainian State Geological Research Institute, Kyiv

Vasyl' Zagnitko, Ruslana Bochevar

Kyiv Taras Shevchenko National University, Kyiv

Carbonate rocks are widespread within the Precambrian metamorphic complexes of the Ukrainian Shield. The rocks comprise of a number of genetic types, including primary sedimentary and geologically later varieties (calc-silicate rocks, carbonatites, carbonate veins, etc.), whose geneses are connected to igneous and metasomatic processes. The discovery of kimberlites and lamproites related rocks carbonate rocks at the Azov Block of the Shield has demonstrated that the carbonate rocks of the Shield are even more diverse and stimulated vivid discussions on their origin.

To divide these families of the carbonate rocks we used system of geological-structural indicators and isotopic (C, O, Sr) signatures of carbonates and some coexisting minerals.

Taking into consideration the obtained data, we determined origin of different kinds of carbonates from objects with more complicated geological history. For example, we examined rocks of the Kapitanivsky ore field (Golovanivska zone of the Shield), where 15 large serpentine (primary dunites and pyroxenites) massives with different metamorphic and metasomatic rocks are present. We identified at least three groups of carbonate rocks here. 1. Primary sedimentary with $\delta^{13}\text{C} = 1 \pm 2\text{‰}$, $\delta^{18}\text{O} = 20 \pm 2\text{‰}$. 2. Metasomatic carbonates with $\delta^{13}\text{C} = -3.2 \pm 2\text{‰}$, $\delta^{18}\text{O} = 16 \pm 2\text{‰}$. 3. Late carbonate veins as a result of intensive alterations of low $\delta^{13}\text{C}$ values (less then -8.0‰). Similar values of the $\delta^{13}\text{C}$ we obtained for late carbonates related to the kimberlites.

Address of corresponding author: V. Guliy: 78 Avtozavods'ka str., Kyiv 04114, Ukraine
e-mail: vgul@ukr.net

Anomalous $\delta^{18}\text{O}$ isotope composition of minerals from North Karelia (Russia)

Aleksandr V. Ignatiev,
Sergey V. Vysotskiy
Far East Geological Institute, Vladivostok

Viktor I. Levitskiy
A.P. Vinogradov Institute of Geochemistry, Irkutsk

Sergey Yu. Budnitskiy, Tatiana A. Velivetskaya
Far East Geological Institute, Vladivostok

The Earth's rocks and minerals commonly have positive $\delta^{18}\text{O}$ values, being enriched in isotope ^{18}O relative to the sea water. Most of silicate rocks are characterized by $\delta^{18}\text{O}_{\text{smow}}$ from +0 to +15‰. The recent findings in Karelian rocks, i.e. anomalously poor in heavy oxygen isotope, suggest very specific conditions of their formation and cause interest to further researches. The corundum-bearing rocks of the northern Karelia composed of few major mineral varieties are characterized by a high diversity of textures and structures, among which zoning is widely presented. Garnet, amphibole and plagioclase of different generations mix with each other in different proportions and form both early corroded relics and late mineral phases, indicating development of paragenetic sequences in a wide range of temperature and pressure.

Oxygen isotope ratios in garnet, corundum, amphibole and plagioclase were analysed. Most of them are anomalously low (from -15.5 to -26‰) that were not known until recently. We believe that minerals may retain the extremely low $\delta^{18}\text{O}$ values, which resulted from interaction of glacial water with their protolith, after metamorphic transformations. The Svecofennian high-alumina corundum-bearing plagioclase was probably formed after the hydrothermally altered Paleoproterozoic rocks formed in the shallow zone of fumarole field under a glacier. Both sufficiently large volume of water with light oxygen isotope composition and long duration of the water-rock interaction were necessary to provide such a deep alteration. The metasomatic processes took place probably in the oldest Huronian glaciation period, which maximum occurred 2.3 billion years ago. Later, these rocks suffered the high-pressure Svecofennian (1.9–1.8 billion years) metamorphism.

We are grateful to the Russian Foundation for Basic Research (No. 10-05-00371-a) for funding our investigation.

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