

Sulfur isotope composition of selected Polish coals

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Abstract Literature studies show that there are few data on sulfur isotope ratio in available the Polish coals. Elaboration of a method for the separation of sulfur from coal and measurement of sulfur isotope ratio of Polish coals is the scope of this work. The aim of the study was the preparation of coal samples and extraction of the particular form of sulfur. The stable compounds (Ag_2S and BaSO_4) were converted into sulfur dioxide. Sulfur isotope ratio in the gas phase was determined using a mass spectrometer. Samples were taken from selected Polish coal mines. Hard coal from Upper Silesia Basin, one sample from the Bogdanka coal-mine and one sample of lignite from the Bełchatów coal-mine.

Key words coal • coal extraction • mass spectrometer • sulfur isotope ratio

Introduction

Industrial activities of man have changed global sulfur cycle flows remarkably. The biggest amount of sulfur is emitted in the form of SO_2 during fossil fuel combustion and exceeds 50 million tons. Previous studies have shown that the isotope ratio value $^{34}\text{S}/^{32}\text{S}$ is higher for natural than anthropogenic (i.e. originating from coal and oil combustion) sources [1]. Therefore, this value can be used as a marker of the sources detected in the environment. However, while the mentioned isotopes ratio is not constant for all regions of the world, they have to be linked to the local fossil fuel sulfur isotopes composition. While the life time of sulfur compounds in the atmosphere is short, they participate in the continental/region range from the emission source.

While in the literature data for American, Australian etc. coals are presented [2], this study seems to be first one performed for the coals of Polish origin. The aim of this work was to establish basic data for the Polish coal, which can be used in further environmental studies.

Application of sulfur isotope ratio for environmental studies

Studies of sulfur isotopes may provide unique information concerning the geological era and mechanism of sulfur incorporation in organic-rich sediments. Figure 1 shows the range of $\delta^{34}\text{S}$ values found in nature for a number of different forms of sulfur. The zero point of the $\delta^{34}\text{S}$ scale is troilite from the Canyon Diablo meteorite. The sulfur isotope geochemistry of sediments is complicated by the fact that sulfur can exist in several oxidation states and chemical forms. In coal, sulfur is present in the form of pyrite (FeS_2) and other metallic sulfides (ZnS , PbS , FeS),

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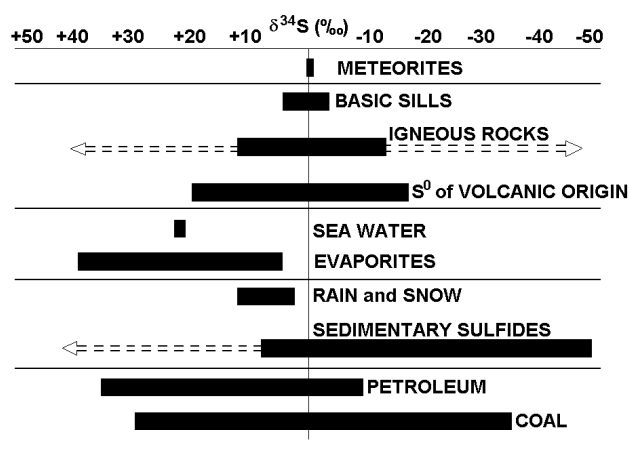


Fig. 1. Sulfur isotope distribution in nature [5].

sulfates (FeSO_4), organic sulfur and elemental sulfur. For this reason, sulfur isotope studies can provide useful information only if the isotopic composition of individual sulfur components is analyzed rather than the total extractable sulfur [6].

Material

In Poland hard coal occurs in three main basins, all of Upper Carboniferous age: Upper Silesia, Lower Silesia and Lublin. There are over 120 recognized deposits, of which around 70 have been developed. Mining is centered at the Upper Silesia Basin, which is located in the south of Poland around Katowice and straddles the border with the Czech Republic. It is the most important coalfield, comprising 103 recognized deposits and covering an area of 4500 km².

Samples from 6 Upper Silesia and Lublin coal mines were selected for this investigation. One sample was taken from the biggest Polish lignite open pit mine Bełchatów. Additionally, coals from Sośnica are from different depths.

Sample preparation and measurement

The work started with the preparation of coal samples and extraction of the particular form of sulfur [7]. By this method, each form of sulfur has been extracted and transformed into a stable compound, which can be subsequently converted into gas phase (SO_2) for mass spectrometric analysis. All the samples, in the form of Ag_2S and BaSO_4 were chemically treated to obtain gaseous SO_2 using the method described by Hałas and Szaran [3]. The sulfides

Table 1. Sulfur isotope for sulfur present in Polish coals.

Coal mine	S [%]	$\delta^{34}\text{S}$ [‰]		
		Pyrite sulfur	Organic sulfur	Sulfate sulfur
Bogdanka	1.23	1.29	-2.50	-1.95
Kazimierz Juliusz	0.79	6.37	6.18	7.27
Chwałowice	0.81	1.97	3.85	1.19
Jankowice	0.64	0.33	15.88	-
Śląsk	0.74	10.50	4.40	13.71
Sośnica	2.06	-6.62	4.66	-1.88
Bełchatów*	0.30	-	9.37	-

* lignite

Table 2. $\delta^{34}\text{S}$ of coals from the Sośnica mine.

Total S [%]	Sulfur content S [%]			$\delta^{34}\text{S}$ [‰]		
	Pyrite	Sulfate	Organics	Pyrite	Sulfate	Organics
0.51	0.36	0.08	0.07	4.05	4.08	4.29
0.75	0.37	0.03	0.35	7.32	10.88	9.71
2.06	1.28	0.10	0.68	-6.62	-1.88	4.66

were heated in a porcelain boat with Cu_2O , the sulfates in a copper boat with NaPO_3 . The sulfur isotope ratio in the obtained sulfur dioxide was measured in the mass spectrometer DELTA plus FINIGAN.

Results and discussion

Organic matter produced from sea – plants is a source of material forming the fossil fuels. This essential part of the process was performed by bacterial action, which transformed organic material and produced H_2S and S, which were then introduced into the layers of peat coal. As the results show (Table 1), the values $\delta^{34}\text{S}$ in mineral fuels are in range from -6.62 to +15.88‰. The obtained results suggest that the sulfur in coal originates from the sulfur originally bounded by plants and is depleted in the isotope $\delta^{34}\text{S}$. The sulfur was probably produced in the process of sulfate bacterial reduction. The precision of the results depended mostly on the precision of mass spectrometric measurements and was found to be 0.34‰.

In some deposits, the isotopic composition is similar at different depths of the whole region, while in some other, deposits this composition can even change within distances of several meters [4]. Three samples from Sośnica coal-mine were taken from different depths (Table 2). There is a big differentiation not only between the concentration of the sulfur, but also between the composition of this isotope ratio as a result of isotope composition of this element in source materials.

This isotope ratio can be used as a tracer for environmental samples (aerosol, rain, superficial water) to track the products of the combustion of a particular coal.

References

- Andrews JE, Brimblecombe P, Jickells TD, Liss PS (1996) An introduction to environmental chemistry. Blackwell Science Ltd., New York
- Derda M (1999) Sulphur isotopes in nature. Determination of sulphur isotope ratios in coal and petroleum by mass spectrometry. Raporty IChTJ. Seria B. No. 6/99 (in Polish)
- Hałas S, Szaran J (1999) Low-temperature thermal decomposition of sulfates of SO_2 for on line $^{34}\text{S}/^{32}\text{S}$ analysis. Anal Chem 71:3245–3257
- Krouse HR (1991) Stable isotope studies of sulfur flows and transformations in agricultural and forestry ecosystems. IAEA, Vienna, IAEA-SM-313/108
- Krouse HR, Grinenko VA (1991) Stable isotopes in the assessment of natural and anthropogenic sulfur in the environment, SCOPE. John Wiley & Sons Ltd., London
- Smith JW, Batts BD (1974) The distribution and isotopic composition of sulfur in coal. Geochim Cosmochim Acta 38:121–133
- Westgate LM, Anderson TF (1982) Extraction of various forms of sulfur from coal and shale for stable sulfur isotope analysis. Anal Chem 54:2136–2139