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The isotopic composition of groundwaters related to native sulphur deposits

Native sulphur deposits of the Carpathian Foredeep contain hydrosulphuric groundwaters. The major components of hydrosulphuric waters (H_2O, HCO_3^-, SO_4^{2-} and H_2S) have been analysed for stable isotope ratios in samples from Machów open-pit mine as well as from selected wells of the area adjacent to native sulphur ores collected in May 1993. The oxygen and hydrogen of recent water from the uppermost layer (at a water table occurring in the Tertiary rocks exposed at Machów) are isotopically very close to the recent infiltration waters. This means that these waters nearly completely replaced the original isotopically heavier waters. Nevertheless, a very high rate of bacterial reduction of sulphate to hydrogen sulphide (within the ore deposits) is indicated by the high concentration of H_2S (292 mg/l) and $\delta^{34}S$ of SO_4^{2-} (26.3‰) and H_2S (−7.9‰). This is further confirmed by high $\delta^{18}O$ of SO_4^{2-} (15.2‰ vs. SMOW).

INTRODUCTION

Major components of groundwaters of Piaseczno and Machów native sulphur open-pit mines (northern, marginal part of the Carpathian Foredeep) have not been isotopically analysed before exploitation or during early stages of sulphur mining. As a result, the isotopic composition of hydrogen and oxygen of the original ore waters can be inferred indirectly on the basis of investigations of secondary gypsum crystals. These crystals were formed only locally in the sulphur bearing series where ore waters have been oversaturated with sulphate. Isotope results indicate that δD and $\delta^{18}O$ of waters from which secondary gypsum orginally precipitated were close to the upper part of the Craig's world meteoric water line (typical for a hot climate) according to the equation:

$$\delta D = 8\delta^{18}O + 10,$$

with the $\delta^{18}O$ ranging from –5.5 to –2.5‰ (S. Hałas, H. R. Krouse, 1982; S. Hałas, 1986; W. Kowalski *et al.*, 1990). Similar $\delta^{18}O$-values (from –6.3 to –5.5‰) have been obtained by A. Zuber and J. Grabczak (1985) for the Tertiary mineralized waters from some wells drilled near Busko and Solec (Nida region). Another way to obtain oxygen isotope composition of original ore waters is the $\delta^{18}O$ of calcite. S. Hałas (1986) obtained $\delta^{18}O$-values ranging from –5.7 to –4.0‰ relative to the average value of oceanic water (SMOW) using this approach.

As it is clear from above, the results obtained by these two methods differ significantly from $\delta^{18}O = -10.5$‰, which is the value typical for shallow groundwaters of Poland (except mountain areas). Thus, it is a possible to estimate (by measuring of $\delta^{18}O$ and δD of the ore waters) a magnitude of the atmospheric water admixture present in the ore waters today. Just such an inquiry comprised of analyses of water samples derived from the Machów native sulphur ore as well as from selected boreholes near Busko and Solec, was carried out in May 1993. In these samples, except oxygen and hydrogen isotope ratios in H_2O, the $\delta^{13}C$ in HCO_3^-, $\delta^{18}O$ in SO_4^{2-} and $\delta^{34}S$ in SO_4^{2-} and H_2S were measured as well.

METHODOLOGY

Isotope composition of hydrogen has been measured with the aid of a cycloidal spectrometer (S. Hałas, 1985) analysing prepared gaseous hydrogen which has been produced at 450°C from 5 µl H_2O with the use Zn (M. L. Coleman *et al.*, 1982). Isotopic composition of oxygen in H_2O has been determined with the aid of *MI-1305* spectrometer from 0.1 µmole CO_2 equilibrated with water samples at 25°C. $\delta^{18}O$ of carbonates has been obtained analysing CO_2 released with the aid of 100% H_3PO_4 in the vacuum line from precipitated $BaCO_3$ (J. M. McCrea, 1950). Oxygen-isotope analyses from sulphates have been analysed after the precipitation of $BaSO_4$ (from water) followed by its reduction at 1000°C with the aid of graphite to CO and CO_2 in a platinum boat put in a vacuum instrument. CO released in this manner was converted to CO_2 by a glow discharge between platinum electrodes (S. Hałas, L. Mioduchowski, 1978).

Sulphur-isotope composition of sulphates has been investigated with a *MI-1305* spectrometer preparing SO_2 in the vacuum line at 850°C from the precipitated $BaSO_4$ with the use $NaPO_3$ (S. Hałas, W. Wołącewicz, 1981). $\delta^{34}S$ of H_2S have been estimated by the analysis of SO_2 obtained from the oxidation of ZnS (previously precipitated from solution) in the vacuum line at 900°C with the aid of Cu_2O. The percentage of the investigated components was determined gravimetrically, and hydrogen ion activity was run in the field (with an accuracy of ± 0.2 pH) using the *MERC* index slips.

The isotope analyses have been carried out with precision and accuracy estimated to be within ±1‰ for hydrogen and to be within ±0.1‰ for the remainder of the elements.

Table 1

Isotopic and chemical results of groundwater analyses

Sample	pH	H_2O		CT		SO_4^{2-}			H_2S	
		δD [‰]	$\delta^{18}O$ [‰]	concentration [mg/l]	$\delta^{13}C$ [‰]	concentration [mg/l]	$\delta^{18}O$ [‰]	$\delta^{34}S$ [‰]	concentration [mg/l]	$\delta^{34}S$ [‰]
Machów, Quaternary*	7.1	–57.2	–9.63	184	–12.77	272	–5.19	6.48	0	n. a.
Machów, Tertiary*	7.0	–64.1	–9.59	0	n. a.	1660	15.16	26.26	292.0	7.94
Busko, spring 8a	6.2	–62.6	–10.05	423	–13.30	1436	13.53	29.06	36.5	–5.96
Busko, spring 13	6.2	–49.5	–9.86	431	–12.94	1368	14.68	28.02	56.7	–6.72
Busko, spring 16	6.2	–59.2	–9.31	400	–13.00	1710	14.89	28.25 (27.4 S)	49.6	–7.31 (–7.0 S)
Solec, Zdrój Solecki	7.0	–31.3	–5.37 (–7.31 T)	356	–17.88	2175 (2890 T)	16.01	31.62 (32.0 S) (32.98 T)	150.2	10.81 (11.66 T)

* — groundwater level; n. a. — not analysed; CT — (carbon total) total inorganic carbon dissolved in groundwater; in brackets: S — results of J. Szaran (1973) sampled in 1970, T — results of A. Trembaczowski (1989) sampled in 1979

RESULTS AND DISCUSSION

Both the obtained and older archival isotope results are listed in Table 1. Carbon total (CT) in Table 1 refers to total inorganic carbon contained in the analysed solutions and means that around pH = 7, except the HCO_3^- ion, a slight admixture of dissolved CO_2 had to occur in the same solution. The $\delta^{13}CT$ values are typical for groundwaters which dissolve marine carbonates, characterized by $\delta^{13}C \approx 0$ (P. Staniaszek *et al.*, 1986). An exception is Zdrój Solecki area where isotopically light carbonates may be dissolved. Such carbonates commonly build up the sulphur ore series (e.g. S. Hałas, 1973; and review of J. Parafiniuk *et al.*, 1994). It has not been possible to estimate the $\delta^{13}C$ of hydrosulphuric waters from the Machów mine where HCO_3^- content was too low.

Presently, the oxygen and hydrogen isotope composition of H_2O from Machów is very close to the values of $\delta^{18}O = -10.5‰$ and $\delta D = -73‰$, i.e. close to the values characteristic for modern shallow groundwaters of Poland. These data confirm the older results (A. Zuber, J. Grabczak, 1985) with regard to the oxygen isotope composition and differ slightly as to the δD-values. The δD-values measured by the authors are less negative than those presented by A. Zuber and J. Grabczak (1985) and J. Grabczak *et al.* (1987).

The $\delta^{18}O$-values obtained in both SO_4^{2-} ion and H_2O may help to estimate the environmental conditions in which the oxidation of sulphide to sulphate ion took place. By plotting of the obtained $\delta^{18}O$-values on a diagram worked out by R. O. van Everdingen and H. R. Krouse (1985), it is possible to estimate how much oxygen of H_2O has been used during the oxidation process. In the case of a water sample (Quaternary) from the Machów mine this has been estimated as high as 100%, while in other cases it is impossible to apply this model because the main process in such waters is the dissolution of sulphates followed by their subsequent (microbiological) reduction to hydrogen sulphide. Sulphate remained in the solution due to bacterial reduction becomes strongly enriched in the heavy isotopes ^{34}S and ^{18}O, while H_2S becomes enriched in the light isotope ^{32}S (see e.g. H. R. Krouse, R. G. L. McCready, 1979). It is interesting to note that the archival data are essentially the same as those reported by the present authors. It means that for 15–20 years there has not been any substantial disturbance of the groundwater dynamic equilibrium in both the Busko (spring no. 16) and Zdrój Solecki areas. The greatest concentration of hydrogen sulphide is observed in the Tertiary ore waters from the Machów mine. The $\delta^{34}S$-values of H_2S from Machów is similar to $\delta^{34}S$-values of hydrogen sulphide from the Busko area. In addition, the groundwater from the Zdrój Solecki area is relatively enriched in the H_2S content and is distinctly isotopically heavier than that groundwater from the Machów mine.

CONCLUSIONS

The presented results indicate that the ore water from Machów sulphur mine are substantially diluted by modern infiltration water or by older Holocene water. The difference between the sulphur isotope composition of SO_4^{2-} and H_2S as well as a high concentration of hydrogen sulphide indicate a high rate of bacterial sulphate reduction in the Tertiary ore waters at Machów open-pit mine. Analogous results are noted only in groundwater of the Zdrój Solecki area. It is noteworthy that the substantial replacement of original isotopically heavy ore waters by modern infiltration waters has not inhibited hydrogen sulphide generation in these groundwaters. Such a high rate of sulphate reduction is also reflected by elevated (around 2‰) content of ^{18}O compared to the $\delta^{18}O$-values of original evaporite sulphates with the values ranging from 12.6 to 13.6‰ (S. Hałas, L. Mioduchowski, 1978).

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REFERENCES

COLEMAN M. L., SHEPHERD T. J., DURHAM J. J., ROUSE J. E., MOORE G. R. (1982) — Reduction of water with zinc for hydrogen isotope analysis. Anal. Chem., **54**, p. 993–995.

EVERDINGEN R. O.van, KROUSE H. R. (1985) — Isotope composition of sulphates generated by bacterial and abiological oxidation. Nature, **315**, p. 395–396.

GRABCZAK J., SZCZEPAŃSKI A., ZUBER A. (1987) — Uwagi na temat genezy i ochrony wód mineralnych Buska i Solca. In: 25 lat górnictwa uzdrowiskowego, p. 91–99. Wyd. AGH. Kraków.

HAŁAS S. (1973) — Interdependence between sulphur and carbon isotope composition in native sulphur ores (in Polish with English summary). Prz. Geol., **21**, p. 277–279, no. 5.

HAŁAS S. (1985) — Dual collector cycloidal mass spectrometer for precision analysis of hydrogen isotopes. Inter. J. Appl. Rad. Isotopes, **36**, p. 957–960.

HAŁAS S. (1986) — Stable isotopes as the source of information on deposit-forming processes at the example of the Tarnobrzeg native sulfur deposits (in Polish with English summary). Prz. Geol., **34**, p. 374–379, no. 7.

HAŁAS S., KROUSE H. R. (1982) — Isotopic abundances of water of crystallization of gypsum from the Miocene evaporite formation, Carpathian Foredeep, Poland. Geochim. Cosmochim. Acta, **46**, p. 293–296, no. 2.

HAŁAS S., MIODUCHOWSKI L. (1978) — Skład izotopowy tlenu w wapniowych i strontowych minerałach siarczanowych i siarczanach wód różnych okolic Polski. Ann. UMCS, **AAA 33**, p. 115–130.

HAŁAS S., WOŁĄCEWICZ W. (1981) — Direct extraction of sulfur dioxide from sulfates for isotopic analysis. Anal. Chem., **53**, p. 685–689, no. 4

KOWALSKI W., PARAFINIUK J., HAŁAS S. (1990) — Model of sulfur isotope fractionation in the Polish native sulfur deposits. Freib. Forsch., **C 441**, p. 65–77.

KROUSE H. R., McCREADY R. G. L. (1979) — Reductive processes (p. 315–368), Biochemical cycling of sulphur (p. 401–430). In: Biochemical factors in mineral cycling (eds. P. A. Trudinger, D. Swaine). Elsevier. Amsterdam.

McCREA J. M. (1950) — On the isotope chemistry of carbonates and a paleotemperature scale. J. Chem. Phys., **18**, p. 849–857.

PARAFINIUK J., KOWALSKI W., HAŁAS S. (1994) — Stable isotope geochemistry and the genesis of the Polish native sulphur deposits — a rewiev. Geol. Quart., **38**, p. 473–496, no. 3.

STANIASZEK P., TREMBACZOWSKI A., LIS J., SZARAN J., HAŁAS S. (1986) — Variability in isotopic composition of carbon dissolved in carbonate waters in the Lublin Upland (in Polish with English summary). Prz. Geol., **34**, p. 159–163, no. 3.

SZARAN J. (1973) — Skład izotopowy siarki pochodzenia źródlanego i badanie równowagi izotopowej między fazą stałą, ciekłą i gazową. Arch. UMCS. Lublin.

TREMBACZOWSKI A. (1989) — Badania składu izotopowego siarki i tlenu siarczanów w wodach gruntowych. Arch. UMCS. Lublin.

ZUBER A., GRABCZAK J. (1985) — Pochodzenie niektórych wód mineralnych Polski południowej w świetle dotychczasowych badań izotopowych. In: Aktualne problemy hydrogeologii, p. 136–148. Wyd. AGH. Kraków.

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BADANIA IZOTOPOWE WÓD PODZIEMNYCH ZWIĄZANYCH ZE ZŁOŻAMI SIARKI RODZIMEJ

Streszczenie

Przebadano skład izotopowy wodoru (H_2O), tlenu (H_2O, SO_4^{2-}), węgla (HCO_3^-) i siarki (SO_4^{2-}, H_2S) występujących w wodach utworów trzeciorzędowych kopalni siarki rodzimej w Machowie oraz w wodach siarczkowych Buska i Solca. Wyniki badań izotopowych wodoru i tlenu (tab. 1) wskazują, że woda usuwana z górnych warstw utworów trzeciorzędowych ma charakter współczesnej wody infiltracyjnej, tj. charakteryzującej się wartościami $\delta D = -70‰$ i $\delta^{18}O = -10.5‰$ względem średniej wody oceanicznej (SMOW).

Z badań izotopowych tlenu w H_2O i SO_4^{2-} wynika, że jedynie w wodzie utworów czwartorzędowych istnieją warunki utleniające oraz że praktycznie cały tlen w jonie SO_4^{2-} tej wody pochodzi z H_2O. Skład izotopowy siarki siarczanowej i siarczkowej oraz znaczna koncentracja H_2S ($\delta^{34}S = 15.16$ i $-7.94‰$ odpowiednio) wskazują na znaczną intensywność bakteryjnej redukcji siarczanów, zachodzącej współcześnie w wodzie z Machowa. Podobną intensywność wykazuje jedynie woda ze Zdroju Soleckiego (tab. 1).

Skład izotopowy węgla w HCO_3^- wód siarczkowych, a ściślej całego węgla nieorganicznego rozpuszczonego w wodzie (CT), jest dość typowy dla HCO_3^- wód gruntowych, którego obecność wynika z rozpuszczania węglanów morskich przez glebowy CO_2. Wyjątek, być może, stanowi tu woda ze Zdroju Soleckiego i Machowa. Ta ostatnia nie została przeanalizowana na $\delta^{13}C$ z powodu niskiej koncentracji HCO_3^-.