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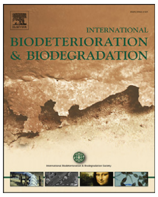

Using multi-isotopes (^{34}S, ^{18}O, ^{2}H) to track local contamination of the groundwater from Hongshan-Zhaili abandoned coal mine, Zibo city, Shandong province

Jianwei Zhou [a, *], Qiuxia Zhang [a], Fengxin Kang [b], Yanpeng Zhang [a], Lei Yuan [a], Dong Wei [c], Shanghua Lin [c]

[a] *School of Environmental Studies, China University of Geosciences, Wuhan, Hubei, 430074, PR China*
[b] *Shandong Provincial Bureau of Geology and Mineral Resources, Jinan, 250000, PR China*
[c] *Shandong Geo-Mineral Engineering Group Co. Ltd., Jinan, 250000, PR China*

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ABSTRACT

The Hongshan-Zhaili coal mine was extensively mined for several decades, lies in Zibo city, Shandong province. After closed in 1994, the coal strata water level raised above the Ordovician limestone water level, then led to the cross strata pollution, which greatly affected the normal use of local people. The Ordovician limestone aquifer is the important drinking water aquifer for local community which covered under the coal strata. Thirty-two domestic water wells near the former coal mine were sampled for water chemistry and stable-isotope analysis of water and dissolved SO_4^{2-}. Groundwater plots close to the Global Meteoric Water Line and reveals evidence of recharging from atmospheric precipitation. The analysis of sensitive components NO_3^-, SO_4^{2-}, ^{34}S in groundwater shows an oxidation environment, promoting the pyrite oxidation. The result of ^{34}S isotopes indicates that the Ordovician limestone water SO_4^{2-} mainly derived from the atmospheric precipitation SO_4^{2-}, and the contamination of the Ordovician limestone water from coal strata water has occurred locally in the study area, the Ordovician limestone water is enriched in SO_4^{2-} and depleted ^{34}S in sulfate.

1. Introduction

Coal mining is an important industry in China, and has made outstanding contribution to the sustainable development of national economy. Although most active mines have policies with respect to release of mine water to the environment, this is often not the case for abandoned mines, hence, after closure, leaving behind various geological environmental problems, such as contamination in groundwater, surface water, soil and plants near the abandoned coal mine, and even endemic disease (Equeenuddin et al., 2010; Bhattacharya et al., 2012; Olías et al., 2012; Sadek, 2012; Khalil et al., 2013). Hongshan-Zhaili abandoned coal mine lies in Zibo city, Shandong province, is a typical case. Groundwater produced from the Ordovician limestone aquifer, provides an important source of water in Zibo city. The aquifer is extensively utilized as a source of potable and producing water by rural residents in the mine area. Acid mine drainage (AMD) produced from Hongshan-Zhaili abandoned underground coal mines is an important threat to local drinking water supplies, which greatly affected the life and production of citizen, and it has attracted attention from the national government and scientists. A large number of scholars have conducted comprehensive research bout the formation mechanism and influencing factors of mine water (Martins et al., 2011a, 2011b), exploring the new way of mine water treatment and mine geological environment restoration has become a new hot spot (Johnson, 1995; Rodriguez et al., 2010).

Based on trends in the concentration of total dissolved solids (TDS) and SO_4^{2-} concentration in domestic water wells, which is similar to the characteristic of mine water, it concluded that localized AMD contamination of Ordovician limestone aquifer was occurring (Xu and Xu, 2003; Zhang, 2001; Lv et al., 2005; Feng, 2006; Yi et al., 2007; Dong and Dong Sh., 2009; Wang, 2012).

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* Corresponding author. No. 388, Lumo Road, Wuhan, 430074, PR China.
E-mail addresses: jw.zhou@cug.edu.cn (J. Zhou), edu652524@163.com (Q. Zhang), kangfengxin@126.com (F. Kang), yanpeng1028@126.com (Y. Zhang), 3360874yl@163.com (L. Yuan), weidong_68064@126.com (D. Wei), lin_shanghua@163.com (S. Lin).

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Among several possible processes, it is widely accepted that the evolution of hydrogeological condition in groundwater after mine closure is responsible for groundwater pollution (Chang et al., 1999). While elevated TDS concentrations in the vicinity of the mine area may be suggestive of AMD incursion, additional methods are required for a qualitative assessment of the magnitude and spatial distribution of this contamination. Previous studies showed that the stable isotopic compositions of aqueous SO_4^{2-} from sulfate oxidation associated with the abandoned coal mine is very different from the stable isotopic composition of SO_4^{2-} in the Ordovician limestone aquifer. The isotope can be used to evaluate which SO_4 source is responsible for groundwater pollution. However, combined use of hydrochemical (major elements) and stable isotope (H, O, S) for investigating the SO_4 contamination mechanism in coal mine has rarely been attempted in China. A multiple isotope approach is strongly needed for comprehensive understanding of groundwater environments (Avner et al., 2002; Widory et al., 2004) to determine the essential factors controlling groundwater pollution.

Stable isotopes are useful for tracing the origin of waters and the sources of polluted constituents. Many investigators have used several isotopes in groundwater environment studies, including ^2H and ^{18}O isotope in water molecules, ^{34}S and ^{18}O in SO_4. ^2H and ^{18}O isotope have commonly been used to investigate the origin and mixing of H_2O in groundwater (Fritz and Fontes, 1980; Gat and Gonfiantini, 1981; Clark and Fritz, 1997). Stable isotope analyses of sulfur in SO_4 have been used for decades to identify and quantify sources of sulfates and related mixing processes (e.g., Holt and Kumar, 1991; Krouse and Grinenko, 1991; Krouse and Mayer, 2000; Nordstrom et al., 2007).

Sulfur is an essential biological element (Fors et al., 2008; Schmalenberger et al., 2011), and is intimately linked with redox cycling of oxygen, carbon, and nitrogen in earth surface environments (Turchyn and Schrag. 2006). SO_4^{2-} may retain the sulfur isotopic signatures of its sources due to minimal isotopic fractionation during sulfur transformations under aerobic conditions (e.g., Tuttle et al., 2009) such as mineral precipitation/dissolution and oxidation of reduced sulfur (Li et al., 2015), in turn, microbial sulfate reduction process leads to enrich ^{34}S.This leads to potentially distinctive sulfur isotopic compositions associated with different sulfate sources (e.g. Samborska et al., 2013), and thus sulfur isotopic composition can be used as a fingerprint of different sulfate sources.

In the present study, advantage is taken of this high contrast in isotopic signal to approach extent of AMD contamination in water wells completed in the Ordovician limestone aquifer in the mine area. This is the first time to use a combined geochemistry-stable isotope (H, O, S) approach the document contamination of the Ordovician limestone water from high- SO_4^{2-} waters derived from weathering of pyrite-rich coal in the study area. This may be the case in other locations where drinking water sources are potentially threatened by low-quality high- SO_4^{2-} mine water.

2. Materials and methods

2.1. Study area

Hongshan-Zhaili coal mine is located in Zichuan area, Zibo city, Shandong province with the area of 67.9 km^2 (Fig. 1). After a long mining history, especially large-scale exploitation of the 20th century, they were abandoned in 1994. The study area is located in a zone of subtropical humid monsoon climate. The mean annual precipitation is 660.0 mm, and most residents in the area receive their drinking water from deep wells completed in the Ordovician limestone.

The major stratigraphic units in the area are: Cambrian system ($\in$), ordovician (O_2), carboniferous (C), Permian (P), Triassic (T), Jurassic (J) and Quaternary (Q).

The Zichuan groundwater system can be divided into three major aquifer systems, loose pored aquifers of Quaternary (Q) with sand and sandy gravel, which is supplied by the atmospheric precipitation recharge, and then flow from south to north. Fissure water aquifers including the sandstone fissure water aquifer of Permian (P_2k) and the limestone karstic fissure water aquifer of Carboniferous (C_2b), the limestone karstic fissure water is recharged by atmospheric precipitation, river infiltration, and locally accept loose poured water from Quaternary, the coal seams in the study area occur in the middle of Carboniferous formations, and due to the mining of coal, the aquifer is impacted by serious acid mine water. The Ordovician aquifer (O_2) is recharged where it crops out in the mountainous regions, and there are 10–30 m thick of sandstone and shale between the Ordovician limestone aquifer and Carboniferous limestone aquifer.

2.2. Water samples and analytical methods

Two sets of groundwater samples were collected in this study. The first set was collected in 2013, while the second set was sampled in 2014, including 23 Ordovician limestone waters, 7 mine waters, and 2 rain waters (the sample location is shown in Fig. 1). Z-16 was collected from shallow sandstone aquifer group (P) with 4–8 depth, Z-17 was mine drainage from the original ventilation shafts, Z-04 was sampled in the coal seam with the depth of 200 m, has not reached the Ordovician limestone roof (400 m). Rain water Z-24, Z-25 were sampled in two precipitation events. Ordovician limestone water was sampled as close to the well head as possible by purging the well for at least 15min while monitoring field parameters (pH, temperature and specific conductance). Samples for isotopic analysis of dissolved SO_4^{2-} were collected unpreserved into 5 L Nalgene bottle, samples for isotopic analysis of water were filtered with 0.45 μm PES syringe filters into 50 mL PVC bottle. Alkalinity titrations were performed in 24 h, using a titrator, 0.025 mol/L HCl cartridges, and pH indicator dyes. Samples for analysis of major and trace elements were filtered as above into 50 mL PVC bottle and preserved with 0.6 mL of Trace Metal grade HNO_3. These samples were analyzed by inductively-coupled plasma atomic-emission spectroscopy (ICP-AES) at the China University of Geosciences (Wuhan).

Preparation of the samples for isotopic analysis of dissolved SO_4^{2-} followed the procedures of Carmody et al. (1998). Sulfate for isotopic analysis was then extracted as $BaSO_4$ with pH adjusted to less than 2 to prevent formation of $BaCO_3$. The resultant $BaSO_4$ precipitates, all of which were white in color, were filtered, rinsed several times with deionized water, dried overnight at 50 °C, and weighed to determine the SO_4 yield.

Stable-isotope analysis of the samples were performed at the China University of Geosciences (Wuhan) using a Micromass Iso-Prime stable isotope ratio mass spectrometer (IRMS). Water-$\delta^{18}O$ analyses were performed using a Micromass MultiPrep device interfaced to a dual inlet and the IRMS, and all other isotope analyses were performed using a Eurovector elemental analyzer interfaced to the IRMS. Isotope values are reported in the usual δ notation in units of ‰, vs. VCDT for S and vs. VSMOW for O and H. Based on replicate laboratory analyses, similar analytical uncertainties were obtained for the samples: ±0.2‰ for $\delta^{34}S_{sulfates}$, ±0.4‰ for $\delta^{18}O_{sulfates}$, ±0.1‰ for $\delta^{18}O_{water}$, and ±1‰ for δ^2H_{water}.

3. Results and discussion

The chemical and isotopic composition data for the

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