The Indicative Significance of Sulfate and its Stable Isotope to Antimony in the Water and Soil System of Xikuangshan Mining Area in Hunan Province

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Abstract

Sulfate has important indicative significance for the environmental behavior of antimony (Sb). Using sulfur and oxygen isotopes, combined with the valence state test of antimony, the groundwater of Xikuangshan in Hunan Province was analyzed. The results show that 50–75% of the $\delta^{18}O$ in groundwater and surface water comes from water, and the $\delta^{18}O$ in mine water mainly comes from sulfate. As sulfate concentration increased, the Sb(III)/Sb(total) ratio rose from 2.39% to 88.63%, and antimony is more sensitive to the response mechanism of endogenous sulfate. This research offers new insights for preventing groundwater antimony pollution.

Keywords: Migration and transformation, water environment, sulfate, stable isotope, valence state analysis

Introduction

Hunan Xikuangshan in China is the world's largest antimony deposit, known as the 'antimony capital of the world'. Nearly a hundred years of mining activities have caused a series of mine geological environment problems, among which the problem of antimony pollution in groundwater and other water environment is particularly prominent (Jia *et al.*, 2022; Jia *et al.*, 2024; Zhou *et al.*, 2022;Zhou *et al.*, 2024a).

However, the source of Sb in the water environment and its migration and transformation are very complex processes, and traditional hydrogeochemical methods such as hydrochemistry are difficult to study in depth and systematically (Wen, 2017; Li *et al.*, 2022; Zhou *et al.*, 2023). Therefore, the selection of typical isotope tracers based on the geological characteristics of the Xikuangshan deposit and the biogeochemical behavior of antimony is a necessary means to study the source, migration and transformation process of antimony in the water environment of the Xikuangshan deposit. Antimony minerals in Xikuangshan are mainly stibnite (Sb2S3) (Zhou *et al.*, 2024b; Jia *et al.*, 2023). Sulfur is the main associated element of antimony minerals in Xikuangshan. The oxidation of sulfide minerals (stibnite) will release a large amount of SO_4^{2-} into the water body. Therefore, the sulfur and oxygen isotopes of sulfate are the direct media to study the source and migration and transformation process of Sb in the water environment of Xikuangshan.

Methods

The hydrochemical data obtained in the process of this study are derived from the field collection work in 2024, including groundwater (spring) samples and surface water (ore-bearing drainage) samples, which are strictly preserved in accordance with the sampling requirements and tested and analyzed in the first time. Among them, the analysis and test of anion and cation and antimony valence state were tested by the laboratory, and the stable isotopes δ^2H_{H2O}, $\delta^{18}O_{H2O}$, $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ were tested by the State Key Laboratory of Biogeology and Environmental Geology of China University of Geosciences (Wuhan).

Results and Discussion

The $\delta^{34}S_{SO4}$ values of mine drainage ranged from −7.29‰ to +7.86‰, with an average of +6.2‰, and the $\delta^{18}O_{SO4}$ values ranged from +1.1‰ to +11.1‰, with an average of +6.2‰. The $\delta^{34}S_{SO4}$ values of groundwater ranged from-3.10‰ to +7.82‰, with an average of +3.79‰, and the $\delta^{18}O_{SO4}$ values ranged from +2.1‰ to +5.8‰, with an average of +3.5‰. The $\delta^{34}S_{SO4}$ values of surface water ranged from -8.04‰ to +3.56‰, with an average of 0.0‰, and the $\delta^{18}O_{SO4}$ values ranged from +1.4‰ to +5.1‰, with an average of +3.8‰ (Fig. 1a). Both surface water and groundwater are controlled by sulfate oxidation, and part of the mine drainage is distributed around atmospheric precipitation, which is presumed to be directly recharged by atmospheric precipitation. It can be seen from Fig. 1b that 50–75% of $\delta^{18}O$ in groundwater and surface water comes from water. However, two sets of data in mine drainage show that only 0–25% of $\delta^{18}O$ comes from water, mainly from sulfate, which indicates that the formation process of mine drainage is mainly controlled by the oxidation process of stibnite, and the $\delta^{18}O$ of other mine drainage is in the range of 50–75% H_2O, indicating that the formation process of mine drainage is affected by atmospheric precipitation leaching.

Through sulfur and oxygen isotopes, it is found that the hydrochemical samples in the study area are mixed by background surface water, atmospheric precipitation and ore-bearing groundwater (Fig. 2). Further analysis of the three-end element mixing ratio of different types of water shows that the contribution of atmospheric precipitation is higher in TG and XG than in BG. It's due to the aquifer in the Batangshan River Basin belongs to the limestone layer, the core is relatively complete, and the cracks are not developed. The aquifer in the Tanjiaxi River Basin belongs to the siliceous limestone layer, and the karst is more developed. The aquifer in the Xuanshan River Basin is argillaceous limestone layer, which is easier to be eroded, so that the atmospheric precipitation in the Tanjiaxi and Xuanshan River basins can enter the aquifer faster to form a recharge. XR receives 61% of the upstream background value, mainly receiving upstream water supply, and is weakly recharged by atmospheric precipitation and groundwater lateral runoff. On the contrary, the contribution of atmospheric precipitation to the TR is as high as 80%, and the contribution of the upstream background value is only 6%. It shows that the slope confluence process of atmospheric precipitation has a great influence on the water body during the runoff process of Tanjiaxi, and the water body has changed

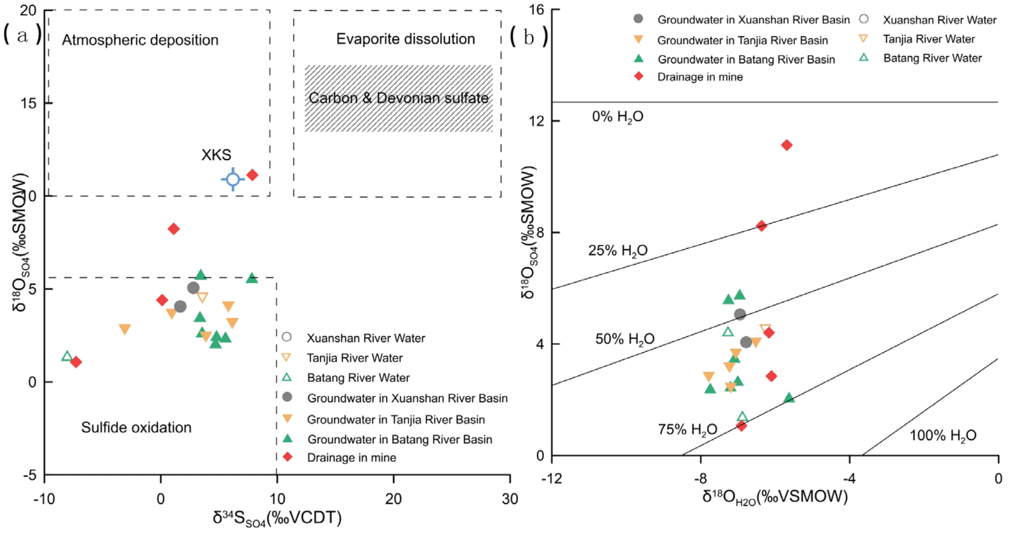

Figure 1 $\delta^{34}S_{SO4}$–$\delta^{18}O_{SO4}$*(a) and* $\delta^{18}O_{H2O}$–$\delta^{18}O_{SO4}$ *(b) correlation diagram(Li* et al.*, 2022).*

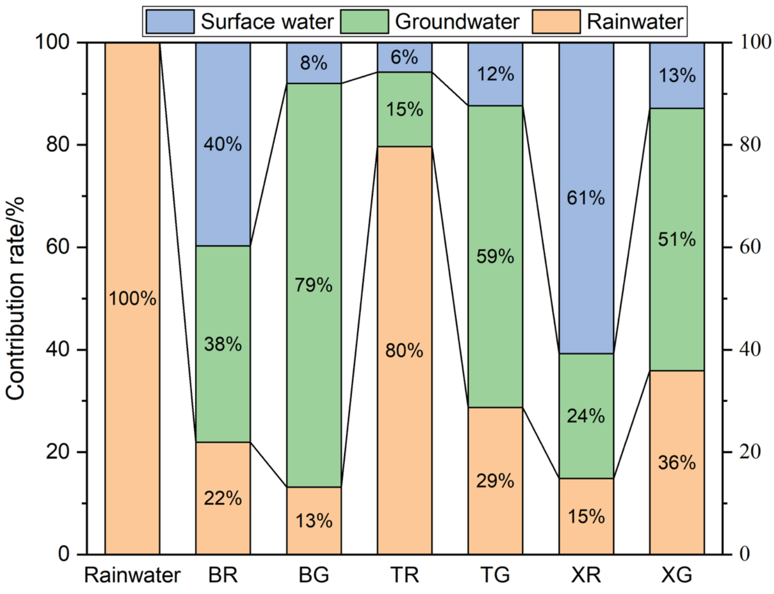

Figure 2 *The contribution of three endmembers (background surface water, atmospheric precipitation and ore-bearing groundwater) in different types of water (BR - Batangshanxi River, BG – Batangshanxi Groundwater, TR- Tanjiaxi River, TG – Tanjiaxi Groundwater, XR – Xuanshan River, XG – Xuanshan Groundwater).*

greatly during the runoff process.

By analyzing the correlation between the ratios of the main ions, the source of the leaching effect experienced during the formation of the water body can be identified, as shown in Fig. 3. The surface water and groundwater in the study area are closer to the mixing of carbonate rocks and evaporite rocks. It is worth noting that 80% of the contribution of TR comes from atmospheric precipitation. In addition to direct recharge, the more important process of atmospheric precipitation recharge to surface water is slope confluence. This process occurs on the surface so that the slope confluence can take away part of the evaporated salt formed on the surface of the slope, making TR closer to the dissolution of evaporated salt rock. The drainage formation process is not entirely a natural process, and is greatly affected by human activities. Therefore, it is not completely controlled by three types of rock salt.

When we shifted the research question from how groundwater is formed to how antimony is released and migrated during the formation of groundwater, we began to explore the migration process of antimony by exploring the changes of antimony and related parameters along the runoff path. In Fig. 4a of the TR, the source is characterized by high antimony (Sb) concentrations and a certain degree of reducing properties due to the influence of waste dumps and extensive livestock breeding by surrounding residents. During the runoff process, the antimony is gradually diluted and oxidized. However, after passing through TJ3, a direct discharge of high Sb-containing water occurs, which leads to an increase in antimony concentration in the river. The characteristics of XR are quite different from those of TR (Fig. 4b). Since the aquifer in the Xuanshan River Basin does not contain ore-bearing layers and there is no slag heap in the upstream, the concentration of antimony in the upstream section is extremely low. After flowing through XS5 (a large tailings reservoir nearby), the concentration of antimony increased significantly. In order to further confirm the impact of the tailings pond on the river, we tested the water directly discharged from the tailings pond into the river. A large amount of polyferric sulfate (PFS) was added to make the antimony concentration

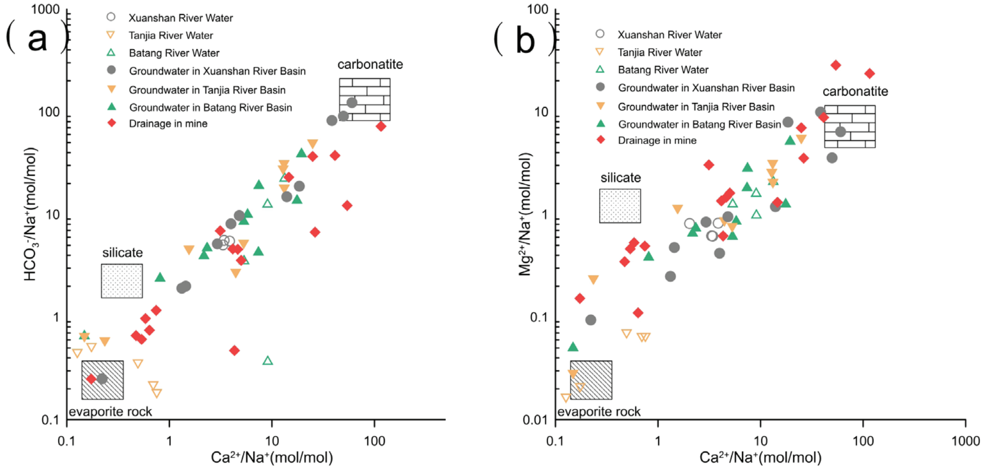

Figure 3 The relationship between different types of rocks and the main ion types of groundwater(a–γ(HCO_3^-/Na^+)-γ(Ca^{2+}/Na^+), b-γ(Mg^{2+}/Na^+)-γ(Ca^{2+}/Na^+)).

lower than 0.5 mg/L, and the whole was in an acidic anaerobic environment, indicating that the tailings pond can cause a large amount of antimony to enter the water environment through other ways besides direct discharge, such as atmospheric precipitation leaching, bottom leakage and other uncontrollable ways.

Atmospheric precipitation recharge, slag heap leaching and antimony-containing wastewater recharge need to be considered in the process of surface water runoff, while the reason for the increase of antimony in the process of groundwater runoff is relatively simple. It is usually due to the oxidation of stibnite in the aquifer during the groundwater runoff process through the silicified limestone section of the ore-bearing layer-Shetianqiao Formation, which causes a large amount of antimony to be transformed into free state and enter the groundwater. This is the case for TG and BG (Fig. 4d, e). In this process, in addition to the increase of antimony concentration, sulfate concentration and $\delta^{34}S_{SO4}$ will also increase, which is due to the large amount of SO_4^{2-}produced during the oxidation of stibnite. However, the increase of antimony concentration in XG does not belong to this situation. Considering that

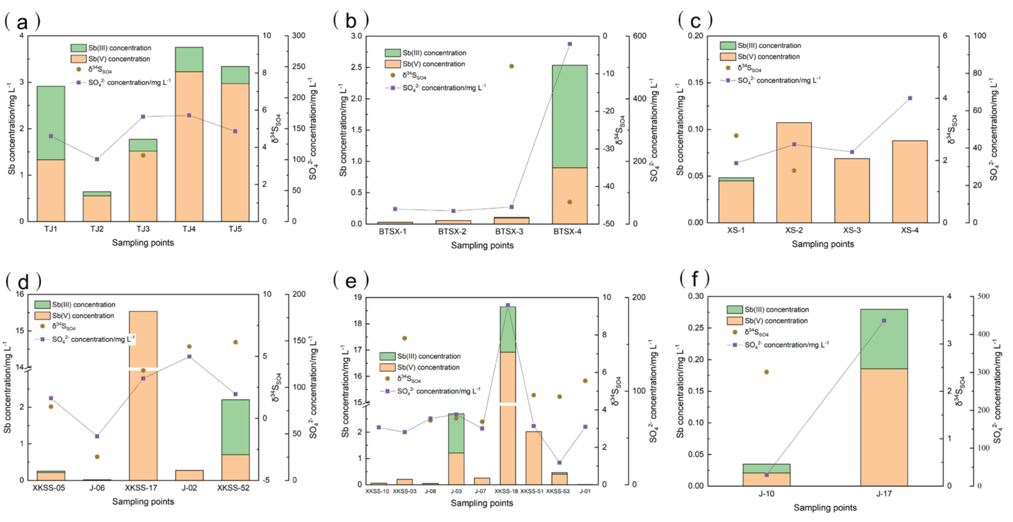

Figure 4 The change process of antimony, sulfate and $\delta^{34}S_{SO4}$ along the runoff path (a-TR, b-BR, c-XR, d-TG, e-BG, f-XG).

J17 is located not far downstream of XS5, it is speculated that the increase of J17 concentration is affected by the tailings pond, or there is an interaction process between surface water and groundwater, which is affected by the high antimony surface water downstream of XR.

We define the sulfate produced during the oxidation of stibnite as the endogenous sulfate produced by the hydrochemical process in the aquifer, and the sulfate injected into the PFS agent to regulate the Sb concentration in the water body is defined as the exogenous sulfate caused by human activities. Due to the strong correlation between endogenous sulfate and exogenous sulfate and the migration and transformation process of Sb, there is a certain relationship between the occurrence form of Sb in water and the concentration of sulfate. The specific performance is that with the increase of SO_4^{2-}concentration, the ratio of Sb (III)/Sb(V) in the water body increases, the proportion of Sb (III) in the water is higher, and the water body is more inclined to the reducing environment. The variation of Sb(III)/Sb(V) in groundwater (under the control of endogenous sulfate) is more sensitive to the nonlinear response trend of SO_4^{2-}concentration change than that in mine drainage and surface water (under the control of exogenous sulfate). However, this can only show that there is a strong correlation between sulfate and the occurrence of antimony, and it is not enough to show that sulfate can affect the occurrence of antimony in water, which needs further research to confirm.

Based on the content described above and previous research, the conceptual model of antimony migration and transformation on the two-dimensional profile of the study area was optimized(Wen, 2017). After atmospheric precipitation, slag heap leaching occurs on the surface, which causes antimony to dissolve from the solid phase medium and enter the surface water for migration. The underground aquifer can accept part of the antimony released by the slag heap leaching carried by the infiltration of atmospheric precipitation, and more of it comes from the oxidation of stibnite to directly produce free antimony. In the process of migration, the occurrence form of antimony changes with the change of redox conditions.

Conclusions

The formation process of groundwater in the study area is controlled by the lithology of the aquifer. The lithology of the Batangshan River Basin is relatively complete, and it is basically not recharged by surface water and atmospheric precipitation. The Tanjiaxi and Xuanshan River Basins are able to receive atmospheric precipitation recharge. The formation process of surface water is mainly affected by the upstream background surface water and atmospheric precipitation. The water of the Xuanshan River is mainly recharged by the upstream

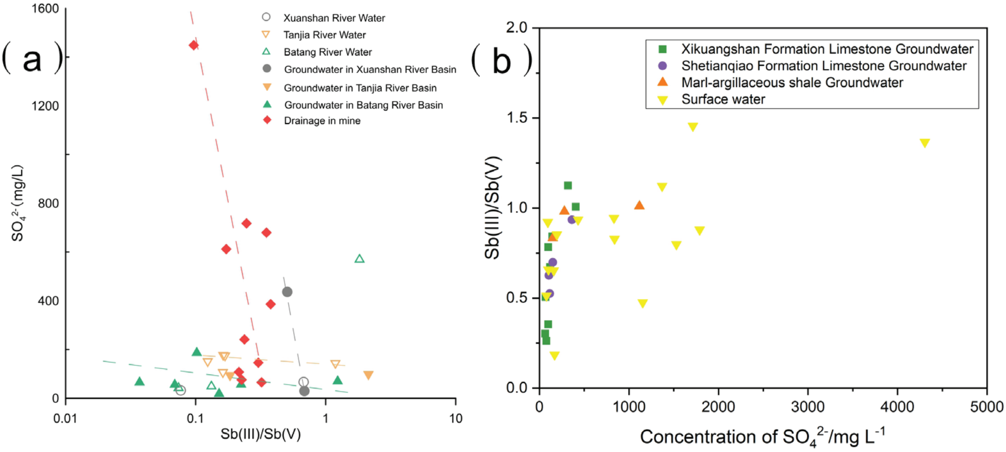

Figure 5 *Synergistic relationship between sulfate and Sb(III)/Sb(V) in water(a-groundwater in different basins,b-groundwater from different aquifers).*

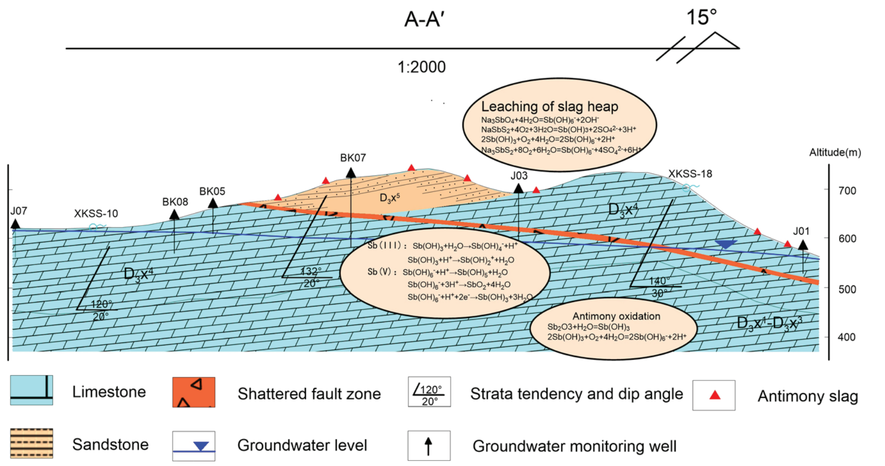

Figure 6 *Conceptual model of antimony migration and transformation in tin mine.*

water, while the Tanjiaxi River is recharged by the slope confluence of atmospheric precipitation. During the recharge process, the slope confluence can leach part of the surface evaporation salt, which makes the ion composition of the Tanjiaxi River closer to the end member of the evaporation salt rock.

In the process of surface water runoff, the concentration of antimony can be increased by the direct supply of external high antimony water or the interaction process of surface water and groundwater. In the process of groundwater runoff, the channel for the release of antimony is usually the oxidation of stibnite. The solid phase Sb_2O_3 is oxidized to free antimony and enters the aquifer. In this process, a large amount of SO_4^{2-} is produced, which increases the sulfate concentration and a. The source analysis of sulfur and oxygen isotopes on the drainage of high antimony ore also confirms this conclusion.

In the process of groundwater migration, the valence state of sulfate and antimony showed a high degree of regularity, and the fluctuation of antimony valence state in summer was more intense in response to sulfate concentration. Further study of the effect of sulfate sources on antimony found that Sb(III)/Sb(V) was 91.91% and 59.28%, respectively, at high endogenous sulfate concentration and high exogenous sulfate concentration, indicating that the valence state of antimony was more sensitive to the response of endogenous sulfate.

Acknowledgements

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