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The geochemistry of rare earth elements (REE) in acid mine drainage from the Sitai coal mine, Shanxi Province, North China

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Abstract

In this paper, geochemical characteristics of rare earth elements (REE) in acid mine drainage (AMD) from the Sitai coal mine of Shanxi Province, North China were investigated by determining concentrations of dissolved REEs and major solutes in the AMD samples, concentrations of REEs in the AMD precipitate samples and country rock samples (mudstone and coal), and modeling REEs species in the AMD. The results show that AMD in the Sitai coal mine have high REEs and SO_4^{2-} concentrations in comparison with several terrestrial waters worldwide. The REE speciation modeling indicates that sulfate complexes ($LnSO_4^+$, > 60%) and free metal species (Ln^{3+}, 20%–40%) are dominant REEs species in the AMD. AMD of the Sitai coal mine also shows a middle REE-enriched NASC (North American Shale Composite)-normalized pattern. The authors suggest that both REE sulfates ($LnSO_4^+$) in the AMD and country rock of coal measures are possible reasons for middle REE-enriched NASC-normalized pattern of the Sitai coal mine AMD. Further work on the AMD precipitates is needed to obtain more information on the origin of the middle REE-enriched NASC-normalized patterns.
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Keywords: Acid mine drainage (AMD); Rare earth elements (REEs); Sitai coal mine; Speciation

1. Introduction

Acid mine drainage (AMD) occurs worldwide and represents a serious environmental problem for international mining industries. AMD can occur during the exploitation of coal and coal-bearing measures, and ore bodies containing acid-forming metal sulfides such as pyrite (FeS_2). The oxidation of such sulfides exposed to atmospheric O_2 during or after mining activities generates acidic waters with high dissolved SO_4^{2-}, Fe, and heavy metals. The low pH may cause further dissolution of local country rock and the leaching of additional metals into water (Tabaksblat, 2002), and thereby adversely impact aquatic life and the surrounding vegetation (Gray, 1997; Geller et al., 1998; Bell et al., 2001; Cherry et al., 2001). Consequently, the behavior of heavy metals in AMD has been exhaustively

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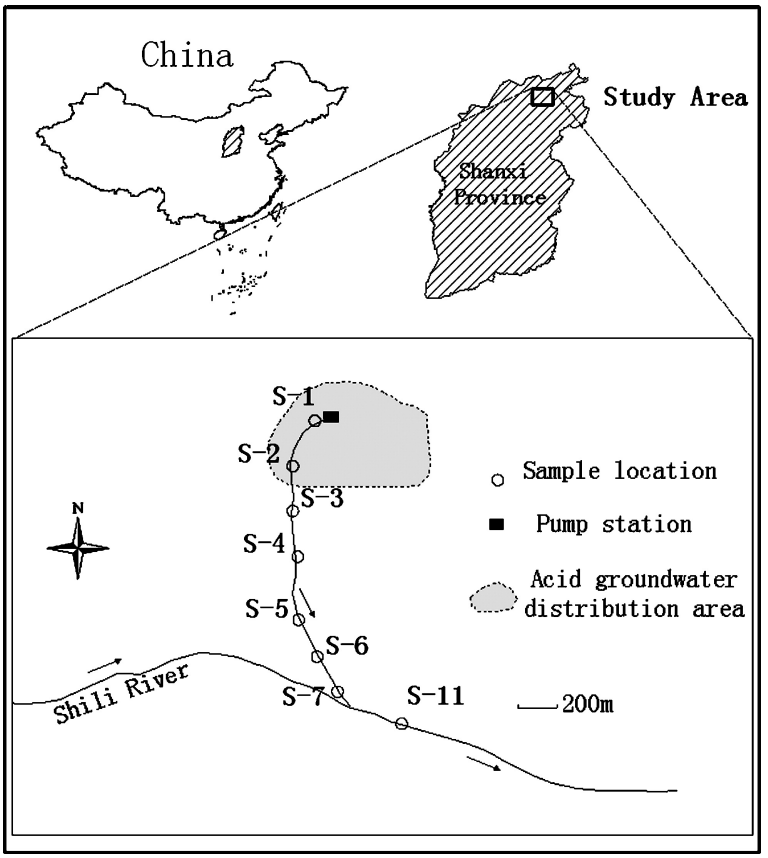


Fig. 1. Sampling location map of the study area.

studied (Johnson, 1986; Yu, 1996; Schemel et al., 2000; Black and Craw, 2001; Kim and Chon, 2001; Lee et al., 2002). Less research has been focused on the rare earth elements (REE) in AMD, possibly because REE are typically considered to have less toxic effect than heavy metals.

However, it has been proven that high concentrations of REE in soil or water may be harmful to human beings

Table 1
Major-ion concentrations in the AMD from the Sitai coal mine (mg/L)

Sample	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-11[a]	Average[b]
pH	3.62	3.55	3.52	3.56	3.65	3.75	6.76	7.76	3.61
Eh(mv)	568	413	416	409	420	394	192	177	437
F^-	0.28	0.37	0.40	0.34	0.99	0.40	0.33	0.63	0.46
Cl^-	189	181	167	163	184	160	203	435	174
NO_3^-	1.74	3.82	4.02	3.81	4.77	4.31	–	34.6	3.75
SO_4^{2-}	2128	1790	1856	1747	1842	1798	911	1296	1860
Na	119	110	106	152	117	115	141	475	120
Ca	242	246	267	246	229	261	181	194	249
Mg	99.2	99.2	90.2	132	97.4	99.2	63.3	119	103
K	37.0	35.3	13.8	13.0	12.0	13.0	15.6	20.6	20.7
Fe	16.2	2.09	3.48	3.62	1.67	1.29	0.16	0.06	4.73
Mn	5.28	3.61	3.55	5.18	3.45	4.02	0.20	0.79	4.18
Al	10.8	7.64	7.64	10.9	7.34	8.66	0.07	0.03	8.83

[a] Water sample of the Shili River.
[b] Average of S-1 to S-6.

and animals (Wu et al., 1983; Zhu et al., 1997). REE are widely used to study the geochemical reactions between and within rocks, groundwater and surface water (Elderfield et al., 1990; Smedley, 1991; Hall et al., 1995; Johannesson et al., 2000). Therefore, a detailed investigation of the geochemistry of REEs is important for comprehensive assessment of the potential environmental impacts of AMD.

AMD is also a serious problem for some Chinese coal mines; however, limited research has been conducted on the geochemistry of AMD.

In this paper, preliminary results of a study on REE concentrations, distribution patterns and speciation in AMD from the Sitai coal mine, Shanxi Province, North China are presented.

2. Site description

The Sitai coal mine is located in the northwestern part of the Datong Coal Field. The Shili River is the main stream in the studied area and flows from west to east (Fig. 1).

The Middle Jurassic Datong Formation is the major coal sequence, and primarily consists of sandstones, mudstones, shales and coal seams. The thickness of coal measures range from 103 m to 224 m. The Datong Formation contains 21 coal seams; however, only the No. 8, No. 10 and No. 11 coal seams are currently being mined.

The Nos. 2 and 3 coal seams were mined underground decades ago and AMD comes from the abandoned workings of these seams. The total amount of AMD is nearly 3.0×10^5 m^3. AMD seeps affect current exploitation of Nos. 8 and 11 coal seams below it. Recently, an extensive discharge program was adopted by the Sitai Coal Authority, and 4.0×10^3 m^3 of AMD was pumped from deep wells. This AMD is discharged along a small valley, and then enters the Shili River (Fig. 1). The AMD pollution is easily recognized in the field by a red Fe-bearing precipitate in the stream channel.

3. Sampling and methods

Samples were collected at the Sitai coal mine in November 2002. Seven acidic water samples (S-1, S-2, S-3, S-4, S-5, S-6, S-7) were collected along a small valley at about 200 m intervals (Fig. 1). One water sample (S-11) was collected from the Shili River. Redox potential, pH and temperature were measured in the field with portable instruments that were recalibrated during the sampling programme. Water samples were filtered through 0.45 μm pore-size membrane and collected into acid-cleaned polyethylene bottles that were rinsed three times with sample water. The sample bottles were completely filled to eliminate the headspace. The samples for metal analysis were immediately acidified to less than pH 2 using high-purity HNO_3; all samples were stored at less than 4 °C until analyzed.

Concentrations of REE and most of cations in the water samples were determined using an inductively coupled plasma mass spectrometer (ICP-MS). Internal standards were used to correct for instrumental drift and matrix suppression for each sample. The following REE isotopes were chosen in order to minimize matrix or polyatomic interferences: ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{173}Yb, and

Table 2
The REE concentrations in the acid mine drainage samples from the Sitai coal mine (μg/L)

Sample	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-11[a]	Average[b]	NASC[c]
La	8.26	6.44	10.4	7.73	6.65	7.15	0.030	0.116	7.77	32.0
Ce	22.0	17.4	18.0	20.4	18.5	19.8	0.130	0.010	19.4	73.0
Pr	3.18	2.60	2.66	2.87	2.61	2.75	0.017	0.004	2.78	7.90
Nd	14.6	11.9	12.7	13.4	12.6	12.7	0.084	0.022	13.0	33.0
Sm	3.36	2.54	2.64	3.60	2.64	3.09	0.017	0.005	2.98	5.70
Eu	1.08	0.77	0.74	0.98	0.84	0.83	0.016	0.016	0.87	1.20
Gd	4.27	3.18	3.50	4.31	3.69	3.70	0.012	0.008	3.78	5.20
Tb	0.77	0.66	0.62	0.81	0.66	0.68	0.005	0.002	0.70	0.85
Dy	4.44	3.75	3.32	4.92	3.96	3.99	0.018	0.012	4.06	5.80
Ho	1.00	0.74	0.73	1.03	0.86	0.83	0.005	0.005	0.87	1.00
Er	2.86	2.03	2.08	3.09	2.29	2.25	0.023	0.008	2.43	3.40
Tm	0.41	0.27	0.29	0.40	0.32	0.32	0.003	0.001	0.34	0.50
Yb	2.21	1.84	1.48	2.65	1.79	1.95	0.027	0.028	1.99	3.10
Lu	0.36	0.25	0.24	0.39	0.32	0.32	0.004	0.005	0.31	0.48
∑REE	68.8	54.4	59.4	66.6	57.7	60.4	0.391	0.242	61.2	173

[a] Water sample from the Shili River.
[b] Average of S-1 to S-6.
[c] North American Shale Composite (μg/g, Taylor and McLennan, 1985).

Table 3
The REE concentrations in water samples of this work and other locations (μg/L)

Place	The Sitai Coal mine	Colour Lake, Canada[a]	Osamu Utsmi, Brazil[b]	Odiel River, Spain[c]	Metalliferous Hills, Italy[d]	Mississippi River, USA[e]	Zhujiang River, China[f]
Sample	Average	Cl-23	GW-58	OR1	BC18	Average	Average
pH	3.61	4.7	4.43	3.25	3.10		
∑REE	61.21	1.90	1046	42.62	929	0.0418	0.355
La	7.77	0.32	567	13.23	185	0.0039	0.035
Ce	19.35	0.57	124.01	36.16	390	0.0073	0.075
Pr	2.78	0.07	0		45.75	0.0014	0.012
Nd	12.98	0.32	250	19.72	172	0.0073	0.053
Sm	2.98	0.09	28.57	4.85	34.82	0.0021	0.037
Eu	0.87	0.03	7.75	1.09	8.65	0.0007	0.015
Gd	3.78	0.19	22.64	5.78	40.18	0.0036	0.031
Tb	0.70	0.02	0	0.83	5.00	0.0005	0.006
Dy	4.06	0.13	23.24	4.96	23.66	0.0045	0.028
Ho	0.87	0.02	5.28	0.90	4.18	0.0012	0.006
Er	2.43	0.05	12.21	2.20	10.50	0.0041	0.023
Tm	0.34	0.01	0	0.30	1.21	0.0006	0.006
Yb	1.99	0.03	5.54	1.73	7.07	0.0039	0.023
Lu	0.31	0.05	0.52	0.26	0.94	0.0007	0.005

[a]Johannesson and Lyons, 1995. [b]Miekeley et al., 1992. [c]Elbaz-Plulichet and Dupuy, 1999. [d]Protano and Riccobono, 2002. [e]Hannigan and Sholkovitz, 2001. [f]Wang et al., 1998.

^{175}Lu. Isobaric interferences of Ba and light REE oxides and hydroxides were corrected during analysis. Detection limits are less than 0.001 mg/L.

Sodium and magnesium in the water samples were determined by Atomic Absorption Spectrometry (AAS). The anions were determined by ion chromatography (IC).

The BST1 and SST1 samples are AMD precipitates collected from underground workings. The SST4 sample is a channel sediment collected at the AMD outfall shown in Fig. 1. The coal sample (SST5) was obtained from the No. 3 coal seam. The SST2 and SST3 samples are mudstones collected from the coal measures. These samples were digested with high-purity HNO_3 and $HClO_4$, and then analyzed by ICP-MS to determine their REE contents. X-ray diffraction was employed to examine the mineral composition of these solid samples.

Speciation calculations were performed with the PHREEQCI code, a comprehensive aqueous geochemical modeling code developed by the USGS (Charlton and Parkurst, 2002). In order to model REE speciation, PHREEQCI includes stability constants of the REE sulphates ($LnSO_4^+$, where Ln represents any of the lanthanide series elements), chlorides ($LnCl^{2+}$), fluorides (LnF^{2+}), and hydroxide complexes ($LnOH^{2+}$) calculated by Millero (1992), and the carbonate complexes ($LnCO_3^+$, $Ln(CO_3)_2^-$) determined by Lee and Byrne (1993). The REE phosphate complexes were not considered in this modeling because of their extremely low concentrations. In this study, activity coefficient calculations were performed by means of the Davies approximation because all of the ionic strengths of the AMD are <0.1 mol/L (Shen et al., 1993).

4. Results

Major ion concentrations, pH and Eh for each water sample are presented in Table 1. The pH of the AMD water samples (S-1 to S-6) ranges from 3.52 to 3.75, and Eh values between 394 mV and 568 mV. The dominant cation is Ca^{2+} (229–267 mg/L) in these samples, followed by Na^+ (106–152 mg/L) and Mg^{2+} (99.2–132 mg/L). The concentration of SO_4^{2-} in Sitai coal mine

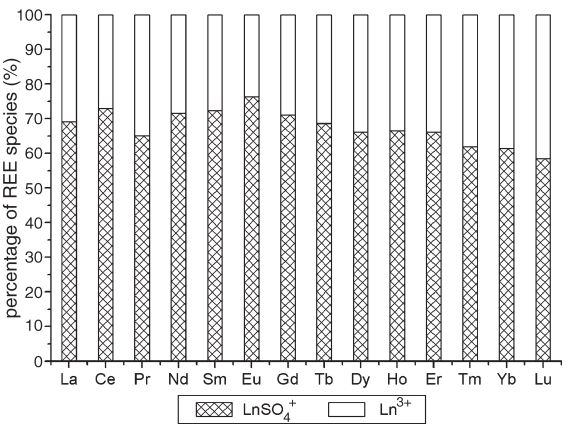


Fig. 2. The speciation of REE in AMD samples from the Sitai coal mine.

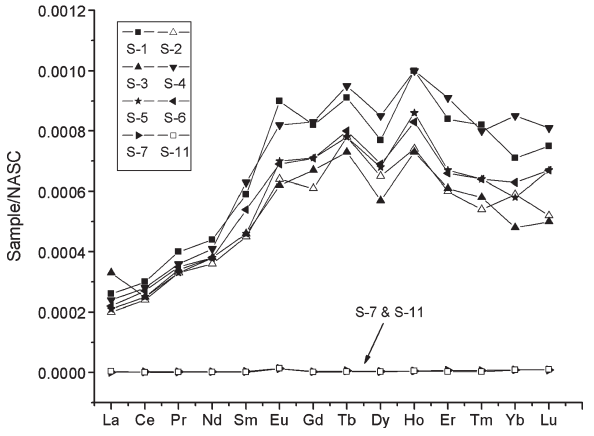


Fig. 3. The NASC-normalized REE patterns for the Shili River and the AMD of the Sitai coal mine (S-1 to S-6: AMD, pH=3.52–3.75; S-7: AMD, pH=6.76; S-11: the Shili River, pH=7.76).

AMD is very high (1742–2128 mg/L) compared to the drinking water upper limit of 250 mg/L (Freeze and Cherry, 1979). Cl^- is also high, whereas concentrations of NO_3^- and F^- are relatively low, and PO_4^{3-} was below detection limits. High concentrations of SO_4^{2-} (Table 1) are from pyrite oxidation from the coal measures, whereas Na and Al are from weathering of the alumosilicates (e.g. albite). Although Ca and Mg can also be derived from aluminosilicate it is more likely derived from carbonates. The AMD samples have higher Fe, Al and Mn concentrations and lower pH than S-7 and the sample from the Shili River (S-11).

4.1. REE concentrations in the AMD

The REE concentrations in the AMD samples are listed in Table 2. Table 3 compares average REE concentrations (S-1 to S-6) from this study with other published results (Miekeley et al., 1992; Johannesson and Lyons, 1995; Wang et al., 1998; Elbaz-Plulichet and Dupuy, 1999; Hannigan and Sholkovitz, 2001; Protano and Riccobono, 2002). The total concentration of REEs (∑REE) in the AMD samples range from 54.37 μg/L to 68.80 μg/L (Table 2), which are about two or three orders of magnitude higher than total REE concentrations in the acidic Colour Lake (1.90 μg/L, Johannesson and Lyons, 1995), neutral Zhujiang River (0.355 μg/L, Wang et al., 1998) and Mississippi River (0.0418 μg/L, Hannigan and Sholkovitz, 2001). However, the total concentrations of REE in AMD from the Sitai coal mine are less than those reported for AMD from Osamu Utsmi (1046 μg/L, Miekeley et al., 1992) and Metalliferous Hills (929 μg/L, Protano and Riccobono, 2002), and are similar to those from Odiel River (42.62 μg/L, Elbaz-Plulichet and Dupuy, 1999). The REE concentrations of the Shili River and S-7 water samples (pH=6.76) are 0.242 μg/L and 0.391 μg/L, respectively, which are similar to that of Zhujiang River (0.355 μg/L, Wang et al., 1998).

4.2. Speciation modeling of REE in the AMD

Average results of speciation modeling for the AMD samples from the Sitai coal mine are presented in Fig. 2,

Table 4
REE concentrations in AMD sediment and country rock samples from the Sitai coal mine (μg/g)

Sample no.	BST1	SST1	SST4	SST2	SST3	SST5
Lithotype	AMD precipitate	AMD precipitate	AMD channel Sediment	Mudstone	Mudstone	Coal
La	47.2	7.74	33.2	30.5	55.4	3.65
Ce	78.3	17.6	70.0	64.2	105	7.02
Pr	9.10	2.08	7.88	7.00	11.2	0.76
Nd	38.8	8.99	31.0	27.4	42.4	3.08
Sm	5.99	1.87	5.37	4.85	6.35	0.51
Eu	1.24	0.58	1.14	1.3	2.31	0.18
Gd	6.72	3.31	6.01	5.68	8.05	0.67
Tb	0.91	0.52	0.72	0.762	1.00	0.12
Dy	5.16	3.04	4.12	4.11	5.57	0.74
Ho	1.13	0.68	0.74	0.798	1.15	0.15
Er	2.97	1.70	2.16	2.18	3.1	0.44
Tm	0.56	0.23	0.34	0.313	0.439	0.07
Yb	3.05	1.28	2.48	2.29	2.8	0.41
Lu	0.57	0.17	0.34	0.314	0.385	0.06
ΣREE	202	49.8	166	152	245	17.9
S/Fe	0.09	0.03	0.06	nd	nd	nd

BST-1 and SST1 are AMD precipitate samples (mainly goethite) collected from underground workings.
SST4 is a channel sediment sample (quartz, goethite and feldspar) collected at the AMD outfall located on Fig. 1. SST2 and SST3 are mudstone (kaolinite, quartz, feldspar, calcite) samples collected from the coal measures.
SST5 is a coal sample obtained from No. 3 coal seam. S/Fe: atomic ratio. nd: not detected.

where the percent abundance of each aqueous REE species is plotted against REE atomic numbers. Speciation modeling indicates that the REE sulfate complexes ($LnSO_4^+$) are the primary form of dissolved REE, and always account for more than 60% of the dissolved REE concentration. Moreover, the partitioning of dissolved REE into SO_4^{2-} complexes decrease as atomic number increases, especially from Eu (Fig. 2). Free metal cations (Ln^{3+}) are the next most abundant dissolved REE species and are responsible for between 20% and 40% of the REE in solution. The partitioning of dissolved REE into free metal species (Ln^{3+}) increases as atomic number increases. The proportion of dissolved REE present as other inorganic complexes such as $LnCl^{2+}$, LnF^{2+} and $LnOH^{2+}$ is less than 1%.

4.3. Distribution patterns of REE in the AMD

The normalization of REE concentrations to those in North American Shale Composite (NASC, Taylor and McLennan, 1985) can act as an indicator of REE enrichment. Fig. 3 illustrates the NASC-normalized patterns of the REE concentrations in the AMD samples, a near neutral water sample (S-7) from the Sitai coal mine, and the Shili River sample (S-11). As can be seen in Fig. 3, the AMD samples display a pronounced convex-up NASC-normalized REE pattern without Ce- or Eu-anomalies. Therefore, middle rare earth elements (MREE) are enriched over both light rare earth elements (LREE) and heavy rare earth elements (HREE) in the AMD samples in comparison with NASC. However, the near neutral water (S-7) and the Shili River samples (S-11) do not display the MREE enrichment.

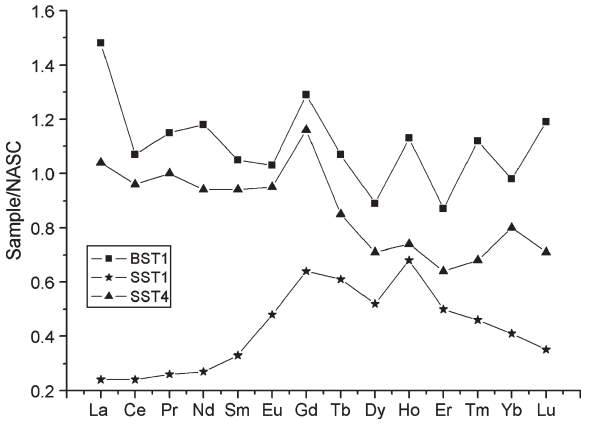


Fig. 4. The NASC-normalized REE patterns for AMD precipitate samples from the Sitai coal mine (BST1 and SST1: AMD precipitate samples; SST4: AMD channel sediment sample).

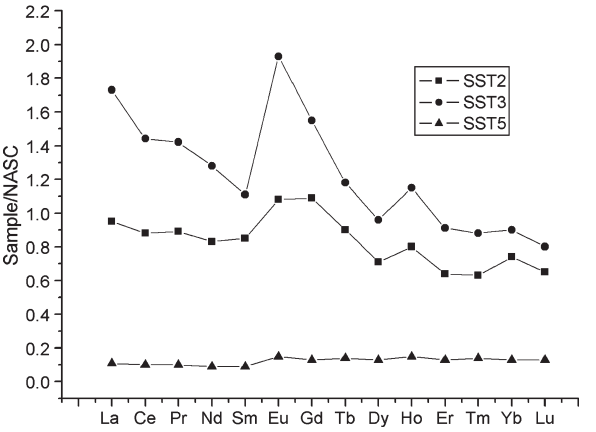


Fig. 5. The NASC-normalized REE patterns for mudstone and coal samples of coal measures from the Sitai coal mine (SST2 and SST3: mudstone samples; SST5: coal sample).

4.4. Concentrations and distribution patterns of REE in AMD precipitates and country rock samples

Table 4 presents REE concentrations in AMD precipitate samples (BST1 and SST1), an AMD channel sediment sample (SST4), two mudstone samples from the coal measures (SST2 and SST3), and a coal sample (SST5). Based on the XRD results, the BST1 and SST1 samples consist mainly of goethite; the SST4 sample consists of quartz, goethite and minor feldspar; the SST2 sample is mainly composed of quartz, kaolinite, feldspar, dolomite, and minor mica; the SST3 sample is mainly made up of kaolinite, quartz, feldspar, and minor calcite. The minerals in the SST5 sample are quartz, kaolinite, calcite, dolomite and gypsum. Table 4 shows the total concentrations of REE in mudstone samples (SST3 and SST2) and in AMD precipitate samples with the highest S/Fe atomic ratios for BST1 and SST4.

Fig. 4 shows the NASC-normalized REE patterns for AMD precipitate samples (BST1, SST1 and SST4); and Fig. 5 for the country rock samples (SST2 and SST3) and the coal sample (SST5). As can be seen in Figs. 4 and 5, most of these solid samples do not demonstrate the typical characteristic of MREE-enriched NASC-normalized REE pattern. However, the SST1 sample shows a similar NASC-normalized REE pattern to that for AMD samples.

5. Discussion

5.1. Enrichment mechanism of REEs in acidic water

Previous investigations indicate that pH, and the presence of colloids and complexes play a major role in controlling REE concentrations in natural waters

(Sholkovitz, 1995; Protano and Riccobono, 2002; Tabaksblat, 2002; Astrom and Corin, 2003). Concentrations of REE in low-pH waters dominated by SO_4^{2-} may significantly increase because of formation of more stable $LnSO_4^+$ (Johannesson and Lyons, 1995; Tabaksblat, 2002). Coagulation and aggregate precipitation of iron and aluminum colloids may effectively remove REE in mine water with increases in pH (Zanker et al., 2003).

In the present study, the concentrations of SO_4^{2-} appear to control concentrations of REEs in AMD samples from the Sitai coal mine. Higher concentrations of SO_4^{2-} lead to the formation of stable $LnSO_4^+$, thereby resulting in higher concentrations of REEs in AMD samples. The concentrations of Fe, Al, Mn and SO_4^{2-} in AMD samples decrease with increases in pH, implying that coagulation and precipitation of Fe–Al–Mn oxide/hydroxide colloids occur. It also implies that REE sulfate complexes ($LnSO_4^+$) are possibly adsorbed onto the Fe–Al–Mn oxide/hydroxide colloids and then co-precipitate with them, thereby resulting in the REEs scavenging from AMD samples with the increase in pH, especially for the S-7 sample (pH = 6.76). Compared with the AMD samples (S-1 to S-6), the Shili River sample (S-11, pH = 7.76) has a lower concentration of SO_4^{2-}; consequently, it also has a lower REE concentration.

REE and SO_4^{2-} in AMD precipitate samples are from the AMD. Data in Table 4 indicate that concentrations of REE are higher in the AMD precipitate samples with higher S/Fe atomic ratios than in those with smaller S/Fe atomic ratios, which also implies that concentrations of SO_4^{2-} control concentrations of REE in AMD samples.

5.2. Mechanism of MREE enrichment in the AMD

Similar MREE enrichments to that in AMD from the Sitai coal mine have been reported for acidic lakes, rivers affected by AMD and acidic groundwater (Johannesson and Lyons, 1995; Elbaz-Plulichet and Dupuy, 1999; Serrano et al., 2000). Therefore, the convex-up NASC-normalized REEs pattern of AMD is one characteristic of acidic natural water although Bozau et al. (2004) recently reported that LREEs in an acidic mine water (Lusatia, Germany) are enriched.

However, the processes controlling MREE enrichment observed in acidic terrestrial waters are still not well understood and it is unclear whether observed distributions relate to the source or aqueous processes. Hall et al. (1995) studied a lake in Newfoundland (Canada), and found that the REE distribution pattern is generally similar to that of the associated sediments, reflecting the REE patterns of the host rocks. Johannesson and Zhou (1999) found that the leaching or dissolution of MREE enriched in the minerals and/or amorphous phases occurs in local rocks by acidic waters at Colour Lake (Canada), and are the most likely source of the MREE enrichment in the lake waters. On the contrary, many researchers have argued that such a feature depends mainly on water chemistry, including the solution pH, and the presence and concentration of complexing ligands, rather than on country rock geology (e.g. see Moller and Bau, 1993; Sholkovitz, 1995).

In the current study, the average proportions of MREE sulfate complexes (70.21%) appear to be higher than those of LREE sulfate complexes (69.67%) and HREE sulfate complexes (61.99%). The sulfate complex ($LnSO_4^+$) is probably one of the reasons for MREE enrichment in the AMD.

Although REE in the mudstone and coal samples from the coal measures do not show a typical MREE-enriched NASC-normalized REE pattern (Fig. 5), some of the MREE (Eu, Gd and Tb in the SST2 sample; Eu and Gd in the SST3 sample and, Eu, Gd, Tb, Dy and Ho in the SST5 sample) show higher NASC-normalized concentrations than the HREE and most of the LREE. Therefore, country rocks (mudstone and coal) of the coal measures possibly contribute to enrichment of MREE in the AMD from the Sitai coal mine.

Different AMD precipitate samples demonstrate different NASC-normalized REE patterns (Fig. 4). Similar MREE-enriched NASC-normalized REE patterns of the SST1 sample to that of the Sitai coal mine AMD probably imply that REE concentrations of the SST1 sample are partly from pore water within the sample. However, contribution of AMD precipitates to MREE-enriched NASC-normalized REE patterns of the Sitai coal mine AMD is still unclear based on current data. Further work is needed to elucidate the contribution of AMD precipitates to MREE-enriched NASC-normalized REE patterns of the AMD.

6. Conclusions

When compared with several terrestrial waters, the AMD of the Sitai coal mine have high REEs and SO_4^{2-} concentrations, and concentrations of SO_4^{2-} control concentrations of REE in the AMD. The REE speciation modeling indicates that REE sulfate complexes ($LnSO_4^+$, > 60%) and free metal species (Ln^{3+}, 20%–40%) are the dominant REE species in the AMD, while other possible inorganic complexes such as $LnCl^{2+}$ and LnF^{2+} are negligible. The AMD of the Sitai coal mine also shows a typical MREE-enriched NASC-normalized REE patterns. Both REE sulfate ($LnSO_4^+$) in the AMD and country rock of the coal measures are possible causes for MREE-enriched NASC-normalized REE patterns of the Sitai coal mine AMD.

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