Specific REE patterns observed in sulfurous hot springs from a hydrothermal alteration area in Manza, Japan

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Abstract

Concentrations of rare earth elements (REEs) in acidic spring waters collected from sulfurous alteration zones in the Manza area belonging to the Kusatsu-Shirane volcano region, Japan were investigated. Based on the correlation in concentrations between REEs and major dissolved components, the common convex shape found in the heavy REEs in their REE patterns probably reflects the hydrothermal reservoir beneath the Manza area. Moreover, the varying distribution patterns in the light REEs presumably resulted from precipitation and/or dissolution of secondary sulfate minerals, such as alunite and anhydrite.

Keywords: rare earth elements; hydrothermal fluids; hot springs; alunite; anhydrite;

1. Introduction

The rare earth elements (REEs) are widely utilized as tracers for the study of geological and geochemical processes. Their distribution patterns or REE patterns in geochemical samples give us meaningful information on the mechanisms involved in geochemical processes connected to the occurrence of the samples. In volcanic hydrothermal fields, REE patterns observed in hot spring waters (not in high-temperature geothermal fluids) reflect geochemical processes involving water-rock interactions at a relative shallow depth that are directly connected with the environment in the area. In this study, we attempt the interpretation of various REE distribution patterns found in acidic spring waters issuing from a sulfurous hydrothermal alteration zone located in the Kusatsu-Shirane volcano area, Japan.

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2. Geological background

The Kusatsu-Shirane volcano is located at the central Japanese islands and well known as an active volcano having a large number of fumaroles and hot springs around its summit and on its mountainside. Extensive surface sulfurous hydrothermal alteration zones having relatively low temperature fumaroles surround the summit area. The Manza hot spring area spreading over southwest of the summit is typical of alteration areas. It is composed of siliceous and argillaceous zones originating from andesitic rock formations [1]. Those altered zones expand along rivers in the area.

3. Experimental operating conditions

Seven spring waters were collected from three subareas, (A) Manza-karafuki, (B) Manza-yubatake and (C) Oku-Manza, in the Manza area on Sep., 28, 2011. All the springs are located within about 1 km². The sampling locations are shown in Figure 1. The water temperature, pH and ORP were measured at the sites. After the sampling, the waters were immediately filtered through a 0.45 µm membrane filter, and HNO₃ was then added to them for preservation until the chemical analysis.

![Fig. 1. Location map of the Manza area with sampling sites (marked with the filled circles).](image)

The major chemical components in the sample waters were determined by conventional analytical methods. Na⁺ and K⁺ were determined by flame photometry. The other cations except Fe were determined by ICP-OES. The Fe²⁺ and Fe³⁺ were determined by 2,2'-bipyridine colorimetry using analytical solutions prepared at the sampling sites. Anions were determined by ion chromatography. The content of H₂S was determined by volumetric techniques [2]. REE in the samples were determined by ICP-QMS after the chemical isolation using a chelate resin (Chelex 100®, Bio-Rad). Then the chondrite-normalized REE patterns were obtained by dividing the contents of REEs in the samples by those of the corresponding REEs in the Leedey chondrite [3, 4].
4. Results and Discussion

The analytical results are listed in Tables 1 and 2. All of the spring waters are acidic with a pH range of 2 to 3. Their temperatures and redox states (Eh and Fe$^{2+}$/Fe$^{3+}$ ratio) vary from sample to sample as well as their chemical compositions, even though the springs are located within a relatively short range.

Table 1. Water chemistries of spring waters.

| Sample | WT (ºC) | pH  | Eh (mV) | Na$^+$ | K$^+$ | Mg$^{2+}$ | Ca$^{2+}$ | Al$^{3+}$ | Mn$^{2+}$ | Fe$^{2+}$ | Fe$^{3+}$ | Si | Cl$^-$ | SO$_4^{2-}$ | H$_2$S |
|--------|---------|-----|---------|-------|------|---------|--------|-------|------|-------|--------|-----|------|-----------|-----|
| A1     | 94.5    | 1.8 | +381    | 385   | 115  | 205     | 75.1   | 74.4  | 21.3 | 11.4  | 0.1    | 181 | 893  | 5902      | --  |
| B1     | 73.3    | 2.1 | +123    | 93.9  | 25.0 | 51.0    | 46.8   | 9.2   | 3.5  | 5.1   | 0.1    | 47.3 | 143  | 865       | 82  |
| B2     | 11.7    | 2.9 | +654    | 9.8   | 2.9  | 8.5     | 16.5   | 6.2   | 0.4  | 0.2   | 0.3    | 19.3 | 9.6  | 265       | --  |
| C1     | 41.7    | 2.8 | +58     | 27.5  | 5.5  | 20.2    | 106    | 10.2  | 0.8  | 2.2   | 0.0    | 25.4 | 77.6 | 587       | 229 |
| C2     | 8.3     | 3.1 | +333    | 4.9   | 2.5  | 4.4     | 14.5   | 8.3   | 0.2  | 0.1   | 0.0    | 20.3 | 24.2 | 194       | --  |
| C3     | 12.3    | 2.6 | +714    | 0.7   | 0.5  | 0.4     | 1.6    | 13.0  | 0.1  | 6.0   | 3.7    | 9.0  | 1.7  | 645       | --  |
| C4     | 10.8    | 2.9 | +689    | 7.0   | 2.9  | 8.1     | 24.6   | 16.0  | 0.2  | 0.2   | 0.2    | 19.8 | 50.1 | 298       | --  |

Table 2. The contents of REEs in µg/dm$^3$ in the spring waters analyzed.

| Sample | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| A1    | 5.1| 13.1| 2.1| 12.4| 3.3| 0.84| 3.7| 0.62| 4.3| 0.91| 2.8| 0.43| 2.8| 0.45|
| B1    | 0.51| 1.2| 0.17| 1.0| 0.33| 0.13| 0.65| 0.14| 1.3| 0.28| 0.77| 0.10| 0.50| 0.056|
| B2    | 0.23| 0.72| 0.12| 0.96| 0.26| 0.09| 0.32| 0.04| 0.33| 0.067| 0.19| 0.03| 0.13| 0.015|
| C1    | 0.082| 0.35| 0.093| 1.3| 0.82| 0.32| 1.5| 0.23| 1.9| 0.39| 1.1| 0.14| 0.68| 0.075|
| C2    | 0.23| 0.73| 0.13| 1.1| 0.36| 0.12| 0.51| 0.065| 0.46| 0.10| 0.28| 0.040| 0.24| 0.025|
| C3    | 1.7| 3.4| 0.32| 1.4| 0.20| 0.051| 0.20| 0.015| 0.099| 0.021| 0.052| 0.007| 0.037| 0.005|
| C4    | 0.16| 0.60| 0.10| 0.59| 0.20| 0.071| 0.28| 0.062| 0.66| 0.14| 0.42| 0.064| 0.28| 0.047|

The chondrite-normalized REE patterns of the samples obtained from the data in Table 2 are shown in Fig. 2a. A wide variety of REE patterns are observed. The REE pattern of A1 sample, which shows the highest water temperature and the highest contents of the dissolved components with the lowest pH value (Fig. 1), is relatively flat. This pattern probably resulted from macroscopic dissolution of rocks on the pathway with high temperature and high acidity.

The REE patterns in the springs from B and C subareas are quite different from that of A1, and varied from sample to sample although their shapes in the heavy REEs (HREEs) are similar to each other. The convex shapes found in the HREEs originally reflect the liquid phase of the Cl-SO$_4$ type hydrothermal reservoir beneath the Manza area, since the contents of HREEs in the samples show correlation with that of Cl and not with SO$_4$. In the Manza area, the Cl in the hot springs solely comes from the hydrothermal reservoir, while the SO$_4$ in them is composed of that from hydrothermal reservoirs and secondary SO$_4$ formed from sulfur species like S and H$_2$S in surface and subsurface environments in sulfuretted alteration zone. Contrary to HREEs, a large variation in the REE pattern is observed in light REEs (LREEs) to middle REEs (MREEs). This is attributable to precipitation and dissolution of secondary mineral phases at a relatively shallow depth. The REE pattern of C3 which is enriched in LREEs with a steep negative slope looks like that of alunite [3] which is a common secondary mineral widely found in the altered zones in the Manza area (Fig. 2b). Thus, C3 probably has contacted with a vein of alunite on its pathway. On the other hand, B1, B2, C1, C2 and C4 are depleted in LREEs, although the shapes in LREEs and
MREEs are different from each other. The distribution patterns in LREEs may be connected to the formation of anhydrite because the La/Nd content ratio in those springs shows a good correlation with the Ca/SO₄ ratio. The REE patterns of some kind of anhydrite are depleted in LREEs [6]. Another possibility is that these springs have precipitated LREE-enriched minerals like alunite on their pathways contrary to the case of C3.

Fig. 2. (a) The REE patterns of spring waters; (b) The REE patterns of Takai lava, the basement rock of the Manza area, and alunite samples (the shaded area) in Kusatsu-Shirane volcano [5].

5. Conclusion

The spring waters collected from the Manza area showed a wide variety of REE distribution patterns even though their locations were close to each other. The variation in the distribution pattern of REEs was significant in the LREE. The varying distribution patterns in the LREEs presumably resulted from precipitation and/or dissolution of secondary sulfate minerals like alunite and anhydrite, since the common convex shape found in the HREEs in their REE patterns probably reflects the hydrothermal reservoir beneath the area.

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