

Mechanisms for anhydrite and gypsum formation in the Kuroko massive sulfide–sulfate deposits, north Japan

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Abstract The Sr, Ba, and rare earth elements (REEs) concentrations and Sr isotopic composition of anhydrite and gypsum have been determined for samples from the Matsumine, Shakanai, and Hanaoka Kuroko-type massive sulfide–sulfate deposits of northern Japan to evaluate the mechanisms of sekko (anhydrite and gypsum) ore formation. The Sr isotopic compositions of the samples fall in the range of 0.7077–0.7087, intermediate between that for middle Miocene (13–15 Ma) seawater (0.7088) (Peterman et al., *Geochim Cosmochim Acta*, 34:105–120, 1970) and

that for country rocks (e.g., 0.7030–0.7050) (Shuto, *Assn Geol Collab Japan Monograph* 18:91–105, 1974). The Kuroko anhydrite samples exhibit two types of chondrite-normalized REE patterns: one with a decrease from light REEs (LREEs) to heavy REEs (HREEs) (type I), and another with a LREE-depleted pattern (type II).

Based on the Sr content and isotopic ratio (assuming an Sr/Ca (mM/M) of 8.7 for seawater), anhydrite is considered to have formed by mixing of preheated seawater with a hydrothermal solution of Sr/Ca (mM/M)=ca. 0.59–1.36 under the condition in which the partition coefficient (K_d) ranges between ca. 0.5 and 0.7. This results in the formation of anhydrite with higher Sr content with an Sr isotopic value close to that of seawater under seawater-dominant conditions.

Larger crystals of type II anhydrite are partly replaced by smaller ones, indicating that anhydrite dissolution and recrystallization occurred after or during the formation of sekko ore. Gypsum, which partially replaces anhydrite in the Kuroko deposits, also exhibits two distinct chondrite-normalized REE patterns. Because LREEs are likely to be more readily mobilized during dissolution and recrystallization, it is hypothesized that LREEs are leached from type I anhydrite, resulting in the formation of type II anhydrite with LREE-depleted profiles.

Keywords Kuroko deposits · Anhydrite · Gypsum · Sr isotope ratio · Rare earth elements (REEs)

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Introduction

Sulfur and oxygen isotopic studies of sulfates from the Kuroko massive sulfide–sulfate deposits of northern Japan have suggested that seawater has an important role in the

formation of these polymetallic deposits (Sakai et al. 1970; Kajiwaru 1971; Sasaki and Kajiwaru 1971; Yamamoto 1974; Kusakabe and Chiba 1979). Farrell et al. (1978) and Farrell and Holland (1983) demonstrated that the Sr isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) of anhydrite and gypsum (0.7082–0.7087) fall between that of the country rocks (0.7030–0.7050) (Shuto 1974) and that of middle Miocene (13–15 Ma) seawater (0.7088) (Peterman et al. 1970), indicating the potentially important role of seawater–country rock interaction and seawater–hydrothermal solution mixing in the formation of the Kuroko deposits. Shikazono et al. (1983) analyzed the Sr content of anhydrite from the Matsumine, Shakanai, and Fukazawa Kuroko deposits. Shikazono and Holland (1983) concluded that the Kuroko anhydrites were formed from the mixing of seawater and hydrothermal solution with high Ca concentration (500–1,000 ppm) and low Sr concentration (1–5 ppm) based on the experiments of Sr partitioning between anhydrite and aqueous solution and the measured Sr contents of Kuroko anhydrites (about 150–2,000 ppm).

On the basis of these previous studies, two main explanations for the genesis of anhydrite in the Kuroko deposits have been proposed: (1) anhydrite formed by the simple heating of

seawater due to a decrease in anhydrite solubility with increasing temperature (Kajiwaru 1971; Farrell et al. 1978; Kusakabe and Chiba 1979), and (2) anhydrite formed by the mixing of ascending hydrothermal solution with seawater (Sato 1973; Shikazono 1983; Shikazono et al. 1983).

Anhydrite has also been found in large amounts beneath active submarine hydrothermal deposits on mid-ocean ridges and in back arc basins, for example the Trans-Atlantic Geotraverse (TAG) hydrothermal mound at 26°N at the Mid-Atlantic Ridge (Humphris et al. 1995). It is considered that anhydrite in these occurrences formed by the subseafloor mixing of hydrothermal solution with seawater because the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios exhibited by anhydrite are intermediate between those of seawater and hydrothermal solution (Teagle et al. 1998a,b; Mills and Tivey 1999) and the $\delta^{34}\text{S}$ value of the anhydrite is very close to that of seawater (Chiba et al. 1998).

On the other hand, the 250°C clear fluids, which are considered to be caused by the phase separation (boiling) and sulfide precipitation beneath the mounds, are venting at the Grimsey field, 66°N on the mid-Atlantic Ridge, north of Iceland, where numerous anhydrite chimneys are found (Hannington et al. 2001). The $\delta^{34}\text{S}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of

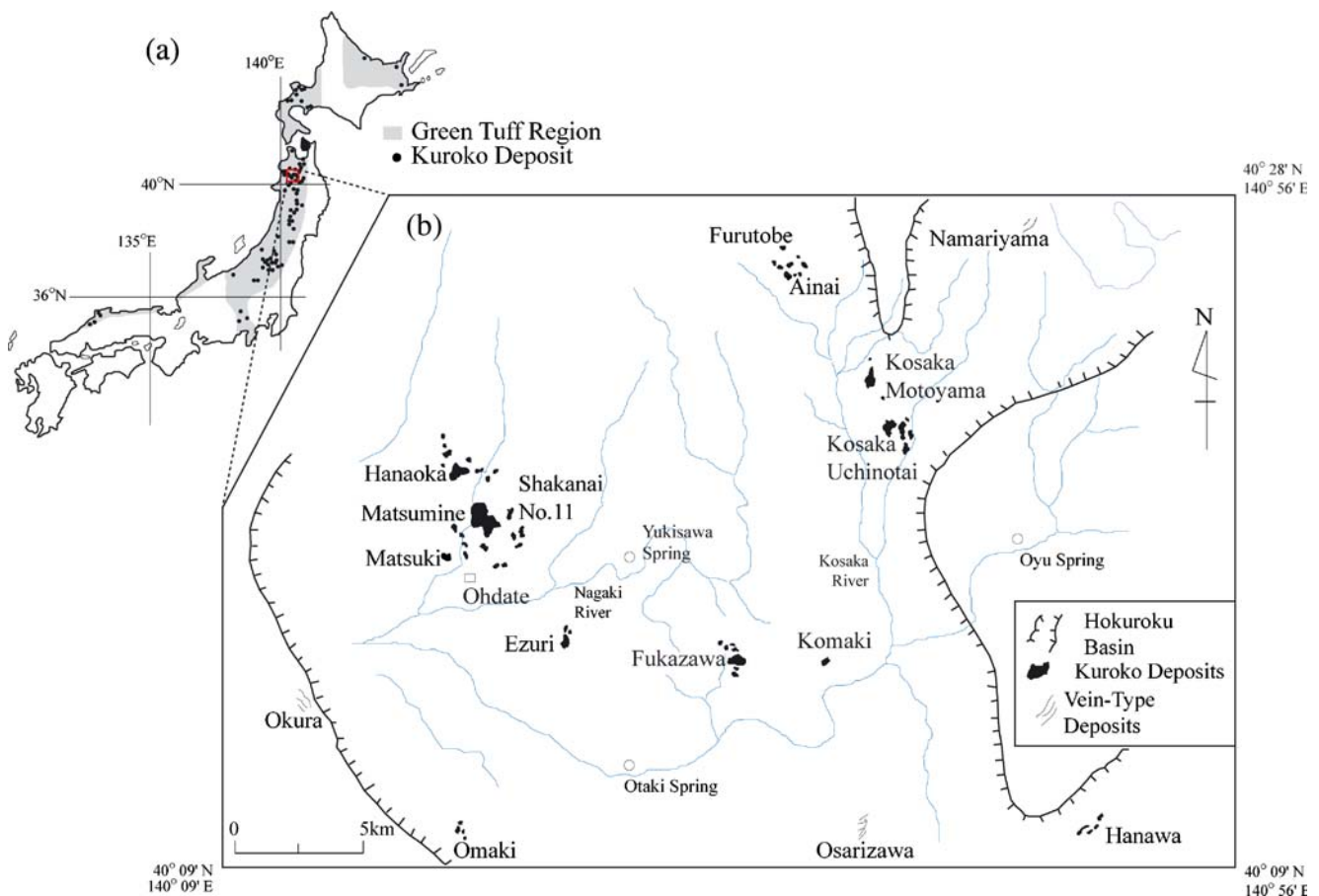


Fig. 1 Distribution of the Kuroko deposits in Japan. **a** Green Tuff region and distribution of the Kuroko deposits. **b** Location of study area; Hokuroku district, Akita Pref., Northern Japan

anhydrite from this site also suggest the anhydrite formation by the mixing of seawater and hydrothermal solution, and it has been suggested that large amounts of anhydrite probably precipitated beneath the Grimsey hydrothermal deposits (Kuhn et al. 2003). The retrograde solubility of anhydrite means that precipitation and dissolution of subseafloor anhydrite with cooling have the potential to modify the structure of hydrothermal deposits, and anhydrite solubility is thus an important aspect of both modern and ancient submarine hydrothermal deposits (Mills and Tivey 1999).

In the present study, the Sr and rare earth element (REE) concentrations and Sr isotopic compositions of anhydrite in the Kuroko deposits were analyzed to consider the potential similarities between the formation mechanism of the sekko ores in ancient Kuroko deposits, which are composed of anhydrite and gypsum, and the processes occurring in active submarine hydrothermal VMS-forming systems (TAG and Grimsey fields).

Anhydrite and gypsum in the Kuroko deposits

There are large numbers of Kuroko deposits in Green Tuff area in Japan, which are situated in an altered submarine volcanic pile of Miocene age (Fig. 1a) in the Hokuoku district of Akita in northern Japan (Fig. 1b). In this study, we considered the mechanism of formation of sekko ore from chemical analyses of anhydrite and gypsum samples from Matsumine, Shakanai, and Hanaoka Kuroko deposits, which are distributed in the western Hokuoku Basin.

Schematic cross sections of the Matsumine and Shakanai No. 11 orebodies are shown in Fig. 2. The sekko ore contains gypsum and anhydrite, which is distributed in the lower horizon of dacitic tuff below black sulfide ore (kuroko) containing sphalerite and galena and yellow ore (oko) containing chalcopyrite and pyrite. Sulfide–anhydrite ores named sekko kuroko or sekko oko occur between the sekko ore and sulfide ore; the term sekko kuroko defines ores containing anhydrite, gypsum, barite, sphalerite, and galena, and the term sekko oko defines ores containing anhydrite, gypsum, chalcopyrite, and pyrite.

Anhydrite is usually nodular in form. It occurs in dacitic tuff breccia and in tuff and gradually changes to anhydrite associated with sulfide minerals (sekko kuroko and sekko oko) at the upper part of the sekko ore horizon. Anhydrite nodule occurring in the lowest part of the sekko ore is ca. 0.5 cm in diameter, and that in the upper part is ca. 5–20 cm in diameter. Details on the occurrence of sekko ore and geochemical data (Sr content, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}$, and fluid inclusion) of the Kuroko anhydrite and gypsum are summarized in Shikazono et al. (1983).

Analytical procedure

The Ba and REE contents and Sr isotopic ratios of anhydrite samples from Matsumine and Shakanai Kuroko deposits studied by Shikazono et al. (1983) were examined in the present study. Anhydrite from the Hanaoka deposit and gypsum from the Matsumine and Hanaoka deposits were also analyzed, along with coexisting anhydrite and gypsum in samples M-2 and M-21 from the Matsumine deposit. The descriptions of the samples are presented in Table 1.

The anhydrite and gypsum samples were analyzed for REE and Ba contents by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (VG Elemental, PQ-3 and Perkin Elmer Sciex, Elan DRC II). The samples were prepared by dissolving 500 mg of anhydrite in 50 ml of double-distilled HNO_3 solution at 60°C. The resultant solutions were then diluted to 2,000–5,000 times for analysis. To obtain accurate analytical data, the standard addition method was employed, in which 1 ppb REE and Ba internal standard solution was added into sample solutions. The blank solution was prepared by the same procedure of dissolution as anhydrite and gypsum samples.

The Sr content of gypsum samples and anhydrite samples from the Hanaoka deposit, which were not analyzed by Shikazono et al. (1983), was analyzed by atomic absorption spectrometry (AAS). These samples were dissolved by the same method as for ICP-MS analysis and distilled to 220–2,000 times concentration for analysis. Highly concentrated La solution (about 0.6 wt%) was added to suppress interference.

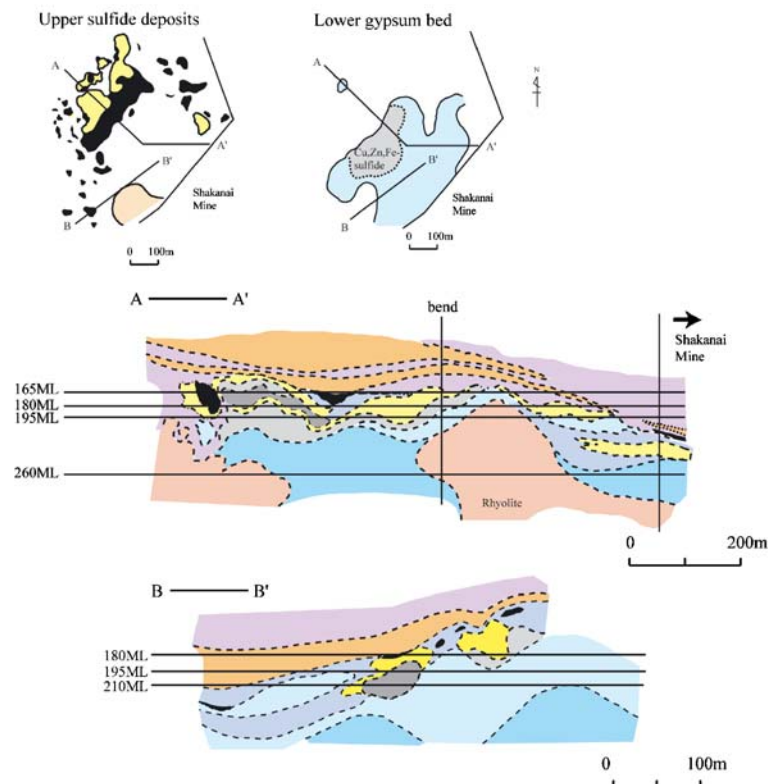
Purification of Sr is necessary for Sr isotope analysis because ^{87}Rb interferes with ^{87}Sr . Sr was separated from dissolved anhydrite sample by the cation-exchange chromatography. Sr samples were loaded onto Ta single filament, and Sr isotope ratios were measured by Finnigan MAT262 mass spectrometry. The obtained $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalized to that for NIST987 (0.71025). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for NIST987 determining during the study were 0.71028 ± 16 ($n=16$). The more detailed procedure was described in Na et al. (1995).

Analytical results

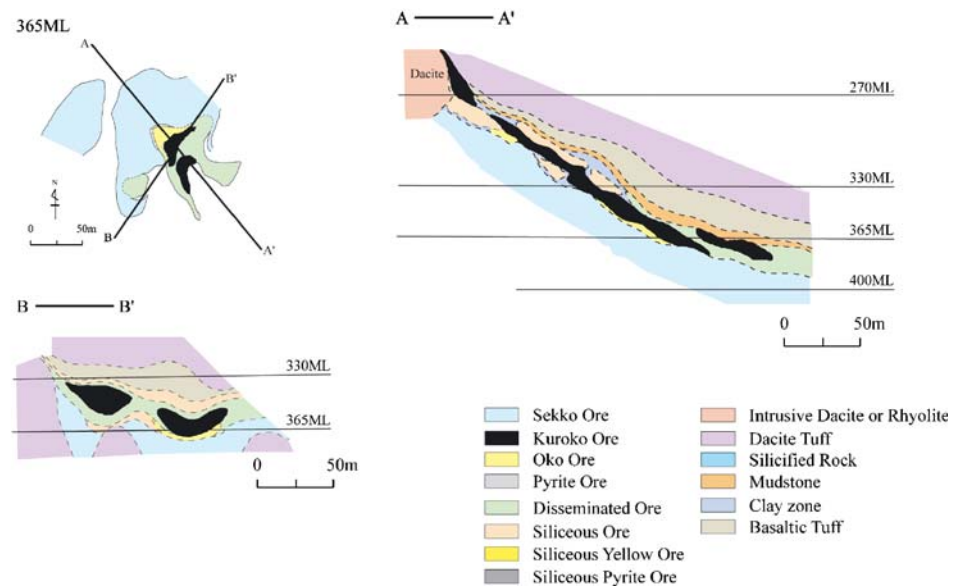
The analytical results for anhydrite and gypsum from the Kuroko deposits as determined by ICP-MS, AAS, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are presented in Table 2, and the chondrite-normalized REE patterns are shown in Figs. 3 and 4. Figure 3 clearly shows that anhydrite in the Kuroko deposits exhibits two different chondrite-normalized REE patterns: (1) a pattern with decrease from light REEs (LREEs) to HREEs (type I) (Fig. 3a,b), and (2) an LREE-depletion pattern with a peak in Sm (type II) (Fig. 3c). Similarly, two

Fig. 2 Schematic cross sections of **a** Matsumine (modified from Suga et al. 1972) and **b** Shakanai No. 11 deposits (modified from Miyazaki et al. 1978)

Matsumine



Shakanai No. 11



types of chondrite-normalized REE patterns have been identified in anhydrite from the Kakkonda geothermal area in Iwate Pref., northern Japan (Sasaki et al. 2003).

Gypsum from the Kuroko deposits also exhibits two types of REE patterns, which are almost similar to those for anhydrite. However, G-1 and G-2 have a slight positive Eu anomaly different from type II anhydrite with negative Eu

anomaly (Fig. 4). The REE concentrations of the two gypsum samples (G-3 and G-4) were too low to obtain chondrite-normalized REE patterns.

The Sr content of type I anhydrite tends to be higher than that of type II. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all anhydrite samples are intermediate between that for middle Miocene seawater (0.7088) (Peterman et al. 1970) and that for country rocks

Table 1 The descriptions of anhydrite and gypsum samples used in this study

Samples	Descriptions
Matusmine Kuroko deposit	
NS-M-1	Massive light purplish, coarsely crystalline anhydrite from sekko horizon containing small amounts of gypsum but no sulfides or pyroclastic debris.
NS-M-3	Specimens from sekko oko horizon, about 50 cm in thickness; sekko oko is composed of anhydrite, gypsum and pyrite; anhydrite is coarsely crystalline.
NS-M-6	Massive, compact, and coarsely crystalline; light purplish anhydrite nodule from sekko horizon; nodule size is about 20–30 cm in diameter; along narrow fractures in anhydrite, gypsum has developed as late-stage hydration product.
NS-M-7	Laminated anhydrite nodules; light gray to white, finely crystalline anhydrite occurs in footwall tuffaceous pyroclastic rocks, which have suffered intense hydrothermal alteration.
NS-M-8	Mineralogy, petrography, and texture are nearly identical to those of NS-M-7; anhydrite is nodular in form, and diameter of anhydrite aggregate is about 10 cm; small amounts of gypsum are contained in specimen; host-rock tuff contains fine-grained pyrite.
NS-M-12	Laminated anhydrite; light gray to white, finely crystalline anhydrite occurs in pyroclastic rocks that have suffered extensive hydrothermal alteration; the dominant alteration mineral is Mg chlorite.
NS-M-13	Petrography and mineralogy are nearly identical to those of NS-M-12.
NS-M-15	Anhydrite–gypsum body about 50–60 cm in diameter; anhydrite is deep purple in color; specimen is from sekko oko zone.
NS-M-22	Laminated, compact anhydrite; anhydrite horizon consists dominantly of felted masses of intergrown anhydrite laths, as well as finely granular compact aggregates.
M-2	Purple anhydrite (M-2 A) surrounded by yellow transparent gypsum (M-2 G.Y.) and fragile white gypsum (M-2 G.W.).
M-21	Purple coarse-grained anhydrite (M-21 A) surrounded by fine gypsum (M-21 G).
Shakanai No. 11 deposit	
NS-S-6	Anhydrite specimen containing small amounts of sphalerite (sekko kuroko); specimen is from horizon immediately underlying black ore horizon.
NS-S-7	Anhydrite collected from sekko horizon immediately underlying sekko kuroko horizon and is nodular in form. Diameter of anhydrite aggregate is about 20–30 cm.
NS-S-10	Massive light purple anhydrite containing pyrite. Pyrite is disseminated.
NS-S-13	Massive, compact anhydrite, 0.3–1 mm in diameter.
NS-S-26	Aggregate of anhydrite nodules containing greenish clay (Mg chlorite); nodule is 5–10 cm in diameter; individual nodules do not display lamination, banding, or flow structure, but it is common for long axes of individual nodules to be parallel to bedding of volcanic pyroclastic units in which anhydrite is developed.
Hanaoka Kuroko deposit	
H-1	Recrystallized anhydrite containing fine pyrite.
H-2	Recrystallized anhydrite containing fine pyrite.
G-1	Medium-grained massive gypsum with small amount of pyrite.
G-2	Medium-grained massive gypsum containing gray layer with small amount of pyrite.
G-3	Coarse-grained gypsum crystal.
G-4	Coarse white transparent gypsum.

(0.7030–0.7050) (Shuto 1974), which is consistent with the analyses from the Fukazawa and Kosaka deposits (Farrell et al. 1978; Farrell and Holland 1983).

Discussions

Similarity of geochemical data between the Kuroko anhydrite and that from the recent submarine hydrothermal deposits

As mentioned in the “[Introduction](#)”, the $\delta^{34}\text{S}$ value and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Kuroko anhydrite are very similar to those of seafloor anhydrite associated with submarine hydrothermal systems, such as the TAG and Grimsey fields on the mid-Atlantic Ridge. Furthermore, the chondrite-

normalized REE pattern of type I anhydrite from the Kuroko deposits in this study is similar to those of TAG anhydrite, except for the Eu anomaly; the latter has uniformly positive Eu anomaly (Humphris 1998), whereas the former has positive, negative, and no Eu anomaly ($\text{Eu}/\text{Eu}^*=0.54$ to 4.0) (Fig. 3a,b). These similarities suggest that anhydrite from the Kuroko deposits may have been formed by the same mechanism as TAG and Grimsey anhydrite, namely, the mixing between seawater and hydrothermal solution.

Shikazono (1983) and Shikazono et al. (1983) proposed that seafloor mixing is the most likely mechanism for the formation of anhydrite in the Kuroko deposits based on two observations: (1) a systematic hydrothermal alteration zone exists around the sekko ore, implying that anhydrite formed in the footwall hydrothermal alteration zone, and

Table 2 Analytical results of Sr, Ba, and REE contents (in parts per million) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of anhydrite and gypsum samples

Matsumine											
	NS-M-1	NS-M-3	NS-M-6	NS-M-7	NS-M-8	NS-M-12	NS-M-13	NS-M-15	NS-M-22	M-2 A	M-21 A
Type	I	I	I	II	II	II	II	I	I	I	I
La	0.437	0.546	0.617	0.265	0.115	0.316	0.361	0.84	0.328	0.239	0.249
Ce	1.01	1.15	1.48	0.687	0.359	0.989	1.06	2.34	0.630	0.573	0.496
Pr	0.129	0.140	0.190	0.111	0.079	0.18	0.18	0.32	0.079	0.076	0.070
Nd	0.581	0.569	0.854	0.603	0.517	1.13	1.02	1.6	0.316	0.302	0.309
Sm	0.142	0.133	0.243	0.243	0.293	0.644	0.346	0.418	0.085	0.055	0.081
Eu	0.056	0.053	0.076	0.075	0.057	0.114	0.049	0.102	0.036	0.032	0.026
Gd	0.145	0.124	0.196	0.241	0.194	0.573	0.318	0.387	0.073	0.058	0.059
Tb	0.015	0.017	0.029	0.026	0.026	0.083	0.038	0.057	0.009	0.006	0.007
Dy	0.050	0.081	0.110	0.100	0.085	0.271	0.123	0.210	0.034	0.031	0.029
Ho	0.010	0.011	0.013	0.012	0.009	0.028	0.012	0.025	0.009	0.005	0.005
Er	0.021	0.021	0.034	0.017	0.016		0.026	0.060	0.016	0.008	0.010
Tm			0.003				0.003		0.003		0.001
Yb			0.013		0.007		0.006	0.015	0.013	0.004	0.005
Lu					0.002			0.004		0.001	0.001
Sr	600	1267	2000	767	770	800	810	1633	1867	1089	1233
Ba	6.11	10.8	15.6	3.82	1.37	7.47	1.97	26.6	12.3	7.38	9.14
$\text{La}_\text{N}/\text{Sm}_\text{N}$	1.94	2.58	1.60	0.686	0.247	0.309	0.657	1.26	2.43	2.75	1.95
Eu/Eu*	1.19	1.26	1.06	0.947	0.731	0.573	0.451	0.775	1.40	1.75	1.16
$^{87}\text{Sr}/^{86}\text{Sr}$	0.708027	0.708378		0.707992		0.70772	0.708074		0.708542		
seawater proportion	0.49–0.73	0.71–0.85		0.48–0.72		0.33–0.64	0.53–0.75		0.82–0.91		

Shakanai					Hanaoka			Gypsum						
	NS-S-7	NS-S-8	NS-S-10	NS-S-13	NS-S-26	H-1	H-2	M-2 GY	M-2 GW	M-21 G	G-1	G-2	G-3	G-4
Type	I	I	I	I	I	I	I							
La	0.936	0.79	0.277	0.169	1.51	0.173	0.173	0.261	0.115	0.338	0.086	0.129	0.0022	0.0120
Ce	1.77	1.75	0.737	0.375	3.27	0.309	0.358	0.556	0.231	0.713	0.333	0.447	0.0021	0.0155
Pr	0.246	0.251	0.111	0.052	0.397	0.036	0.045	0.076	0.031	0.096	0.073	0.093	0.0005	0.0024
Nd	1.16	1.21	0.490	0.253	1.68	0.168	0.207	0.305	0.144	0.430	0.422	0.601	0.0036	0.0098
Sm	0.364	0.389	0.141	0.105	0.427	0.050	0.075	0.065	0.034	0.120	0.136	0.313	0.0030	0.0016
Eu	0.309	0.496	0.185	0.055	0.111	0.010	0.020	0.034	0.021	0.036	0.071	0.179	0.0016	
Gd	0.368	0.365	0.144	0.062	0.414	0.065	0.086	0.062	0.038	0.086	0.125	0.277	0.0038	0.0016
Tb	0.029	0.030			0.040	0.007		0.007	0.005	0.010	0.015	0.044		
Dy	0.103	0.103	0.057	0.025	0.203	0.034	0.042	0.035	0.024	0.037	0.060	0.167		
Ho	0.011				0.029	0.005		0.007	0.003	0.006	0.008	0.025		
Er	0.016	0.033	0.014	0.001	0.068	0.013	0.013	0.012	0.007	0.012	0.010	0.053		
Tm						0.003		0.001	0.001	0.002	0.001	0.004		
Yb		0.013	0.005	0.002	0.041	0.01	0.012	0.009	0.003	0.012	0.003	0.013		
Lu						0.002		0.002	0.001	0.002	0.001	0.002		
Sr	1400	1267	2210	1000	987	3483	2819	866	1062	784	820	863	136	180
Ba	11.0	3.73	73.4	2.79	7.39	6.06	4.24	11.29	10.79	7.26	110	10.04	0.326	0.407
$\text{La}_\text{N}/\text{Sm}_\text{N}$	1.62	1.28	1.24	1.01	2.23	2.18	1.45	2.54	2.11	1.78	0.40	0.26	0.45	4.78
Eu/Eu*	2.58	4.02	3.97	2.08	0.807	0.536	0.761	1.66	1.80	1.08	1.68	1.86	1.41	
$^{87}\text{Sr}/^{86}\text{Sr}$	0.708309	0.708093	0.708017		0.708237	0.708656	0.708661							
seawater proportion	0.67–0.83	0.54–0.76	0.49–0.73		0.62–0.81	0.90–0.95	0.90–0.95							

Sr content data of samples except anhydrite samples from the Hanaoka ore deposit and gypsum samples from the Matsumine and Hanaoka ore deposits are taken from Shikazono et al. (1983). REE data of chondrite were used from Taylor and McLennan (1985)

$^{87}\text{Sr}/^{86}\text{Sr}$

Middle Miocene seawater: 0.7088 (Peterman et al. 1970)

Kuroko hydrothermal solution estimated values by Shikazono (1983): 0.7055–0.7070

Country rock: 0.7030–0.7050 (Shuto 1974)

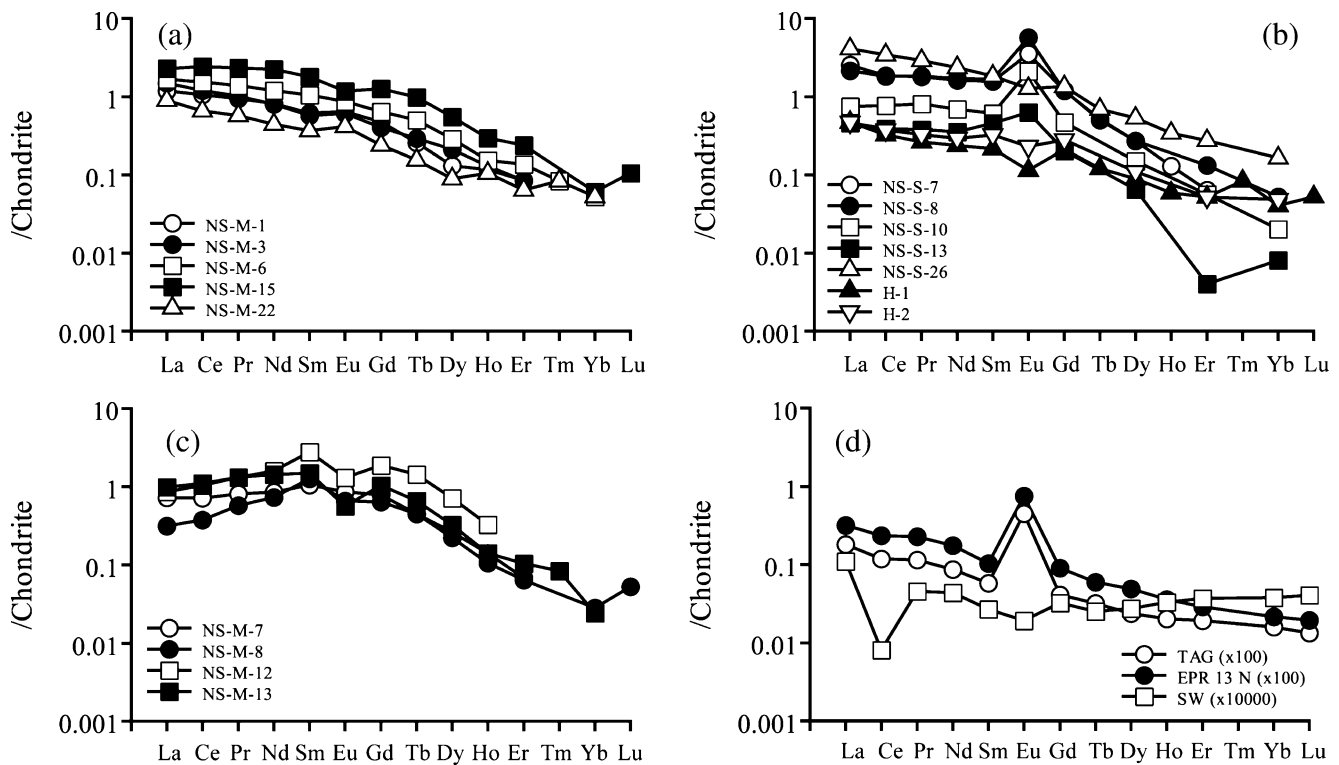


Fig. 3 Chondrite-normalized REE patterns of anhydrite samples from the Kuroko deposits. **a** Type I anhydrite from the Matsumine Kuroko deposit. **b** Type I anhydrite from the Shakanai and Hanaoka Kuroko deposits. **c** Type II anhydrite from the Matsumine Kuroko deposit. For reference, chondrite-normalized REE pattern (ppm/ppm) of TAG and

(2) anhydrite is observed around active chimneys, yet is not observed around relict ones on mid-ocean ridges such as the East Pacific Rise 21°N (EPR 21°N) due to subsequent dissolution by cold seawater (Styrt et al. 1981). Therefore, it seems likely that the Kuroko anhydrites were formed by the mixing of seawater with the hydrothermal solution below the seafloor similar to the saturation mechanism for the TAG subseafloor anhydrite.

Sr contents, $^{87}\text{Sr}/^{86}\text{Sr}$, and saturation of anhydrite of the Kuroko deposits

The conditions of anhydrite precipitation in Kuroko deposits are investigated in this study based on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr content. Similar to the studies of Teagle et al. (1998a,b) and Kuhn et al. (2003), $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are used in this study as indicators of the mixing ratio of seawater and the Kuroko hydrothermal solution. Several parameter values are thus estimated for the Kuroko hydrothermal solution. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of middle Miocene seawater has been defined 0.7088 (Peterman et al. 1970), and that of the Kuroko hydrothermal solution is estimated to be 0.7055–0.7070, as ascertained as follows. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of volcanic rocks in the Kuroko mining district are divided into three zones:

EPR 13°N hydrothermal solution and seawater are shown in (d). REE data of chondrite were used from Taylor and McLennan (1985). The REE data for hydrothermal solutions ($\times 100$) and seawater ($\times 10,000$) were taken from Douville et al. (1999) and Mitra et al. (1994), respectively

greater than 0.7075 near orebodies, less than 0.7048 away from orebodies, and 0.7055–0.7070 between these two boundary zones (Farrell and Holland 1983). If equilibrium between the volcanic rocks and the hydrothermal solution is attained, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Kuroko hydrothermal solution is estimated to be 0.7055–0.7070 (Shikazono 1983). The chemical composition of the Kuroko hydrothermal solution is estimated from chemical analyses of fluid inclusions (Pisutha-Arnond and Ohmoto 1983). The Ca concentration is assumed to be that for an end-member with $\text{Mg}=0$, which was obtained from their data. As the Sr concentration of the Kuroko hydrothermal solution has not been estimated, a wide range of Sr concentration is assumed. The Ca and Sr concentrations ($C_{\text{Ca}(\text{mx})}$ and $C_{\text{Sr}(\text{mx})}$) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio ($R_{(\text{mx})}$) of the mixed solution of seawater and hydrothermal solution are estimated from the following equations:

$$\begin{aligned} C_{\text{Ca}(\text{mx})} &= nC_{\text{Ca}(\text{sw})} + (1-n)C_{\text{Ca}(\text{hs})} \\ C_{\text{Sr}(\text{mx})} &= nC_{\text{Sr}(\text{sw})} + (1-n)C_{\text{Sr}(\text{hs})} \\ R_{(\text{mx})} &= nR_{(\text{sw})} \times \frac{C_{\text{Sr}(\text{sw})}}{C_{\text{Sr}(\text{mx})}} + (1-n)R_{(\text{hs})} \times \frac{C_{\text{Sr}(\text{hs})}}{C_{\text{Sr}(\text{mx})}} = R_{(\text{anhydrite})} \end{aligned}$$

where n is the proportion of seawater in the mixed solution, $C_{\text{Ca}(\text{sw})}$ is the Ca concentration of seawater, $C_{\text{Ca}(\text{hs})}$ is the Ca concentration of the hydrothermal solution, $C_{\text{Sr}(\text{sw})}$ is the Sr

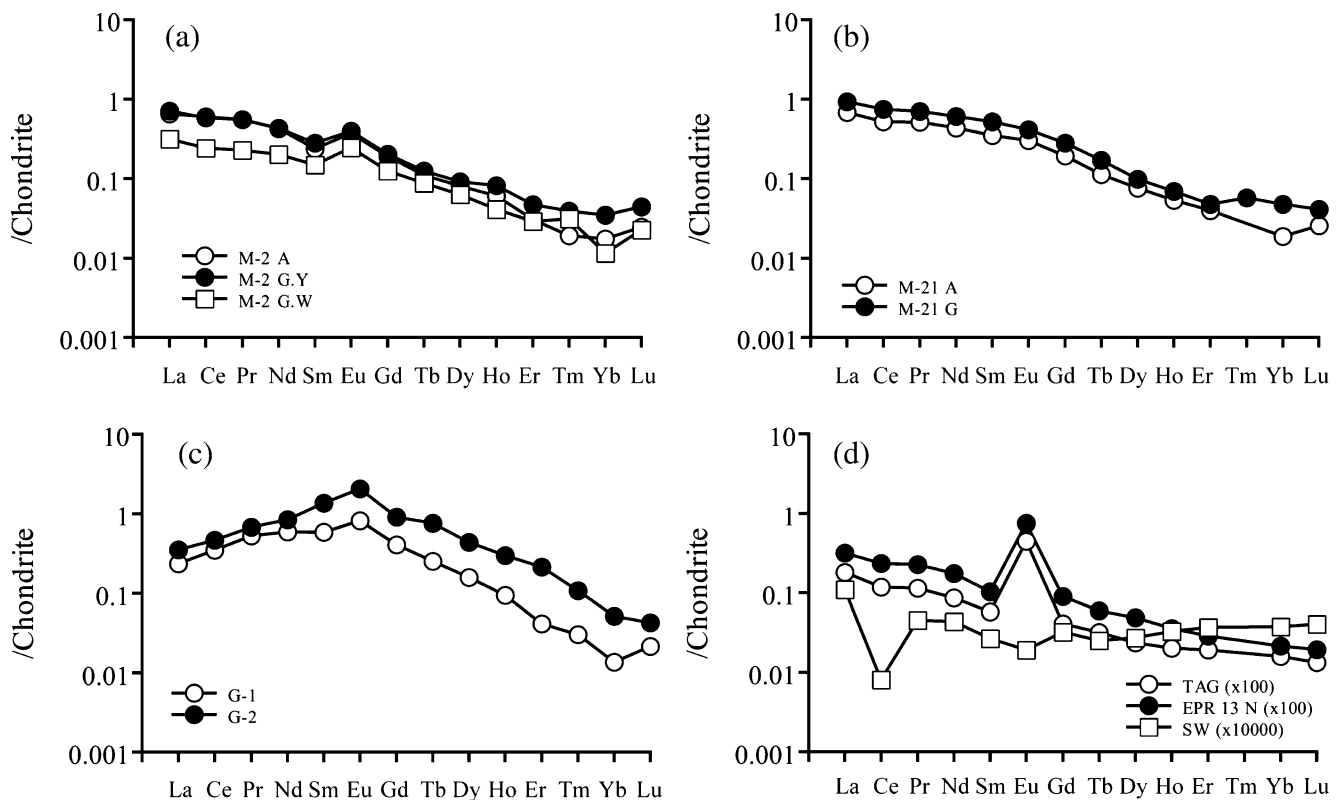


Fig. 4 Chondrite-normalized REE pattern of anhydrite and gypsum samples from the Kuroko deposits. **a** M-2 anhydrite and gypsum samples. **b** M-21 anhydrite and gypsum samples. **c** G-1, G-2 gypsum samples. For reference, chondrite-normalized REE pattern (ppm/ppm) of TAG and EPR 13°N hydrothermal solution and

seawater are shown in **(d)**. REE data of chondrite were used from Taylor and McLennan (1985). The REE data for hydrothermal solutions ($\times 100$) and seawater ($\times 10,000$) were taken from Douville et al. (1999) and Mitra et al. (1994), respectively

concentration of seawater, $C_{\text{Sr(hs)}}$ is the Sr concentration of the hydrothermal solution, $R_{\text{(sw)}}$ is the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater, $R_{\text{(hs)}}$ is the $^{87}\text{Sr}/^{86}\text{Sr}$ of the hydrothermal solution, and $R_{\text{(anhydrite)}}$ is the $^{87}\text{Sr}/^{86}\text{Sr}$ of the anhydrite. The relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca (mM/M) ratios of the mixed solution, as estimated from the above equations, is shown in Fig. 5.

The apparent partition coefficient for Sr ($[\text{Sr}] K_d$) in anhydrite is expressed as

$$[\text{Sr}] K_d = (\text{Sr}/\text{Ca})_{\text{anhydrite}} / (\text{Sr}/\text{Ca})_{\text{solution}}$$

where $(\text{Sr}/\text{Ca})_{\text{anhydrite}}$ and $(\text{Sr}/\text{Ca})_{\text{solution}}$ represent the mole ratios for the anhydrite and the solution, respectively. Shikazono and Holland (1983) estimated that $[\text{Sr}] K_d$ under highly supersaturated conditions is 0.48–0.56 based on the experiments on Sr partitioning between anhydrite and aqueous solution. The $[\text{Sr}] K_d$ values estimated by Berndt et al. (1988) have wider range (0.27–0.73). Those experimental values are similar to the values of anhydrite from the TAG and Grimsey fields (Teagle et al. 1998a,b; Kuhn et al. 2003). Therefore, the experimental value of $[\text{Sr}] K_d$ (0.27–0.73) is used for the present analysis of the

conditions of anhydrite formation. The Sr/Ca (mM/M) ratios of the mixed solution precipitating anhydrite are deduced from K_d value and are plotted in Fig. 5.

Sr partitioning into anhydrite is best explained with a K_d greater than ~ 0.5 (Fig. 5b,c). In Fig. 5c, for example, the Sr/Ca (mM/M) ratios of the solution precipitating anhydrite plot near line c, which represents the assumption that the Sr concentration of the Kuroko hydrothermal solution is half of seawater concentration, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is 0.7055, and K_d is 0.73. This indicates that the Kuroko anhydrite precipitated from a mixture of seawater and hydrothermal solution with Sr/Ca (mM/M) ratio of approximately 0.59.

This investigation is expanded to the estimated wide range parameters, Sr concentration, and $^{87}\text{Sr}/^{86}\text{Sr}$ of the Kuroko hydrothermal solution and K_d , and the relationship among these parameters is summarized in Fig. 6. If the $^{87}\text{Sr}/^{86}\text{Sr}$ of the Kuroko hydrothermal solution is 0.7055 and partitioning occurs at $K_d=0.54$, an upper limit of Sr/Ca (mM/M) of hydrothermal solution can be estimated (ca. 1.36). If the $^{87}\text{Sr}/^{86}\text{Sr}$ of the Kuroko hydrothermal solution is 0.7070 and partitioning occurs at $K_d=0.73$, the lower limit of Sr/Ca (mM/M) of hydrothermal solution could also be estimated (ca. 0.59). Under these conditions, lower

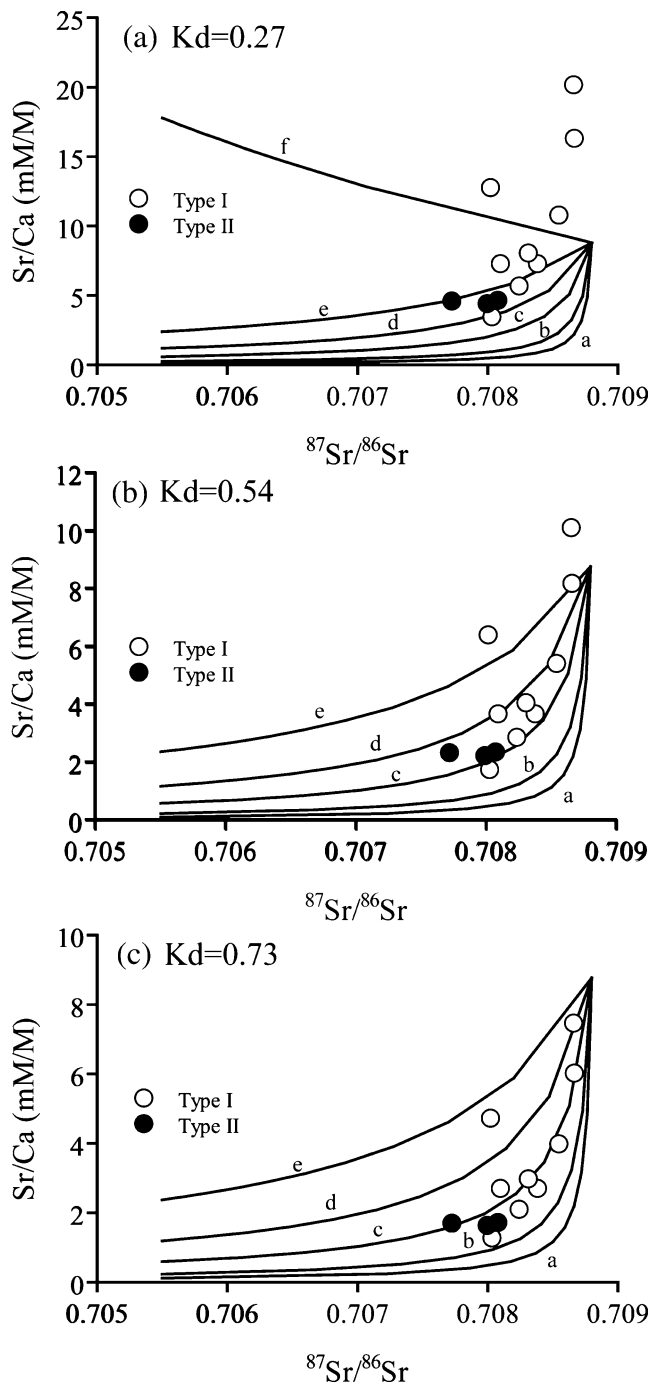


Fig. 5 One example of the estimation of anhydrite formation condition from the calculation based on Sr content and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of mixture of seawater and hydrothermal solution. The assumption for the calculations is that Ca concentration is the value for the end-member one with $\text{Mg}=0$, which is obtained from fluid inclusion data of Pisutha-Armond and Ohmoto (1983). A wide range of possible Sr concentrations of the Kuroko hydrothermal solution is assumed [1/10 (line a), 1/5 (b), 1/2 (c), 1 (d), 2 (e), and 5 (f) times higher than that of seawater]. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Kuroko hydrothermal solution is assumed to be 0.7055. Sr partitioning coefficient for anhydrite (K_d) is assumed to be a 0.27, b 0.54, and c 0.73 as obtained by Shikazono et al. (1983) and Berndt et al. (1988), and Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of parent solution estimated from analytical data and K_d are also plotted

and upper limits of Sr contents of anhydrite formed by the mixing of seawater and hydrothermal solution can be estimated; the relationships between estimated Sr contents and $^{87}\text{Sr}/^{86}\text{Sr}$ of anhydrite are shown in Fig. 7. The Sr contents and $^{87}\text{Sr}/^{86}\text{Sr}$ of anhydrite analyzed are also plotted; almost all samples plot around calculated lines.

The estimated Sr/Ca (mM/M) ratio of the Kuroko hydrothermal solution is ca. 0.59 to 1.36, whereas that of seawater is ca. 8.7. Thus, the Sr/Ca ratio of the parent solution for anhydrite increases with increasing seawater/hydrothermal solution ratio, as related by the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Although K_d affects the Sr content of anhydrite formed, the Sr content is mainly controlled by the Sr/Ca ratio of the parent solution (Fig. 7). Mills and Tivey (1999) predicted that the hydrothermal solution would evolve to a solution with higher Sr/Ca ratio under TAG seafloor due to anhydrite precipitation under a condition with K_d less than 1. This result also indicates that fluid evolution did not occur during the Kuroko hydrothermal

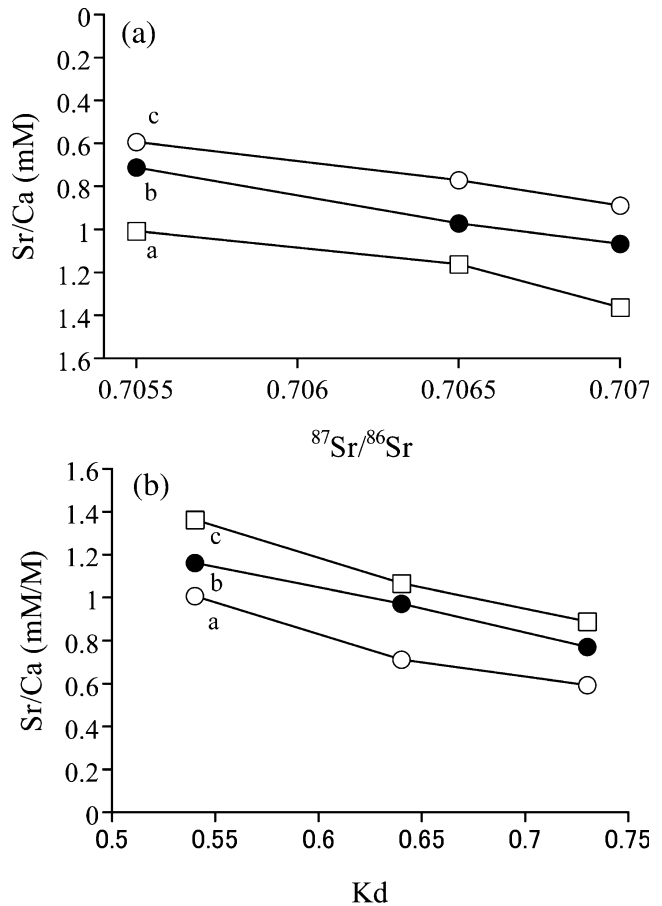


Fig. 6 The possible relationship a between K_d and Sr/Ca ratio of Kuroko hydrothermal solution and b between $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of hydrothermal solution and Sr/Ca ratio of Kuroko hydrothermal solution estimated from Fig. 5. a Line a, $K_d=0.73$, (b) 0.63, (c) 0.54; (b) line (a) $^{87}\text{Sr}/^{86}\text{Sr}=0.7055$, (b) 0.7065, (c) 0.7070

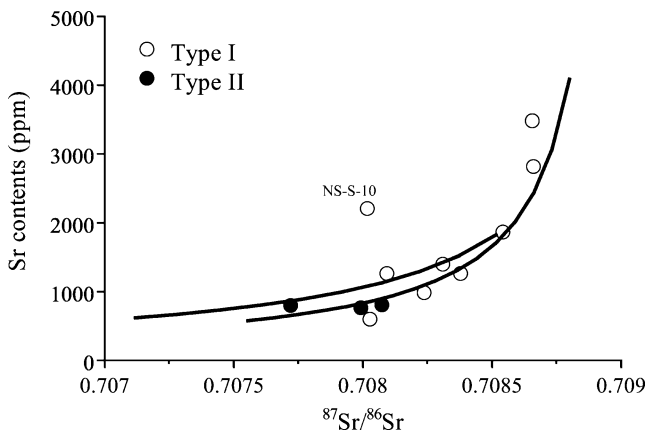


Fig. 7 The possible relationship between Sr content and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of Kuroko anhydrite. Two lines mean the estimation of possible upper and lower limits of Sr content of anhydrite formed by seawater and hydrothermal solution on the basis of Fig. 6

activity. However, the data on sample NS-S-10 deviate from the calculated mixing lines (Fig. 7), and high Sr content of this sample means the possibility that partial fluid evolution occurred. Considering the high Ba content of this sample (Table 2), another possibility is that this sample is not pure, although only anhydrite was detected by XRD.

The saturation indexes (SI) of anhydrite are calculated from the fluid inclusion data obtained by Pisutha-Arnond and Ohmoto (1983) by using GEOMS, which is a revised version of SUPCRT 92 by Ogata and Uchida (2004). For confirming the temperature sensitivity of anhydrite, it is assumed that seawater is heated at 100, 200, and 250°C or unheated (2°C) before the mixing with the hydrothermal solution (330°C). If heated seawater was not involved, some of type I anhydrite would not precipitate because the mixed solution was not saturated (Fig. 8). Thus, it is possible that seawater was heated before the mixing with the hydrothermal solution similar to the TAG hydrothermal system (Teagle et al. 1998a,b). If seawater is heated at 100°C, anhydrite is supersaturated for the possible mixing range. The temperature of formation of Kuroko anhydrite was estimated to be ca. 240–340°C, and the saturation temperature range of three Matsumine samples is ca. 250–300°C (Shikazono et al. 1983). If all samples analyzed in this study were formed in this temperature range, seawater is then inferred to be heated to at least 100°C before the mixing (Fig. 8).

Variation of REE patterns of the anhydrite from Kuroko, TAG, and Pacmanus

There are no correlations evident between Sr and La, and Sm and ΣREE contents (Fig. 9), indicating that REE partitioning into anhydrite is different from Sr. Furthermore,

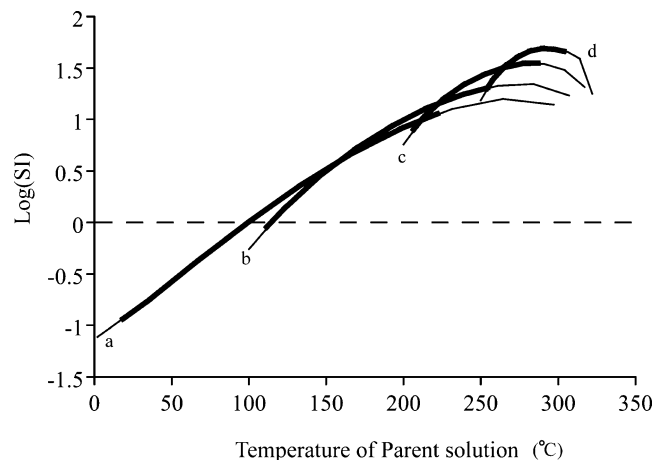


Fig. 8 The relationship between temperature and saturation indexes (SI) for anhydrite of parent solution. The calculation of SI is performed for a seawater was at 2°C as well as at higher temperature b 100, c 200, and d 250°C due to conductive heating. Bold lines represent the possible seawater/hydrothermal solution mixing range

considering the values of $\text{La}_\text{N}/\text{Sm}_\text{N}$ and Eu/Eu^* (ppm/ppm) of hydrothermal solution (1.98 and 28.1, respectively) (e.g., TAG hydrothermal solution: Douville et al. 1999) and seawater (2.59 and 2.00, respectively) (Mitra et al. 1994), both $\text{La}_\text{N}/\text{Sm}_\text{N}$ with less than 1 of $\text{La}_\text{N}/\text{Sm}_\text{N}$ and negative Eu/Eu^* of type II anhydrite are not inherited from the parent solution.

REE partitioning into anhydrite is considered to be crystallographically controlled (Mills and Elderfield 1995). If anhydrite precipitates slowly, more perfect crystals should be formed. Ideally, crystal should have few foreign ions whose ionic radii are dissimilar to principal cation lattice (Ca^{2+}). Indeed, Koeppenkastrup and De Carlo (1992) suggested from experimental results that medium REE (MREE) preferential incorporation in hydroxyapatite may be due to the crystal lattice substitution for Ca^{2+} .

REE–anion complexing (Bach et al. 2003; Humphris and Bach 2005) is also considered to play a significant role on partitioning behavior into anhydrite. Bach et al. (2003) suggest that REE behaviors during TAG anhydrite formation are controlled by only Cl^- and OH^- complexation, resulting in uniform REE patterns. It is considered that the wide variety of REE patterns of Pacmanus anhydrite is due to complexation by magmatic volatiles (HF and SO_2). It has been shown experimentally that the incorporation of ions during nonrapid precipitation is controlled by thermodynamic factors such as the tetrad effect (Kagi et al. 1993). On the other hand, it has also been reported that rapidly precipitating anhydrite incorporates many different ions nonselectively (Kagi et al. 1993). The nonselective incorporation of REEs could inherit the REE signature of the Kuroko hydrothermal solution because REE concentration of Kuroko hydrothermal solution is considered to be much

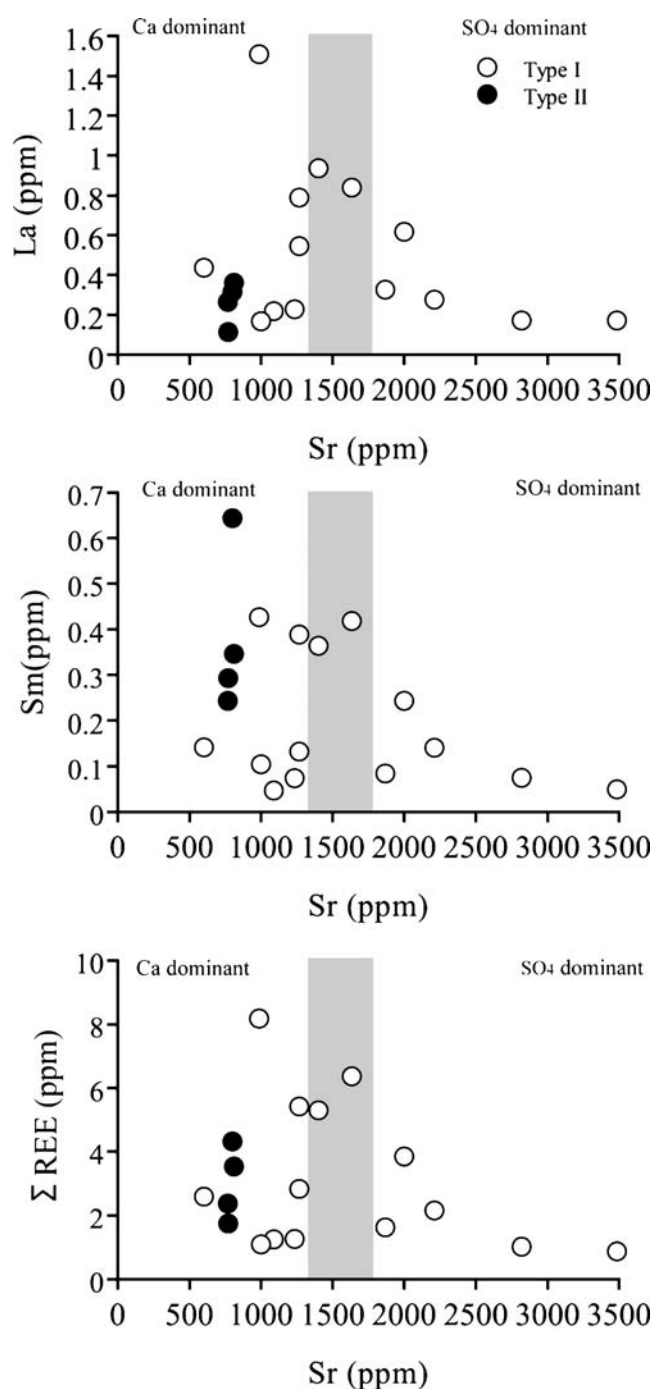


Fig. 9 Relationship between Sr and **a** La, **b** Sm, and **c** ΣREE (ppm) contents of anhydrite. Gray zone means the nearly Ca²⁺-SO₄²⁻ equimolar condition

higher than that of seawater, considering the recent hydrothermal solution (cf. Douville et al. 1999). Thus, anhydrite precipitation rate is considered to play an important role for REE discrimination.

Nancollas and Gill (1979) reported that the SO₄/Ca ratio affects the precipitation rate of calcium sulfate hemihydrate (CaSO₄·0.5H₂O), and the rate of anhydrite precipitation is

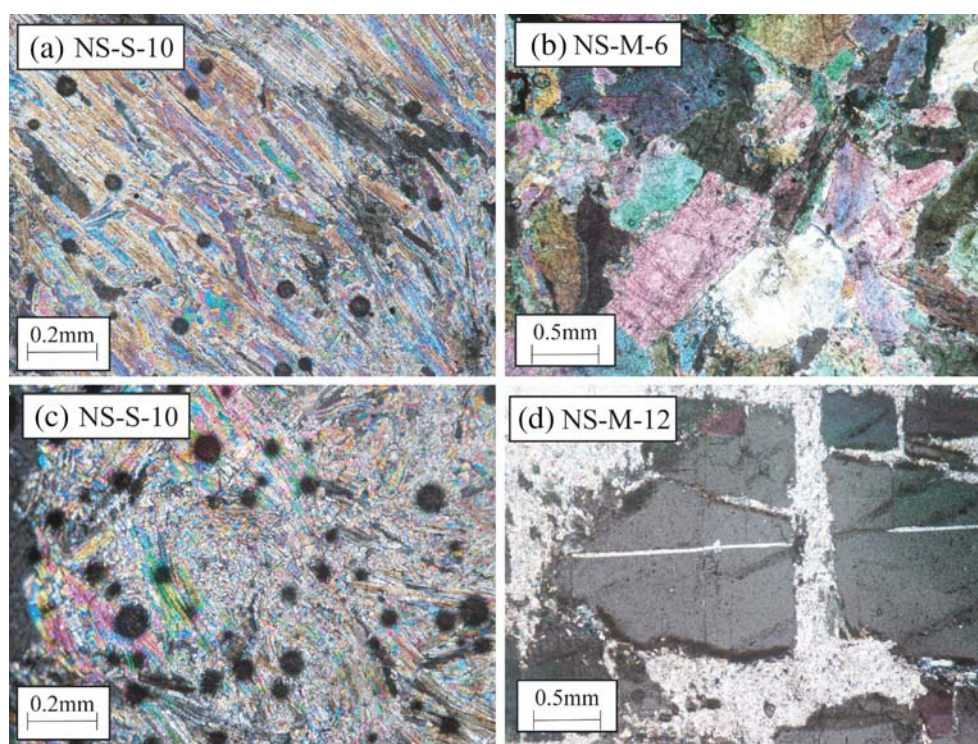
also considered to be affected. On two lines in Fig. 7, representing a seawater/hydrothermal solution mixture of approximately 81/19, the SO₄/Ca ratio is 1 based on the assumption that SO₄ concentration of the Kuroko hydrothermal solution is almost 0. The estimated Sr content of the anhydrite precipitating under such conditions is 1,340 to 1,775 ppm based on K_d values of 0.54 and 0.73. It is roughly estimated that anhydrite whose Sr content is lower than those values precipitated under the Ca-dominant conditions, whereas anhydrite whose Sr content is higher than those values precipitated under SO₄-dominant conditions. This information is added to Fig. 9.

As mentioned above, SO₄/Ca ratio of parent solution is considered to affect the anhydrite precipitation rate. Considering that type I anhydrite precipitated under a wider range of SO₄/Ca compositions, incorporation of REE was not caused by kinetic effects. It seems likely that REE is preferentially concentrated in anhydrite, which is considered to have formed under near SO₄/Ca equimolar conditions, except for type II (Fig. 9). However, anhydrite with low REE contents also exists in this region.

The precipitation rate may also affect crystal size and morphology. Type I anhydrite (NS-S-7), which is considered to be formed from near equimolar concentration, are typically acicular and fine rectangular crystals (e.g., Fig. 10a), indicating fast precipitation. Although NS-M-6 (Sr: 2,000 ppm) and NS-S-10 (2,210 ppm) are considered to be type I anhydrites formed under SO₄²⁻-dominant condition, the former has large rectangular crystals with relatively high REE contents (Fig. 10b), whereas the latter has acicular crystals with relatively low REE contents (Fig. 10c). Therefore, it seems that SO₄/Ca ratio is not correlated with crystal size, morphology, precipitation rate, and REE contents and that crystallographic discrimination of REE did not occur.

MREE enrichment in anhydrites from Pacmanus is interpreted to reflect the abundance of free REE ions (Bach et al. 2003). However, MREE enrichment in type II anhydrites would not have been caused by the complexation process because the REE pattern of many Kuroko anhydrites are uniform (type I) similar to TAG examples. Furthermore, barite from the Kuroko deposit exhibits uniformly type I-like patterns (Shikazono 1999). Variation in REE pattern of Pacmanus anhydrites is considered to be caused by the several types of complexes because of HF and SO₂ components in magmatic volatiles. Although the magnitude of HF input from magma to the submarine hydrothermal system during Kuroko mineralization is unclear, significant SO₂ input is not considered to be important because the δ³⁴S of anhydrite is almost identical to the seawater value (e.g., Sakai et al. 1970) similar to TAG anhydrite (e.g., Chiba et al. 1998). Thus, it seems likely that geochemical situation of REE mobility accom-

Fig. 10 Photomicrograph showing the texture of anhydrite. **a** NS-S-7 (from Shakanai, type I). **b** NS-M-6 (from Matsumine, type I). **c** NS-S-10 (from Shakanai, type I). **d** NS-M-12 (from Matsumine, type II)



panied by the Kuroko anhydrite formation is similar to that during the TAG anhydrite formation rather than that accompanied by the Pacmanus anhydrite formation. Under OH⁻ and Cl-REE complexing conditions similar to TAG, temperature significantly affects the REE fractionation, and REE complexation behaviors during the different mixing scenarios, namely, mixing of hydrothermal solution and cold seawater or conductively heated seawater, cause the variation of REE pattern of TAG anhydrite (Humphris and Bach 2005). As mentioned above, Kuroko anhydrite is inferred to have formed by the mixing of hydrothermal solution and preheated seawater. If REE partitioning into Kuroko anhydrite was also controlled by complexing, primary discrimination of REE (anhydrite formation stage) would not occur.

Type I anhydrite is primary and prevailing Kuroko anhydrite for the following reasons: (1) the type I anhydrite are formed under wider SO₄/Ca conditions, namely, wider seawater/hydrothermal solution mixing ratios (Fig. 8), (2) type I anhydrite is more abundant than the type II one, and (3) the chondrite-normalized REE pattern of Kuroko type I anhydrite is similar to TAG anhydrite and Kuroko barite.

Small crystals (type II) are found enveloping large ones, and these very small crystals are considered to have formed by recrystallization after or during primary anhydrite precipitation (e.g., Fig. 10d). Thus, the secondary processes resulting in dissolution and recrystallization of anhydrite (type II) affect the redistribution of REE.

Elemental mobility during transformation of anhydrite to gypsum: implications for type II anhydrite formation

Gypsum in the Kuroko deposits is considered to be a secondary mineral that was formed by hydration of anhydrite after the Kuroko mineralization (Matsubaya and Sakai 1973). Thus, the elemental mobilities during the transformation of anhydrite to gypsum were also examined. Anhydrite and gypsum coexist in nodules of M-2 and M-21, and these gypsum occurrences are thought to represent transformed anhydrite.

The chondrite-normalized REE patterns of M-2 G.Y. and M-21 G (gypsum) are similar to those of pristine anhydrite (M-2 A and M-21 A) (Fig. 4). On the other hand, the REE pattern of M-2 G.W. (La_N/Sm_N: 2.11) is flatter than those of pristine anhydrite, M-2 A (La_N/Sm_N: 2.75). Therefore, the LREE is likely to become mobile during the transformation of anhydrite (M-2 A) to gypsum (M-2 G.W.).

Gypsum samples G-1 and G-2 are more depleted in LREEs than M-2 G.W. (Fig. 4). The pristine anhydrite from which these gypsum samples formed would likely have a type I REE pattern because type I is considered to be the prevailing primary pattern. Atacamite-bearing minerals with LREE depletion from the TAG field, representing a secondary mineralization, are considered to be formed by recrystallization (Mills and Elderfield 1995). It has been reported that LREEs in these minerals may be released during dissolution and recrystallization controlled by chloro-REE complex formation under acidic Cl-rich conditions (Mills and Elderfield 1995).

LREE mobilities during gypsum formation indicate that secondary processes such as post-ore recrystallization may possibly cause changes in REE pattern similar to TAG atacamite-bearing minerals. It is possible that the phase change from anhydrite (M-2 A) to gypsum (M-2 G.W.) is caused by a Cl-bearing acidic aqueous solution. On the other hand, the phase change from anhydrite (M-2 A and M-21 A) to gypsum (M-2 G.Y. and M-21 G) could be caused by a low Cl solution, such as meteoric water, based on the changes in the LREE abundance observed.

The G-3 and G-4 samples are composed of well-crystallized gypsum, which contain only minor amounts of Sr, Ba, and REEs. It is therefore possible that these elements are controlled mainly by the crystallographic factors during gypsum formation. This is another possible explanation for the depleted LREE character of the M-2 G.W., G-1, and G-2 gypsum samples. On the other hand, G-3 has La_N/Sm_N lower than 1 similar to type II anhydrite and some gypsum samples (G-1 and G-2), whereas G-4 has La_N/Sm_N higher than 1. Thus, the crystallographic effect would not be related with MREE enrichment, although very

low REE contents of these samples make quantitative discussion difficult.

The two possible explanations for the different REE patterns of gypsum could also be applied to the different REE patterns observed in anhydrite, although it is unclear if incorporation of REE is mainly controlled by crystallographic factors or complexing. If REE mobility is controlled by complexization, the type II anhydrite forms as follows. According to the REE speciation distribution calculation (Humphris and Bach 2005), the Cl complex represents as considerable proportion in the TAG hydrothermal solution, which is sensitive to mixing of seawater, resulting in a decrease of Cl complex with increasing seawater proportion. Anhydrite precipitation under seafloor affects the subsurface porosity (Sleep 1991). If entrainment of seawater was inhibited due to anhydrite precipitation, anhydrite dissolution and recrystallization would occur in situ within the hydrothermal solution, where REE–Cl complexing is dominant. Because of the greater stability of LREE–Cl complexes than HREE–Cl complexes, preferential LREE dissolution from anhydrite should occur

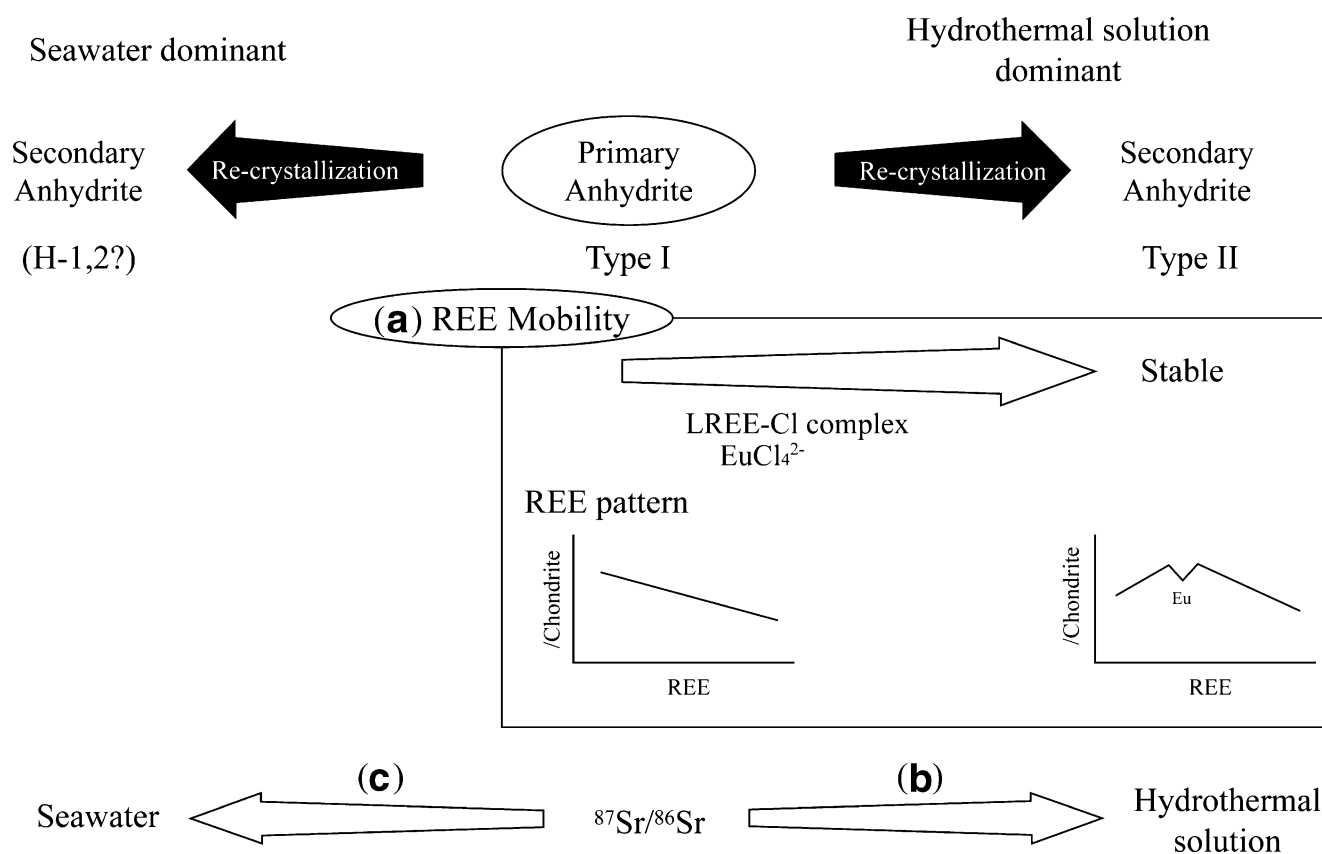


Fig. 11 Possible changes of REE pattern and $^{87}\text{Sr}/^{86}\text{Sr}$ during dissolution and recrystallization of primary anhydrite. **a** Under the hydrothermal solution dominant condition, REE–Cl complexing is dominant. Because of the greater stability of EuCl_4^{2-} complex and LREE–Cl complexes than HREE–Cl complexes, preferential LREE and Eu^{2+} dissolutions from anhydrite should occur, resulting in a negative Eu anomaly like

type II. **b** Under the hydrothermal solution dominant condition, Sr exchange reaction would change the $^{87}\text{Sr}/^{86}\text{Sr}$ of anhydrite to evolve closer to that of hydrothermal solution. **c** Under the seawater dominant condition, Sr exchange reaction would change the $^{87}\text{Sr}/^{86}\text{Sr}$ of anhydrite to evolve closer to that of seawater

(Fig. 11). Under such conditions, almost all Eu is presented as EuCl_4^{2-} complex (Humphris and Bach 2005), and Eu dissolution from anhydrite would occur selectively, resulting in a negative Eu anomaly like type II (Fig. 11). If so, Sr exchange reaction would change the $^{87}\text{Sr}/^{86}\text{Sr}$ of anhydrite to evolve closer to that of hydrothermal solution (Fig. 11). If, in the contrary, anhydrite precipitation prevents the infiltration of the ascending hydrothermal solution, the $^{87}\text{Sr}/^{86}\text{Sr}$ of anhydrite would shift closer to that of seawater (e.g., H-1 and H-2) (Fig. 11).

The precipitation of anhydrite in the TAG mound is considered to affect the REE pattern of the venting hydrothermal solution (Mills and Elderfield 1995). If secondary process, such as dissolution and recrystallization occurred during the hydrothermal activity responsible for the Kuroko mineralization, it is possible that LREE-enriched anhydrite (i.e., type I) may preferentially release LREEs (rather than MREEs and HREEs) during dissolution, potentially resulting in the formation of type II anhydrite by recrystallization. In this case, a substantial change in the REE pattern of the Kuroko hydrothermal solution may have occurred.

Conclusions

Anhydrite in the Kuroko sulfide–sulfate deposits exhibits two different chondrite-normalized REE patterns: one with a decrease from LREEs to HREEs (type I), and another with a relatively LREE-depleted pattern with a peak in Sm (type II). The REE patterns and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Kuroko anhydrite exhibit many similarities with those of the TAG subseafloor anhydrite, suggesting that they have formed by the same process, that is, the subseafloor mixing of heated seawater and hydrothermal solution.

It was estimated from the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and Sr content of anhydrite that anhydrite saturation occurred by the mixing of the Kuroko hydrothermal solution with Sr/Ca (mM/M) ratio of ca. 0.59–1.36 and seawater with Sr/Ca ratio of 8.7 at K_d =ca. 0.5–0.7 conditions. Therefore, anhydrite with higher Sr content is considered to have formed under seawater-dominated fluid mixing conditions.

It is inferred that precipitation rates of anhydrite, which are related to crystal size and morphology, are not important factors for the incorporation of certain trace elements into precipitating crystals. Large crystals of type II anhydrite are partially replaced by the very small ones, indicating that the anhydrite dissolution and recrystallization occurred. Thus, it is possible that LREE in type I anhydrite was leached during secondary processes, resulting to type II formation. Indeed, gypsum, which is a secondary replacement of anhydrite also, has LREE-depleted patterns, indicating the possibility of LREE mobilization during the secondary reactions.

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