

Reexamination of kimuraite: the occurrence of lanthanite in the cleavages of kimuraite

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ABSTRACT

We have measured the Ca and REE compositions of seven kimuraite samples, which are subsamples taken from a spherulitic aggregate kimuraite sample filling a void in the alkali olivine basalt. In the chondrite-normalized REE patterns, all samples yielded parallel concave tetrad patterns, and the mole ratios of $\Sigma(\text{REE}+\text{Y})$ to Ca were calculated to be 2.5 to 3.4, all of which were obviously larger than the ideal value 2.0 of kimuraite. In addition, electron-probe microanalyzer (EPMA) was also applied to determine the compositions of our samples. Though only four rare earth elements (Y, La, Pr and Nd) were able to be measured, the mole ratios of $\Sigma(\text{REE}+\text{Y})$ to Ca of thirty-two point analyses determined with EPMA were 2.1 to 3.3. Both analytical results demonstrated that our kimuraite samples might have excessive amount of REE. In the backscattered electron (BSE) images, besides dark kimuraite grains, the presence of another mineral with brighter BSE intensity along the cleavages of kimuraite grains was confirmed, and almost all analysis spots of EPMA failed to escape from the contamination of this mineral. The most possible candidate for this mineral is lanthanite, both for its close association with kimuraite and for its characteristic chemical composition. The compositions of our kimuraite samples, especially LREE, have been modified due to the presence of a small portion of lanthanite, but the concave tetrad pattern remains, as lanthanite seems to have a similar concave tetrad pattern like kimuraite.

Keywords. rare earth elements, kimuraite, lanthanite, tetrad effect

INTRODUCTION

A new rare earth element (REE) carbonate mineral, referred to as kimuraite $[\text{Ca}(\text{Y},\text{REE})_2(\text{CO}_3)_4 \cdot 6\text{H}_2\text{O}]$, was found in Hizen-Cho, Saga Prefecture, southwest Japan (Nagashima *et al.*, 1986). This mineral occurs as a fissure-filling mineral in the host alkali olivine basalt, and is featured in its considerably high abundances of rare earth elements, especially yttrium. In the pioneer work on kimuraite, Nagashima *et al.* (1986) also studied other two REE carbonate minerals, lanthanite $[(\text{La}, \text{Nd})_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}]$ and lokkaite $[\text{Ca}(\text{Y},\text{REE})_4(\text{CO}_3)_7 \cdot 9\text{H}_2\text{O}]$, which were considered as coeval minerals with kimuraite. In order to account for the high REE abundance in kimuraite, the formation of kimuraite inevitably requires a unique precursor fluid that is highly concentrated in REE. Though Nagashima *et al.* (1986) suggested kimuraite might be a dehydration

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product of lokkaite, they failed to provide further discussions about the source of REE.

Lately, Akagi *et al.* (1993) investigated the REE compositions of three kimuraite samples with ID-MS and ICP-MS, including (1) middle layer kimuraite A, (2) inner layer kimuraite A and (3) kimuraite B, and came out with an interesting result that the chondrite-normalized REE patterns of all three kimuraite samples appeared to show similar tetrad effects with four concave curves. In their subsequent study, Akagi *et al.* (1996) argued that kimuraite should not be simply a dehydration product of lokkaite because the mass balance for the reaction was not fully met, and instead, they developed a new model to illustrate the origin of kimuraite and its tetrad effect. According to their model, the tetrad effect should be probably inherited from the REE-rich aqueous fluid when kimuraite was precipitated from this fluid.

Given that three samples studied by Akagi *et al.* (1993) are the same kimuraite mineral, it is confusing that the REE composition of the inner kimuraite is apparently much different from other two kimuraite samples. Furthermore, Y and Ca, which are major elements in kimuraite, were not determined in their study. In recent studies (Miyawaki *et al.*, 2000 and 2003), two other REE minerals, namely kozoite-(La) and kozoite-(Nd), were reported from the same location where kimuraite was collected. These minerals were concurrently formed from the same fluid with kimuraite, but it is difficult to discuss whether or not they show a tetrad effect like kimuraite by the REE data reported by Miyawaki *et al.* (2000 and 2003).

The study on kimuraite and its tetrad effect is still far from sufficient. Thus, we would like to continue the study of kimuraite. In this work, we examined the chemical composition of kimuraite with ICP-AES and ICP-MS. Meanwhile, electron probe microanalyzer was also deployed to measure the compositions of kimuraite samples on polished sections. Combining the analytical results with the backscattered electron images of kimuraite samples, we came to a conclusion that another mineral, most likely lanthanite, is present in the cleavages of kimuraite.

ANALYTICAL METHODS

In our study, we took seven subsamples from a spherulitic aggregate of kimuraite of 3cm in length and 3cm in width, which was collected from Hizen Cho, Higashi Matsuura Gun, Saga Prefecture, Japan, and each subsample was about 10 mg. According to Nagashima *et al.* (1986), kimuraite seems to lose its absorbed water thoroughly at a temperature around 55°C. Therefore, we planned to determine the content of absorbed water by heating the kimuraite sample in an oven. However, it is nearly impossible to weigh the dried kimuraite sample accurately, as the sample will start to absorb water rapidly from the air. Eventually, we gave up the determination of water. In the next step, all samples were heated at 800°C for two hours, and the residues were dissolved with HCl. Since the abundances of Y and Ca are high enough in kimuraite, these two elements were measured with ICP-AES. Then, the REE abundances of our kimuraite samples were determined with ICP-MS.

The remaining kimuraite aggregate was prepared as a conventional polished section for the analysis with JEOL JCSA-733 electron-probe microanalyzer at Center for Chronological Research, Nagoya University. The analytical conditions are as follows:

The accelerating voltage was 15 kV, the probe current was 25nA, and the probe diameter was 10 μ m with a counting time of 25s. Since kimuraite is rich in volatile components, it was hard to keep the analysis at a high-level precision, and only five elements (Ca, Y, La, Pr and Nd) were able to be measured precisely. In this study, the method explored by Bence and Albee (1968) was adopted for matrix correction, using the α -factor table introduced by Kato (2005) with modification for Pr L β emission.

RESULTS

The analytical results by ICP-MS and ICP-AES are summarized in Table 1. Our kimuraite samples have exceedingly high abundances of REE and Y, which is a typical character of kimuraite. As the contents of water in kimuraite samples were not determined in our study, we cannot obtain the chemical formula of kimuraite, but we can still gain important information from the mole ratio of $\Sigma(\text{REE}+\text{Y})$ to Ca, which ranges from 2.5 to 3.4. Since the recommended mole ratio for kimuraite proposed

Table 1. The chemical compositions of seven kimuraite samples, REE were determined by ICP-MS, while Ca and Y were determined by ICP-AES. The mole ratios of (Y+REE) to Ca are also summarized in this table.

(ppm)	K-1	K-2	K-3	K-4	K-5	K-6	K-7
La	16900	12200	12600	7460	6370	13900	20600
Ce	113	90.8	41.9	18.8	72.7	34.9	17.3
Pr	4430	3920	4170	3380	2910	4720	5360
Nd	29100	28300	27500	24000	19100	31100	33200
Sm	10500	9330	8780	8660	8590	12100	12100
Eu	5130	5800	4140	4420	4160	5820	5730
Gd	28900	31000	25000	26900	20200	33500	32600
Tb	3860	4120	4100	4420	3120	4550	4470
Dy	22600	26500	23300	24800	21600	26400	25100
Ho	5160	5330	5750	6350	5230	5400	5360
Er	11800	12800	12900	14200	18300	12900	12600
Tm	774	810	1110	1240	1020	787	769
Yb	1600	1640	2760	3190	2600	1680	1650
Lu	164	170	319	376	246	170	160
Y	229000	264000	198000	211000	302000	231000	227000
Ca	45100	50400	41900	45500	66200	43700	42300
$\Sigma(\text{Y}+\text{REE})/\text{Ca}$	3.4	3.4	2.8	3.0	2.5	3.3	3.4

by Nagashima *et al.* (1986) is 2.0, it seems incredible that all the mole ratios of our kimuraite samples are much greater than the recommended one. In Fig.1, all REE carbonate minerals found from Hizen Cho have been plotted on the volatile-free basis. The linear trend of our samples implies that they are not pure kimuraite, and have received contributions from lokkaite and/or lanthanite, but neither kozoite-(La) nor kozoite-(Nd).

In Fig. 2, the chondrite-normalized REE patterns of our kimuraite samples are plotted together with those reported by Nagashima *et al.* (1986) and Akagi *et al.* (1993). The extremely negative Ce anomaly is remarkable. Ce is very sensitive to the redox condition, and can be simply separated from the other REE. Akagi *et al.* (1993) attributed such an anomaly in kimuraite to the segregation of Ce^{4+} in aqueous fluid. When compared to the former studies, the abundances of LREE in our samples are much higher, while the HREE show a slight decrease (Fig. 3). The inner layer kimuraite A has a quite analogous REE distribution pattern to our kimuraite samples, especially K-3 and K-5. In the meantime, both the middle layer kimuraite A and kimuraite B reported by Akagi *et al.* (1993) show slight enrichments in middle REE relative to other kimuraite samples. This agrees with the suggestion made by Kawabe *et al.* (2012) that the inner layer kimuraite A is enriched in La, Pr and Nd relative to the middle layer kimuraite A. In spite of these differences, all kimuraite samples exhibit similar concave tetrad effects.

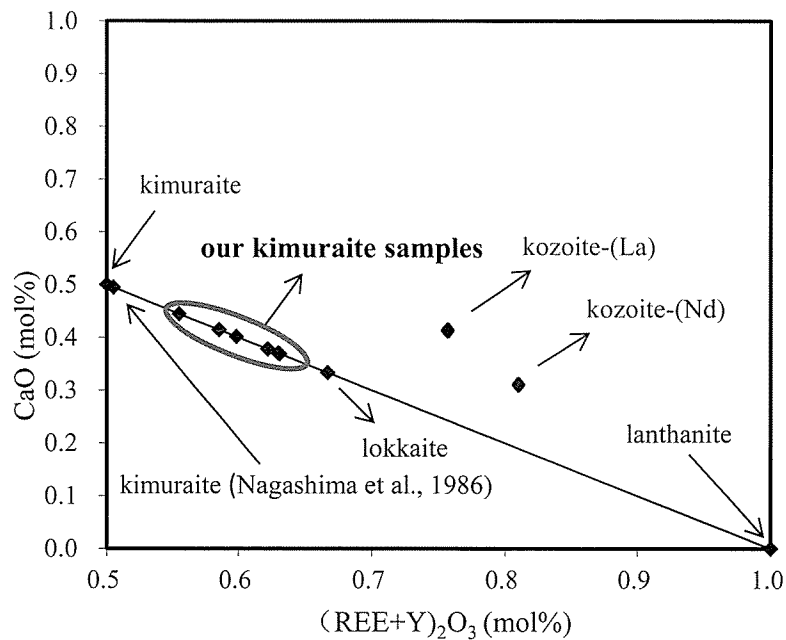


Fig. 1. The CaO mole percentages of kimuraite and lanthanite are plotted against their $(REE+Y)_2O_3$ mole percentages, on condition that the volatile components are not taken into consideration.

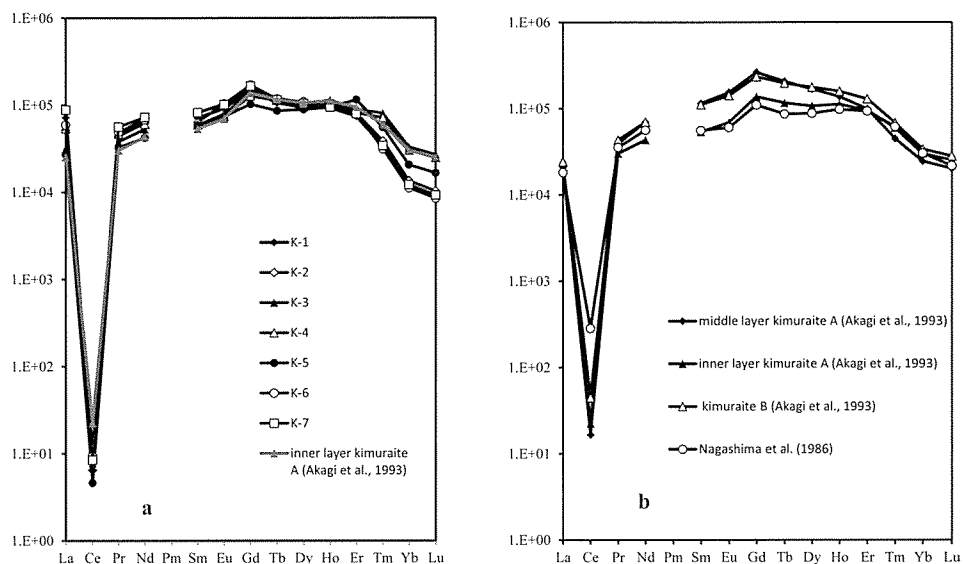


Fig. 2. Chondrite-normalized REE patterns of the kimuraite samples from Hizen Cho. The chondritic values reported by Anders and Grevesse (1989) were used for normalization. a: our kimuraite subsamples and the inner layer kimuraite A from Akagi *et al.* (1993); b: kimuraite samples reported by Nagashima *et al.* (1986) and Akagi *et al.* (1993).

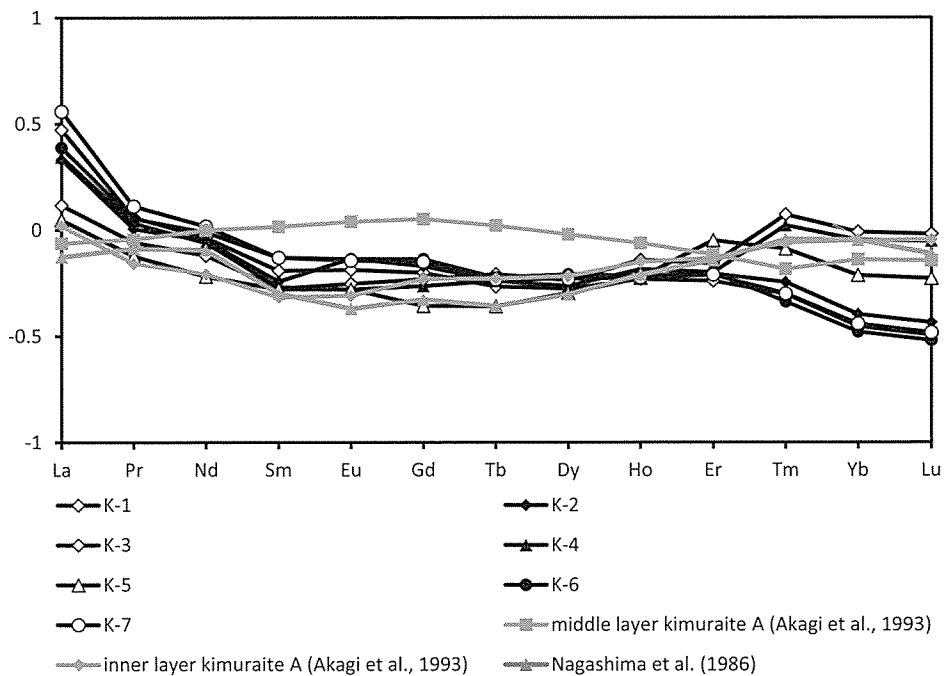


Fig. 3. Kimuraite B from Akagi *et al.* (1993) is taken as a reference sample, and the REE abundances of other kimuraite samples are normalized to this reference in the logarithmic scale. Due to the negative anomaly, Ce is not contained in this plot, as well as Pm.

As the compositions obtained with ICP-MS and AES were much different from that determined by Nagashima *et al.* (1986), we re-examined the kimuraite samples with EPMA. Thirty-two spots were analyzed with EPMA, and the analytical results are displayed in Fig. 4. The content of CaO ranges from 7.0% to 11.6%, and the total amount of other four elements vary from 42.9% to 57.3%. The mole ratios of $\Sigma(\text{Y, La, Pr, Nd})$ to Ca vary from 2.1 to 3.3, all of which are again greater than that proposed ratio. Since only four rare earth elements are determined with EPMA, it is rational to consider that these ratios are consistent with the results obtained by ICP-MS.

In Fig. 5, we show the backscattered electron images of our kimuraite samples. The dark parts are kimuraite grains, since kimuraite is a mineral enriched in Ca and Y, both of which have relatively smaller atomic numbers. When kimuraite is to crystallize, a perfect cleavage will occur along the $\{0\ 1\ 0\}$ crystal plane (Nagashima *et al.*, 1986), and this cleavage can be well discerned in the BSE images. Besides dark kimuraite grains, it is really surprising to find that there is another mineral with bright BSE intensity occurring in the cleavage of kimuraite. The strong brightness in BSE images is a sign that this mineral holds a different chemical composition from kimuraite, probably concentrated in elements of larger atomic numbers. Meanwhile, it seems almost all EPMA analysis spots failed to escape from the contamination of this mineral. In other words, both ICP-MS and EPMA analyses have measured the composition of a mixture that is composed of kimuraite and a small portion of another mineral, and this must be the reason why there was a disagreement on the chemical compositions of kimuraite samples (Fig. 1). In fact, this is for the first time to recognize the existence of another mineral in kimuraite.

DISCUSSION

As for seven kimuraite subsamples in our study, the mole ratios of (REE+Y) against Ca determined with ICP-MS and ICP-AES varied from 2.4 to 3.4, and all these values were much greater than the recommended value of 2.0, indicating our kimuraite samples must be different from the one reported by Nagashima *et al.* (1986). In the BSE images, the presence of another mineral in the cleavage was confirmed for the first time, demonstrating that our kimuraite samples were mixtures of two different minerals rather than pure kimuraite. Due to the presence of this mineral, the compositions of our kimuraite samples were fairly altered, which could be reflected from the mole ratios of REE to Ca. Furthermore, the linear trend in Fig. 1 indicated that this mineral might be lokkaite or lanthanite, both of which have been suggested to have close relationships with kimuraite. However, this mineral is too small for us to directly locate the analysis spot on it, so it is nearly impossible to specifically know its composition.

Like kimuraite, lokkaite is also a carbonate mineral that enriches in Y-group rare earths, and contains a large amount of Ca (Table 2). But there is still a notable difference that lokkaite has much less lanthanum than kimuraite does. If a small amount of lokkaite is mixed with kimuraite, there supposed to be a remarkable reduction in the lanthanum abundance when this mixture is compared with the pure kimuraite. However, this is not in accordance with our result, as the average lanthanum abun-

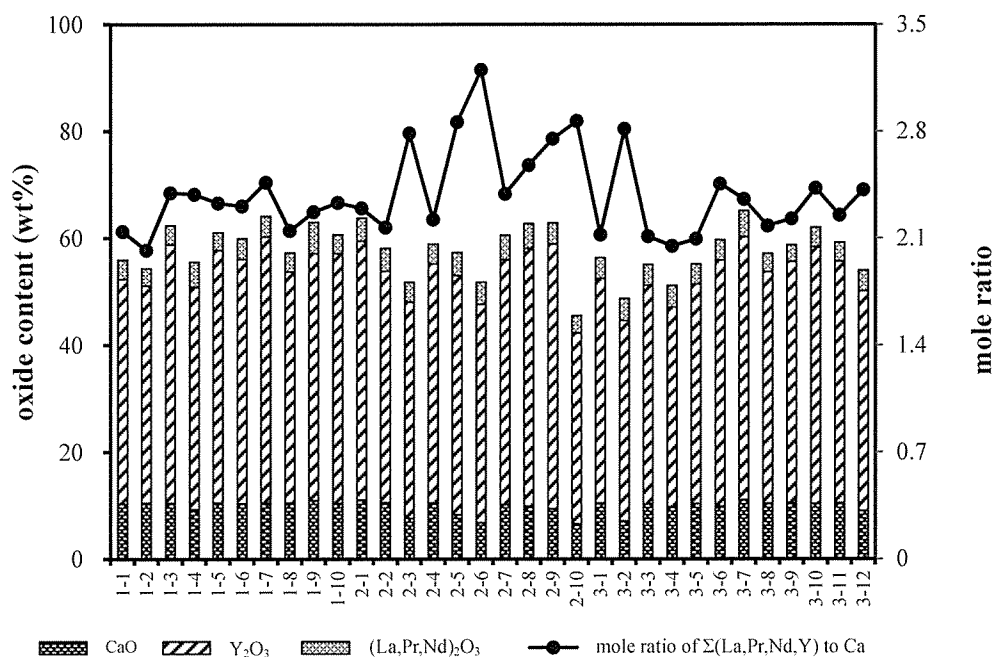


Fig. 4. The oxide contents (wt%) of five elements for thirty-two analytical spot by EPMA. The other REEs and the volatile parts, including CO₂ and H₂O, were not able to be determined in our study.

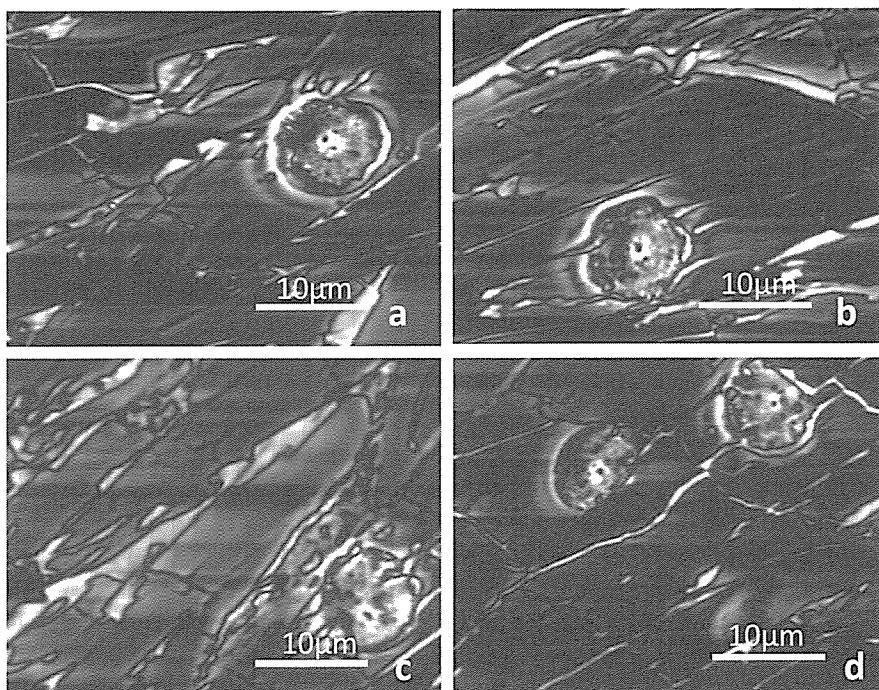


Fig. 5. BSE Images of our kimuraite samples. Circles are the analysis spots.

Table 2. Chemical compositions of REE carbonate minerals from the southwest Japan.

(ppm)	Akagi et al., (1993)			Nagashima et al., (1986)		
	middle layer kimuraite A	inner layer kimuraite A	kimuraite B	kimuraite	lokkaite	lanthanite
La	4940	5970	5700	4260	2810	134000
Ce	10	13.6	27	171	3670	9480
Pr	3490	2690	3860	3160	5210	44300
Nd	31600	19600	31600	25500	61100	201000
Sm	16900	7860	16300	8190	33100	31800
Eu	8650	3880	7900	3370	14900	6910
Gd	51700	27000	45900	21600	64800	15100
Tb	7480	4210	7130	3130	10600	869
Dy	40700	25900	42800	21300	52500	2960
Ho	7630	6220	8800	5410	9780	175
Er	15700	15100	20600	14800	20600	262
Tm	1080	1440	1650	1490	2450	0
Yb	3970	4880	5500	4920	7030	0
Lu	489	614	683	528	879	0
Y	-	-	-	232000	163000	3780
Ca	-	-	-	65900	37500	-

dance for our kimuraite samples is three times as high as the pure kimuraite analyzed by Nagashima *et al.* (1986). Furthermore, the great amount of Y and Ca in lokkaite will result in a weak BSE intensity like kimuraite, which is contradict to the strong brightness in our BSE images. Therefore, it can be inferred that the mineral present in our kimuraite is not lokkaite.

Lanthanite is another mineral closely associated with kimuraite. Akagi *et al.* (1993) reported that one of their kimuraite samples was covered by a layer of lanthanite. However, its chemical composition is quite different from kimuraite. Lanthanite is totally free of Ca and Y, which are two essential constituents in kimuraite. Compared to the tremendous amount of LREE, the HREE in lanthanite is relatively negligible (Nagashima *et al.*, 1986; Coimbra *et al.*, 1989; Graham *et al.*, 2007). On one hand, the absence of lighter elements, like Ca and Y, will allow lanthanite to produce strong signals in the BSE imaging. On the other hand, if kimuraite is mingled with a small amount of lanthanite, the peculiar chemical composition of lanthanite will cause an increase to the LREE while a decrease to the HREE abundance of the mixture, which is coincident with the chondrite-normalized REE patterns of our kimuraite samples. Therefore, lanthanite is the most proper candidate for the contaminant mineral.

The chemical formula, $\text{Ca}(\text{Y,REE})_2(\text{CO}_3)_4 \cdot 6\text{H}_2\text{O}$, tells us that the mole percentages of CaO and $(\text{REE}+\text{Y})_2\text{O}_3$ in a pure kimuraite should be the same value 50%, if the volatile parts are not taken into consideration. Since lanthanite does not contain any calcium, the REE_2O_3 mole percentage for a pure lanthanite will be 100%. In Fig. 1, the kimuraite sample analyzed by Nagashima *et al.* (1986) can be regarded as a pure kimuraite. Our kimuraite samples are distributed in the area close to the pure kimuraite, making up a linear trend toward the pure lanthanite. Although lokkaite is also plotted on this trend, it is impossible for lokkaite to be the contaminating mineral in our samples. One reason is that lokkaite is not capable of generating the strong BSE intensity as we have already seen in the images. In addition, if the contaminating mineral is lokkaite, the proportions of lokkaite need to be about 40%–80%, which is apparently not consistent with the observation of BSE images. Therefore, it can be

concluded that our kimuraite samples have been contaminated by lanthanite to different extents. Judging from this plot, the proportions of lanthanite in our kimuraite samples can also be estimated, ranging from 10% to 20%.

The crystallization of kimuraite consumes a large number of Ca and Y-group rare earths, causing a local depletion of these elements to the residual fluid. Such a fluid is a potential source for lanthanite. For this reason, kimuraite is likely to be accompanied by lanthanite. From our study, an important fact has been addressed that lanthanite of a few micrometers can exist in the cleavages of kimuraite (Fig. 5).

Akagi *et al.* (1996) analyzed the REE compositions of a lanthanite sample from Hizen Cho, and suggested that lanthanite might have a concave tetrad effect like kimuraite. Moreover, the chondrite-normalized REE pattern of another lanthanite from New Zealand has been proved to be a concave tetrad effect (Kawabe *et al.*, 2012). In a word, although lanthanite has a different REE composition from kimuraite, both of them display concave tetrad effects in the chondrite-normalized REE patterns. As a result, even though our kimuraite samples are contaminated by a small portion of lanthanite, their chondrite-normalized REE patterns have not been changed greatly, and still show similar concave tetrad effects to the other kimuraite samples in Fig. 2b, except for their relative enrichment of La.

CONCLUSION

In this study, we have found that all seven kimuraite samples are contaminated by lanthanite. This is the first time to document the precipitation of lanthanite of several micrometers in the cleavage of kimuraite. Though the former studies reported that kimuraite usually occurs together with lanthanite in hand specimens (Akagi *et al.*, 1993 and 1996), they have not recognized the possibility for kimuraite to have a micrometer scale contamination by lanthanite, and have not report the contents of Y and Ca of their kimuraite samples. It is also worth noting that the inner layer kimuraite A reported by Akagi *et al.* (1993) shows a similar REE pattern to K-5, which might raise a suspicion of the same contamination of inner layer kimuraite A.

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