

Deep-sea mud in the Pacific Ocean as a potential resource for rare-earth elements

Yasuhiro Kato^{1*}, Koichiro Fujinaga¹, Kentaro Nakamura², Yutaro Takaya¹, Kenichi Kitamura¹, Junichiro Ohta¹, Ryuichi Toda¹, Takuya Nakashima¹ and Hikaru Iwamori³

World demand for rare-earth elements and the metal yttrium—which are crucial for novel electronic equipment and green-energy technologies—is increasing rapidly^{1–3}. Several types of seafloor sediment harbour high concentrations of these elements^{4–7}. However, seafloor sediments have not been regarded as a rare-earth element and yttrium resource, because data on the spatial distribution of these deposits are insufficient. Here, we report measurements of the elemental composition of over 2,000 seafloor sediments, sampled at depth intervals of around one metre, at 78 sites that cover a large part of the Pacific Ocean. We show that deep-sea mud contains high concentrations of rare-earth elements and yttrium at numerous sites throughout the eastern South and central North Pacific. We estimate that an area of just one square kilometre, surrounding one of the sampling sites, could provide one-fifth of the current annual world consumption of these elements. Uptake of rare-earth elements and yttrium by mineral phases such as hydrothermal iron-oxyhydroxides and phillipsite seems to be responsible for their high concentration. We show that rare-earth elements and yttrium are readily recovered from the mud by simple acid leaching, and suggest that deep-sea mud constitutes a highly promising huge resource for these elements.

At present, 97% of the world's production of rare-earth elements and yttrium (REY) is accounted for by China, although China has only one-third of global reserves and the Commonwealth of Independent States, the United States, and Australia together have another one-third of reserves¹. China's dominance pertains to heavy rare-earth elements (HREE; conventionally Gd to Lu, but Eu is included here), which are especially important materials for high-technology products including electric automobiles and flat-screen televisions⁸. HREE reserves are almost all in ion-absorption-type ore deposits in southern China, whereas light REE (LREE) can be obtained from carbonatite/alkaline igneous complexes in other countries^{1–3}. We report here the great potential of deep-sea REY-rich mud in the Pacific Ocean as a new mineral resource for REY, especially HREE, because the mud commonly has a higher HREE/LREE ratio than the southern China ion-absorption-type deposits, as described below.

We studied drill core samples from 51 sites obtained by the Deep Sea Drilling Project/Ocean Drilling Program (DSDP/ODP) and piston core samples from 27 sites obtained by the Ocean Research Institute, the University of Tokyo (Supplementary Table S1), which cover a major portion of the Pacific Ocean (Fig. 1). Many of the DSDP/ODP holes penetrated a depth greater than 50 m below seafloor (mbsf), whereas most of the University of Tokyo piston

cores are ~10 m long and some are less than 3 m long (Fig. 2 and Supplementary Fig. S1). We measured chemical compositions of 2,037 bulk-sediment samples to evaluate the potential of seafloor sediment as a REY resource (Supplementary Data S1 and also see Methods).

REY-rich mud (generally metalliferous sediment, zeolitic clay, and pelagic red clay in lithology) is mainly distributed in two regions: the eastern South Pacific and central North Pacific (Fig. 1). In the eastern South Pacific (5°–20° S, 90°–150° W), the REY-rich mud has high REY contents, 1,000–2,230 ppm total REY (Σ REY) and 200–430 ppm total HREE (Σ HREE). REY contents of the mud are comparable to or greater than those of the southern China ion-absorption-type deposits (Σ REY = 500–2,000 ppm; Σ HREE = 50–200 ppm; refs 9,10); notably, the HREE are nearly twice as abundant as in the Chinese deposits. The core profiles reveal that the REY-rich mud has accumulated to thicknesses of ~10 m at Sites 76 and 319 (Figs 2b, 3 and Supplementary Fig. S1). The REY-rich mud lies at the surface and is less than 3 m thick at Sites 75 and 597, although the average REY contents there are very high (Σ REY = 1,530 ppm at Site 75 and 1,630 ppm at Site 597; Supplementary Table S2 and Fig. 3). At Site 596, ~2,000 km west of these areas, high- Σ REY mud (2,110 ppm maximum, 1,110 ppm average) occurs in a layer ~40 m thick below 13.5 mbsf, whereas the surface sediment has Σ REY contents of less than 250 ppm (Figs 2b and 3; Supplementary Fig. S1).

The REY-rich mud in the North Pacific east and west of the Hawaiian Islands (3°–20° N, 130° W–170° E; Fig. 1) has moderate REY contents (Σ REY = 400–1,000 ppm, Σ HREE = 70–180 ppm). Deposits in this region are much thicker than those of the eastern South Pacific, mostly >30 m and locally >70 m (for example, Site 1222; Figs 2a, 3 and Supplementary Fig. S1). Cores from east of the Hawaiian Islands commonly show broad peaks of REY content that extend deeper than ~10 mbsf (for example, Sites 1215–1218; Figs 2a, 3 and Supplementary Fig. S1). West of the Hawaiian Islands, some cores have relatively high Σ REY contents, ranging from 680 to 1,130 ppm (Sites 68 and 170). Although the cores are relatively short (less than ~20 m) in the western area, the thickness of the REY-rich mud is probably comparable to that in the eastern area, considering its presence deeper than ~40 mbsf at Sites 164 and 168 (Fig. 2a and Supplementary Fig. S1).

REY-rich mud with moderate REY content is also found in the northeast Pacific, west of the Juan de Fuca Ridge, generally between 5 and 40 mbsf (Fig. 2c and Supplementary Fig. S1). The cores from Sites 33 and 36 contain significant amounts of terrigenous material and have low REY contents, which suggests that these

¹Department of Systems Innovation, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, ²Precambrian Ecosystem Laboratory (PEL), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima, Yokosuka, Kanagawa 237-0061, Japan, ³Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, Japan. *e-mail: ykato@sys.t.u-tokyo.ac.jp.

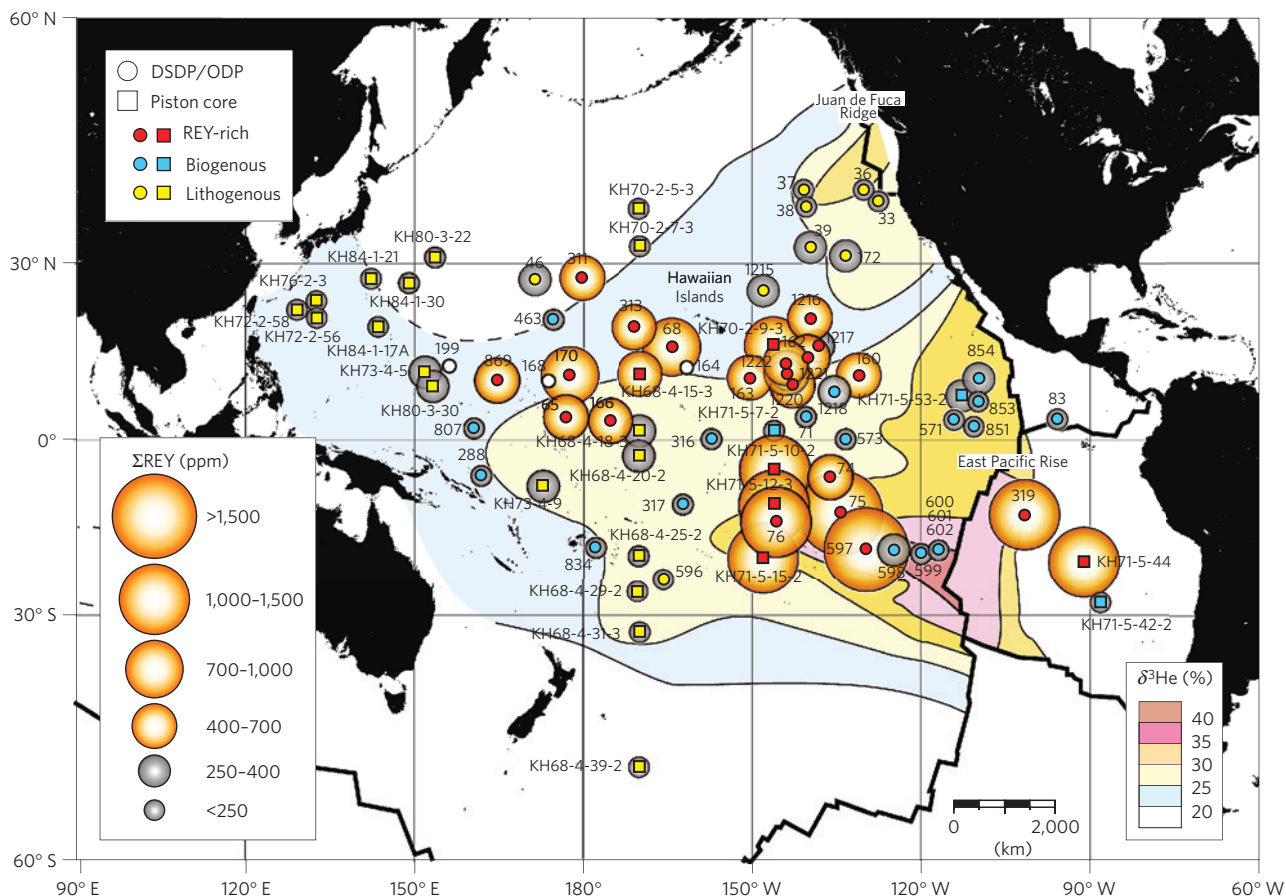


Figure 1 | Distribution of average Σ REY contents for surface sediments (<2 m in depth) in the Pacific Ocean. Circles represent DSDP/ODP sites and squares represent the University of Tokyo piston core sites, with colours corresponding to the dominant origin of surface sediments. Open symbols are sites lacking samples from the sediment surface. Contours represent helium-3 anomalies ($\delta^3\text{He}$) of mid-depth seawater¹². REY-rich mud with average Σ REY >400 ppm is designated as a potential resource in this study.

detrital materials, derived from the North American continent, greatly dilute the REY contents of mud near the coast¹¹.

REY-bearing carbonate is found in areas near the East Pacific Rise above the carbonate compensation depth, where carbonate oozes of near-zero REY content accumulate together with a smaller amount of REY-rich component (for example, Sites 598 and 854; Fig. 1). The Σ REY contents of the REY-bearing carbonate reach no more than about 200 ppm, thus it has poor potential as a REY resource. In areas closer to either mid-ocean ridges or the equator, more intense dilution by rapidly deposited carbonate or siliceous (radiolarian) oozes occurs, leading to extremely low REY contents (for example, Sites 601 and 573).

In addition to REY, the mud is enriched in transition metals including V, Co, Ni, Cu, Zn, Mo, and Mn by up to two orders of magnitude greater than average continental crustal contents (Supplementary Data S1). Hence, the resource value of the mud may be greater if these metals are recovered together with REY. Moreover, the Th and U contents are a small fraction of average crustal abundances. As these radioactive elements can pose environmental problems during the mining and processing of deposits in carbonatite/alkaline igneous complexes, strong depletion of Th and U makes the mud more suitable as a REY resource.

The distribution map of average Σ REY contents for the seafloor sediment, except for areas of dilution by biogenous carbonate/silica and contamination by terrigenous material, is generally consistent with the helium-3 anomaly ($\delta^3\text{He}$) map of mid-depth seawater in the Pacific^{12,13}, which reflects far-field

spreading of hydrothermal plumes from the East Pacific Rise and Juan de Fuca Ridge (Fig. 1). This coincidence suggests that the deposition of the REY is related to mid-ocean ridge hydrothermal activity. Our bulk-sediment data also indicate that one of the main hosts for the REY is an Fe-oxhydroxide precipitate from hydrothermal plumes that has taken up rare earths from ambient seawater (see Methods and Supplementary Figs S2–S7), which is well known as a scavenging mechanism for REY in the submarine environment^{4,14–17}. The distribution of the REY-rich mud evident in Fig. 1 reflects the interplay among mid-ocean ridge hydrothermal activity producing Fe-oxhydroxide particulates, deep or intermediate water currents dispersing these particulates, and biogenous activity entraining carbonate/silica-diluting materials as well as contamination by lithogenous (mainly terrigenous) material. Bulk-sediment compositional data and multivariate statistical analysis (Independent Component Analysis¹⁸) clearly show that a second REY-rich component exists with relatively low Fe and high Al contents, similar to phillipsite in major element composition (see Methods and Supplementary Figs S2–S7). This interpretation is consistent with the long-held notion that phillipsite is one of the main carriers of REY in pelagic sediments¹⁹, although the origin of phillipsite associated with high REY contents is not well understood²⁰. Our measurements demonstrate that the REY-rich mud occurs in pelagic deep-sea regions more than ~2,000 km from mid-ocean ridges (Fig. 1), where high-REY materials were deposited slowly (<0.5 cm kyr⁻¹; Supplementary Fig. S8) without significant dilution by biogenous carbonate or silica. The REY-rich mud extensively and thickly

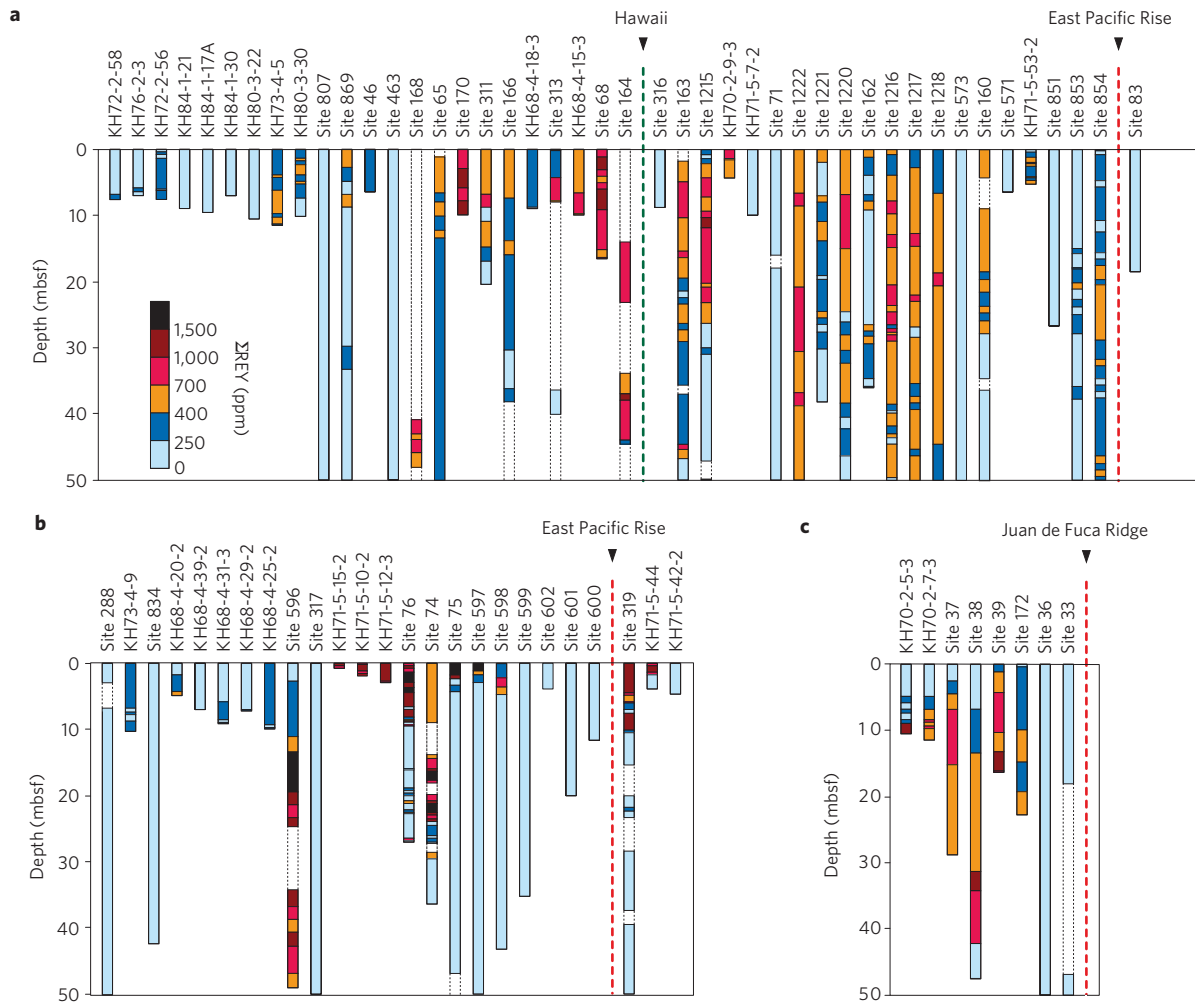


Figure 2 | Colour-coded depth profiles of Σ REY contents in cores. **a**, The northern tropical Pacific Ocean between 0° and 30° N. **b**, South of the equator. **c**, North of 30° N. These are simplified profiles limited to shallower than 50 mbsf. Complete and more detailed depth profiles are given in Supplementary Fig. S1.

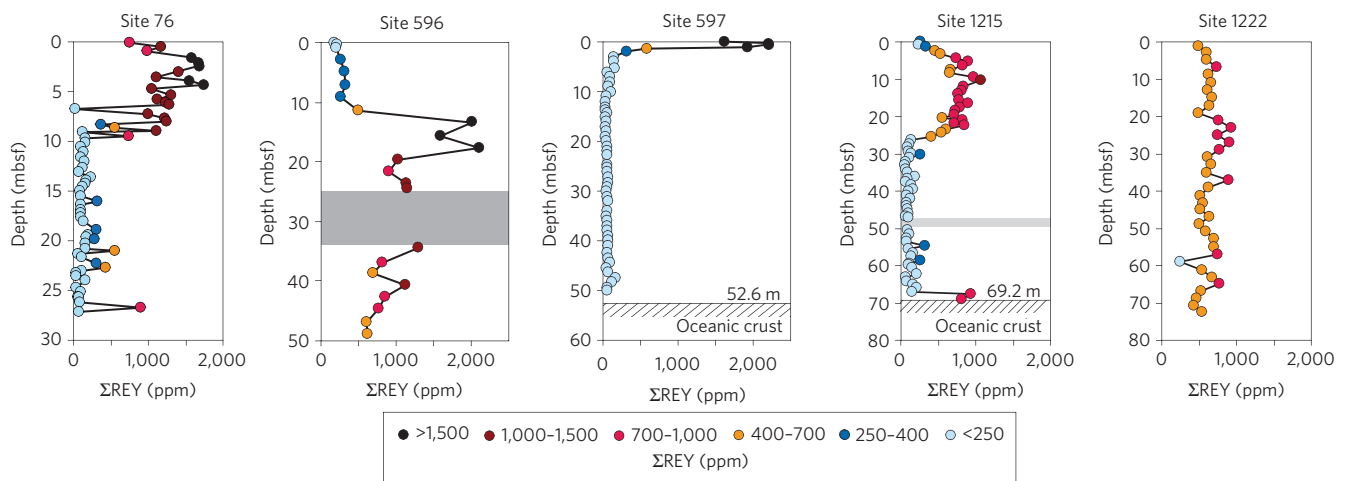


Figure 3 | Detailed depth profiles of Σ REY contents in representative cores. The pale grey intervals represent no core recovery.

distributed in the Pacific Ocean represents accumulation dating from the Palaeogene (partly Cretaceous) period to the present, and constitutes a huge potential REY resource under the sea (Fig. 2).

Assuming an average Σ REY content of $1,180 \pm 189$ ppm (Supplementary Table S2 for the mean value and Supplementary

Fig. S11 for the uncertainty) and dry bulk density of 0.66 g cm^{-3} (ref. 21), the 10-m-thick bed of REY-rich mud in an area of 1 km^2 at Site 76, in the eastern South Pacific, has the potential to yield $9,110 \pm 1,460$ tonnes of REY oxides (tREY-oxides), or one-fifteenth (one-eighteenth to one-thirteenth) of the global

annual consumption of REY in 2010 (134,000 tREY-oxides (ref. 2)). Similarly, assuming an average Σ REY content of 640 ± 102 ppm and dry bulk density of 0.477 g cm^{-3} (ref. 22), the 70-m-thick REY-rich mud layer in an area of 1 km^2 at Site 1222 in the central North Pacific holds nearly $25,000 \pm 4,000$ tREY-oxides; $\sim 5 \text{ km}^2$ (about $2.3 \text{ km} \times 2.3 \text{ km}$) of this material at Site 1222 could possibly supply the majority of current annual REY consumption in the world. Considering that the REY-rich mud shows a thick distribution at many sites throughout the eastern South and central North Pacific (Figs 1, 2 and Supplementary Fig. S1), the seafloor REY resource potentially could exceed the world's current land reserves of 110×10^6 tREY-oxides¹, although more detailed sampling and analysis are needed to properly evaluate this possibility. Irregular bottom topography, local currents, and highly variable rates of biogenous sedimentation together may produce major differences in the REY-rich mud thickness over relatively short distances (Supplementary Table S2), hence resource estimates for large regions cannot be made until more detailed data are available for areas lacking cores.

Our experiments using dilute acids ($0.2 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$ or $0.5 \text{ mol l}^{-1} \text{ HCl}$) reveal that almost all of the REY, except Ce, are readily leached from the mud in 1 to 3 h (Supplementary Fig. S9). In addition, pulverization and beneficiation are not needed before metal leaching. These features enhance the potential of the REY-rich mud as a REY resource. Unless the great water depths (mostly 4,000–5,000 m; Supplementary Table S2) have a significant impact on the technological and economic viability of mining REY on seafloor, the REY-rich mud in the Pacific Ocean may constitute a highly promising REY resource for the future.

Methods

Bulk-sediment analyses. Major element contents of the bulk-sediment samples from the piston cores were measured using a Rigaku 3270 X-ray fluorescence (XRF) spectrometer at the Ocean Research Institute, the University of Tokyo. Details of the XRF analytical procedures are given in refs 23,24. Trace element and REY abundances for all bulk-sediment samples and major element contents of the DSDP/ODP bulk-sediment samples were determined by ICP-MS (Agilent 7500c) at the Department of Systems Innovation, the University of Tokyo, following the procedures described in ref. 25, with some modifications. Analyses are generally within 2% of accepted values of the reference materials issued by the Geological Survey of Japan; reproducibility of replicate analyses ($n = 5$) is typically <3% RSD. Major element data obtained by two analytical methods (XRF and ICP-MS) for the piston core samples agree well with each other (Supplementary Fig. S10). Duplicate analyses of selected core samples from Site 76 by ICP-MS (this study) and INAA (Actlabs, Ontario, Canada) show a good agreement within the analytical uncertainties, integrating those for ICP-MS (<7%) and INAA (<9%; Supplementary Fig. S11).

Analysis of compositional variability. To clarify components controlling the compositional variability, we examined correlation among the ten components (nine major elements as oxides plus Σ REY) in 1,940 samples that have complete data sets. The CaO and SiO₂ variation diagrams (Supplementary Figs S2 and S3) clearly show dilution of the other components by biogenous carbonate and silica, respectively, which is confirmed in the other variation diagrams as a trend converging toward the origin (Supplementary Figs S4–S6). In the TiO₂ versus oxide variation diagrams (Supplementary Fig. S4), a clear but minor trend with low Σ REY contents extends toward an oceanic island basalt (OIB) composition, suggesting that contamination by OIB-derived material is limited to specific geographical areas in the western Pacific (for example, KH80-3-30, KH84-1-17A). Except for these dilution and contamination trends, the remaining variations can be explained mainly by terrigenous and REY-rich components (Supplementary Figs S5 and S6). Data for some samples rich in Al₂O₃ plot near the compositions of average shales, indicating predominance of the terrigenous component in these samples. The Fe₂O₃ versus oxide variation diagrams show that data for some of the REY-rich samples extend toward hydrothermal Fe-rich endmembers (Supplementary Fig. S6; for example, Fe₂O₃ versus Al₂O₃ and K₂O diagrams). This Fe-rich trend is associated with enrichment of REY, although the degree of enrichment is variable, possibly reflecting a wide compositional range of Fe-rich endmembers (Fe₂O₃– Σ REY diagram in Supplementary Fig. S6). Another Σ REY enrichment trend characterized by relatively low Fe contents extends toward a phillipsite-like major element composition having 2,500 to 3,000 ppm Σ REY (Fe₂O₃– Σ REY diagram in Supplementary Fig. S6), which is higher than reported Σ REY contents in phillipsite. Phillipsite has long been considered one of the main

sources for REY in pelagic sediments¹⁹, although the cause of Σ REY enrichment in phillipsite is still ambiguous²⁰. Phillipsite crystals themselves may not contain abundant REY. Instead, Fe-oxyhydroxide inclusions in phillipsite aggregates have been observed to accumulate REY (ref. 20). Apatite has been often proposed as an essential host for REY (ref. 26). In our analysis, however, there is no appreciable trend that consistently extends toward an apatite composition in multi-element space, including Σ REY.

A relatively new multivariate statistical method, Independent Component Analysis (ICA; refs 18,27), supports the arguments made above. ICA of the current data set shows that four independent components (ICs), which account for 91.0% of the sample variance, explain dilution of the terrigenous component by biogenous carbonate and silica (IC1 and IC2 in Supplementary Fig. S7), as well as two trends with high REY contents: Fe-rich and Al-rich trends (IC3 and IC4 in Supplementary Fig. S7). It is noted that the ICs are obtained as vectors or linear trends, rather than points having specific compositions. In this study, ICA has been performed with the algorithm known as FastICA (ref. 28), and the number of ICs has been determined following the procedure described in ref. 18.

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Author contributions

Y.K., K.F., K.N. and H.I. designed the study. K.F., Y.T., K.K., J.O., R.T. and T.N. carried out chemical analyses. Y.K., K.N. and H.I. primarily wrote the manuscript with input from all other co-authors.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at <http://www.nature.com/reprints>. Correspondence and requests for materials should be addressed to Y.K.