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REE-rich mud in the Pacific Ocean



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

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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-oxhydroxides 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 televisions². 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

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

- Geochemical natures and distribution of REE-rich mud
- Possibility of REE-rich mud development

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REY (rare-earth elements and yttrium)

HREE (Tb, Dy, Yb, Y) and Eu
are very important

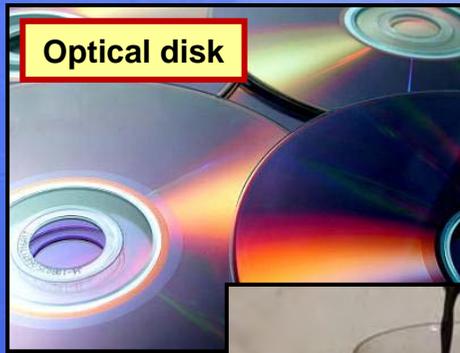
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113	114																	118
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117	118																	122
119	120																	124

light rare-earth (LREE)

heavy rare-earth (HREE)

57-71	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
L lanthanides	La Lanthanum	Ce Cerium	Pr Praseodymium	Nd Neodymium	Pm Promethium	Sm Samarium	Eu Europium	Gd Gadolinium	Tb Terbium	Dy Dysprosium	Ho Holmium	Er Erbium	Tm Thulium	Yb Ytterbium	Lu Lutetium
89-103	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

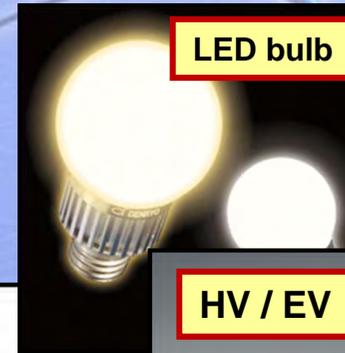
Principal use of rare-earth elements and yttrium (REY)



Optical disk



Flat screen TV



LED bulb



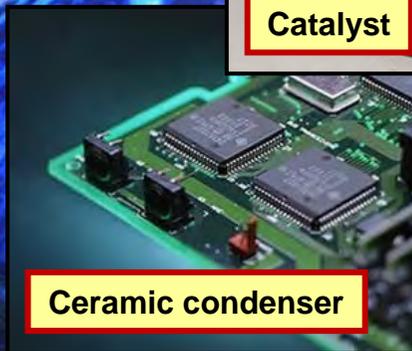
Catalyst



HDD



HV / EV



Ceramic condenser



Fuel cell

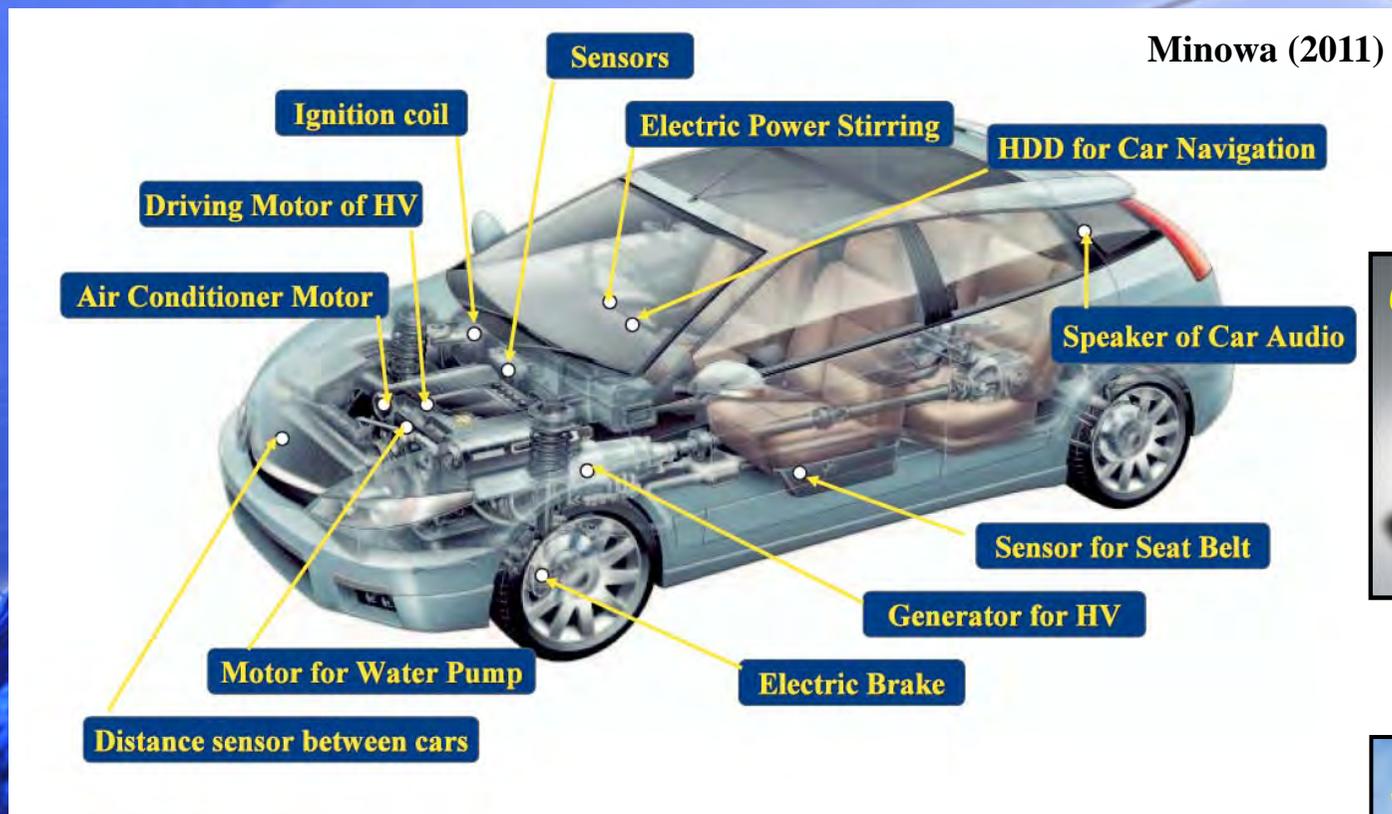


Smartphone

REY are crucial for high-tech products

- green-energy technologies
- novel electronic equipment
- space development industry etc...

REY used in a hybrid vehicle



One hybrid vehicle needs...



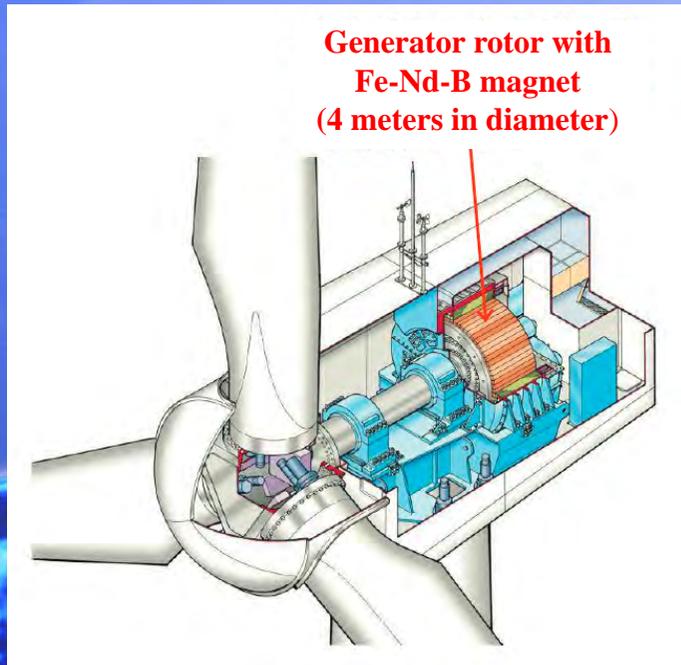
3 tonnes of REY ore !



- Fe-Nd-B magnet:
1.0 kg (Prius, TOYOTA) ~1.8 kg (Estima, TOYOTA)
- Nd (30%) : 300 g ~ 540 g
- Dy (3% ~ 8%) : 80 g ~ 144 g

Dy is a key element for a hybrid vehicle !

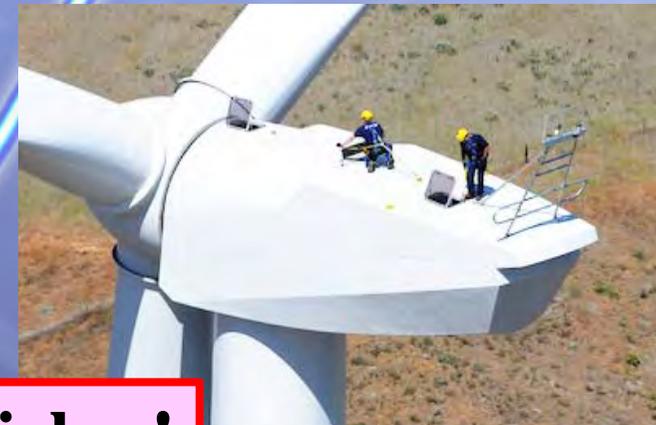
REY used for wind power generation



Permanent Magnet Synchronous Generator

- Fe-Nd-B magnet: 1.5 t ~ 2.0 t
- Nd (30%): 450 kg ~ 600 kg
- Dy (3% ~ 8%): 45 kg ~ 160 kg

1,500 ~ 2,000 hybrid vehicles !



(Ueda, 2011)

Principal uses of REY: Advanced military technology

Missile guidance and control system
(Nd, Pr, Sm, Dy, Tb)



Laser targeting system
(Y, Eu, Tb)

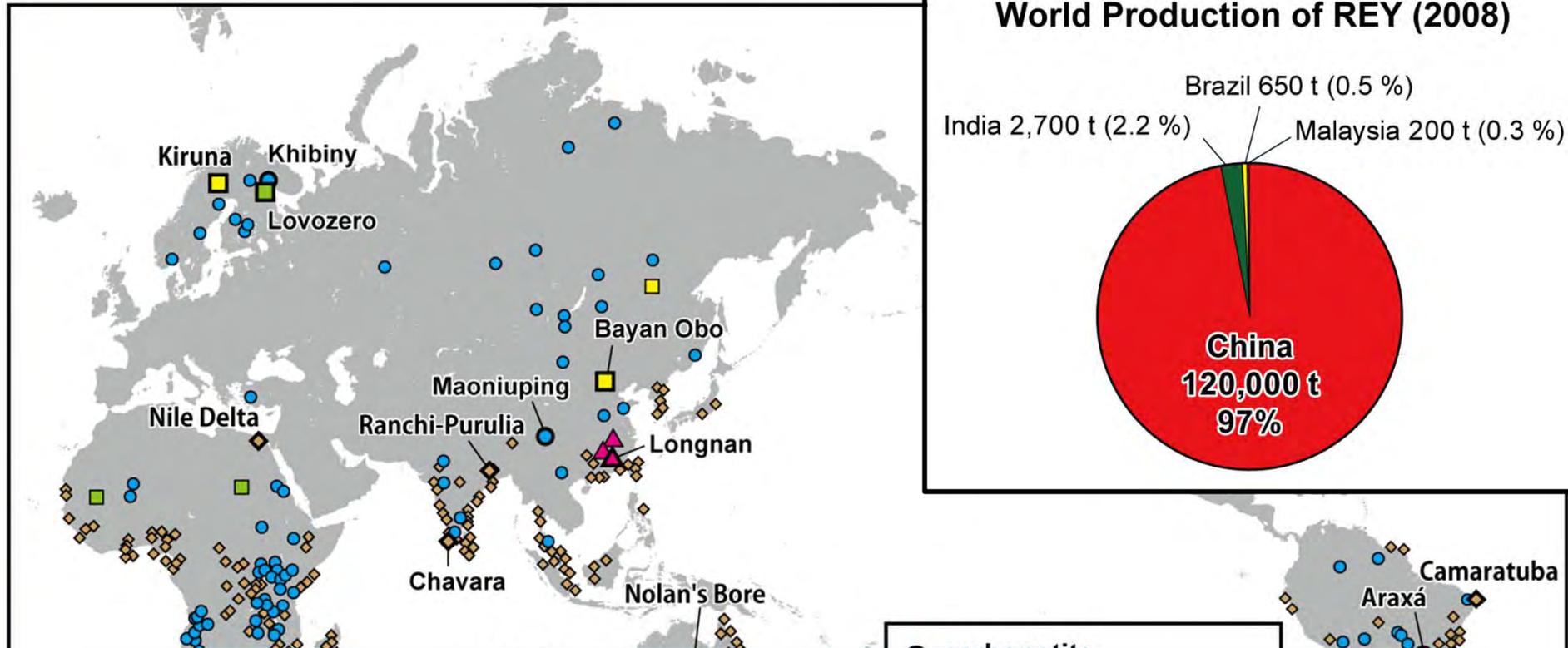


Radar surveillance system
(Nd, Y, La, Lu, Eu)



REY are also indispensable for security

REY deposits in the world

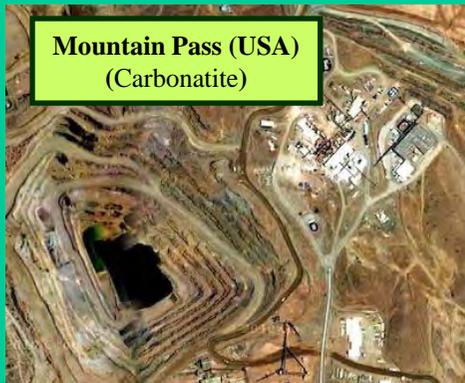


- Almost all deposits are of LREE
- Ion-absorption-type deposits in southern China exclusively produce HREE

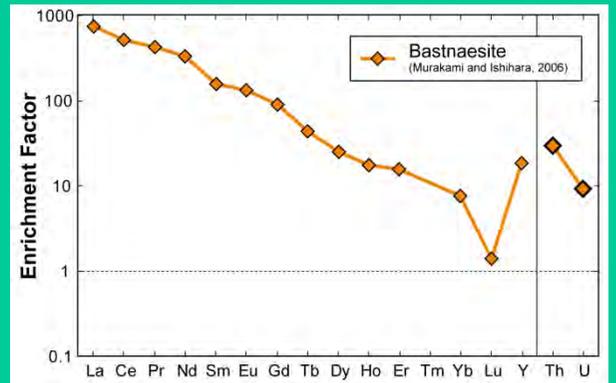
- 97 % of REY are mined and produced by China

(2008)

LREE deposits on land

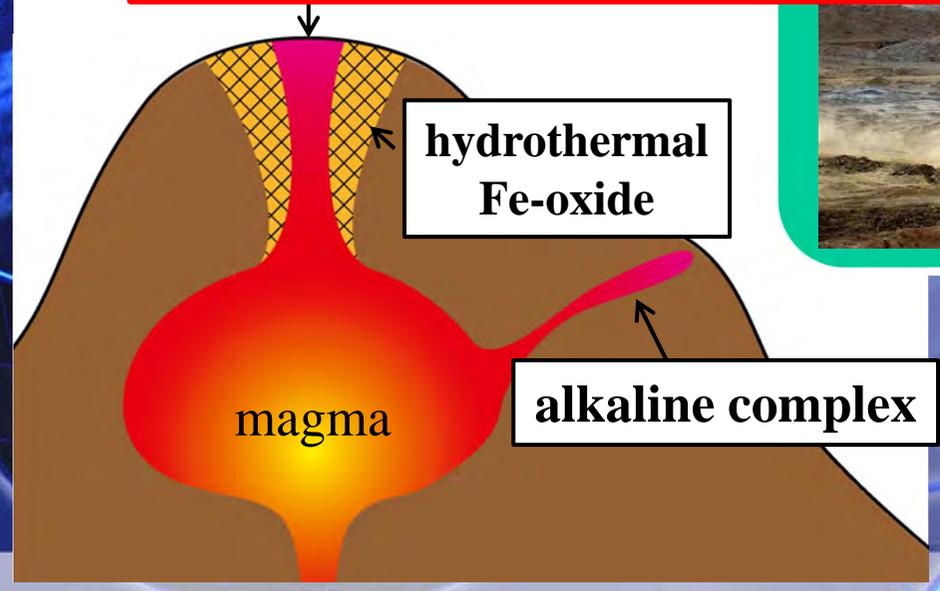


Mountain Pass (USA)
(Carbonatite)

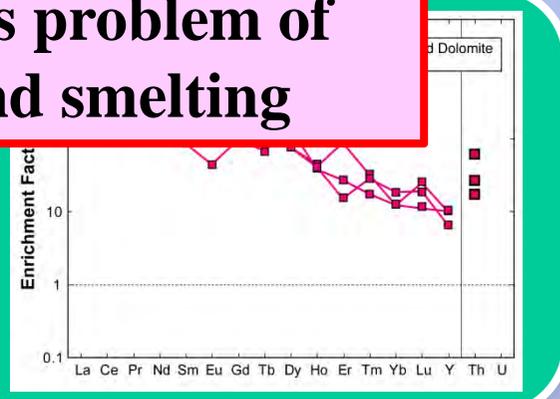


- LREE deposits are formed by magmatic activity and hydrothermal alteration (ex. carbonatite, hydrothermal Fe-oxide, alkaline complex).
- Radioactive elements (Th and U) are also enriched by fractional crystallization.

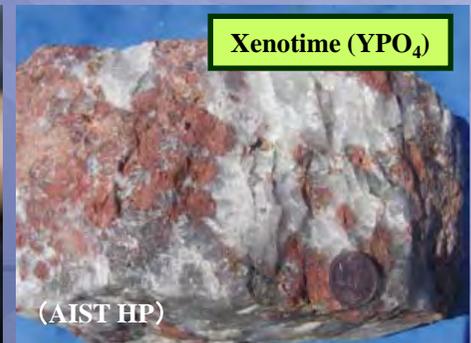
Enrichment of Th and U causes a serious problem of radioactive waste during the mining and smelting



Bayan Obo (China)
(hydrothermal Fe-oxide)



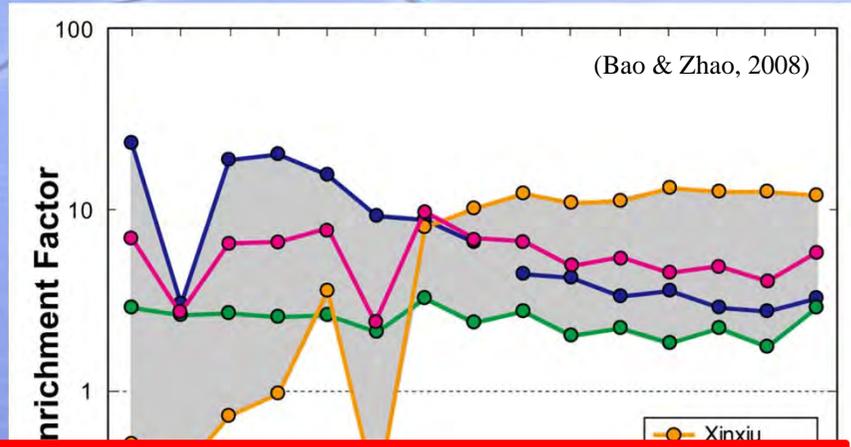
bastnaesite ((REE)(CO₃)F)



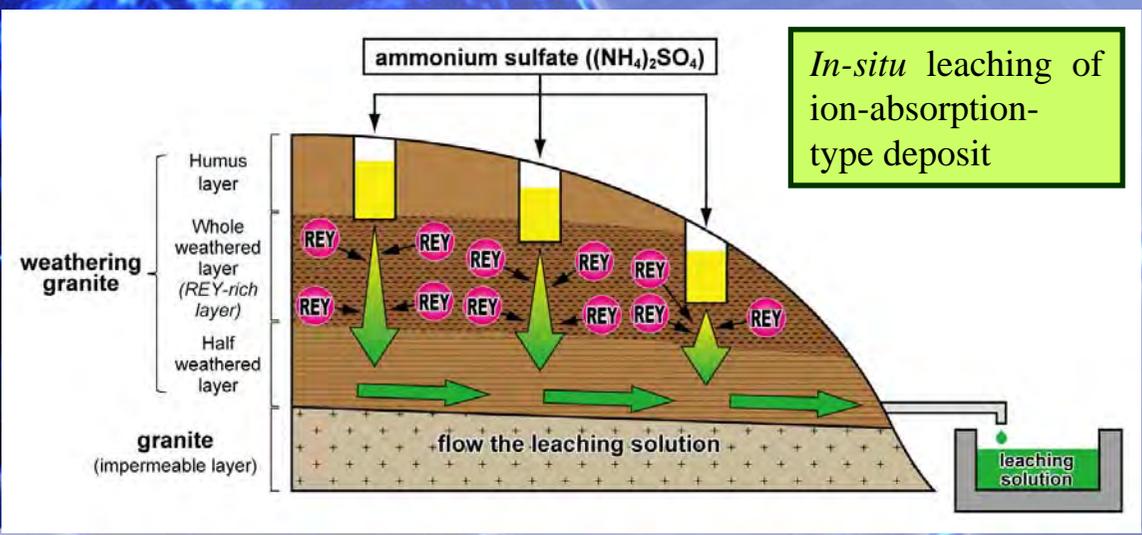
Xenotime (YPO₄)

(AIST HP)

HREE deposits on land (ion-absorption-type deposit)

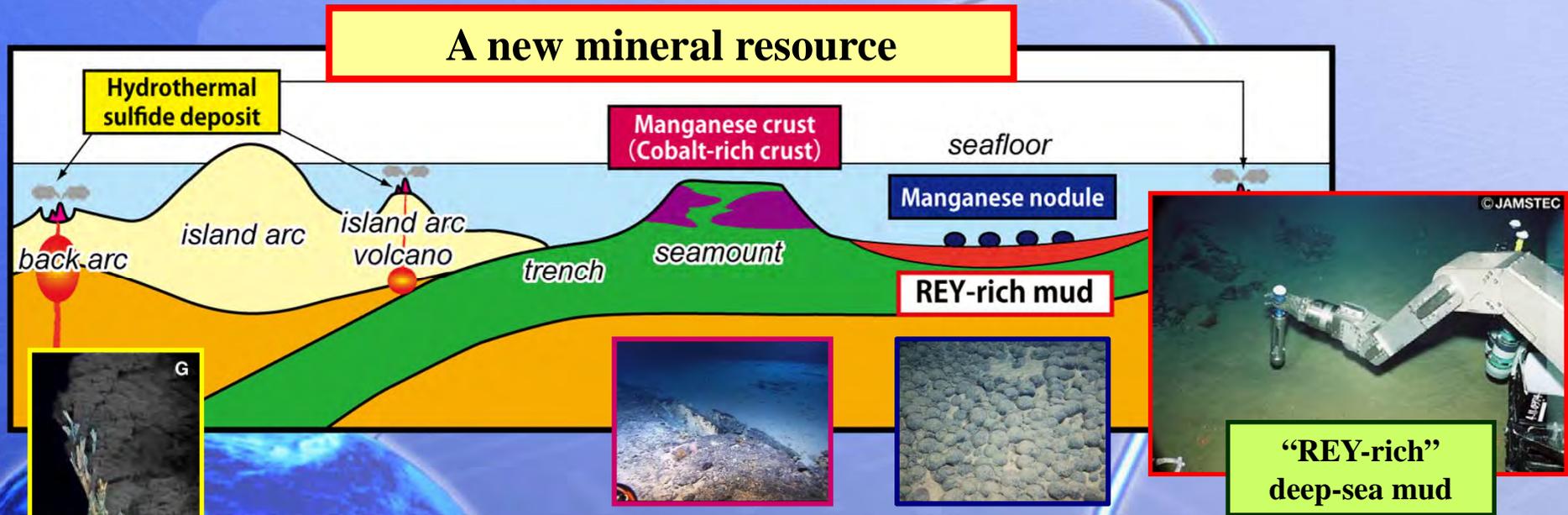


Leaching acids injected into outcrops are uncollected, and cause a severe environmental pollution



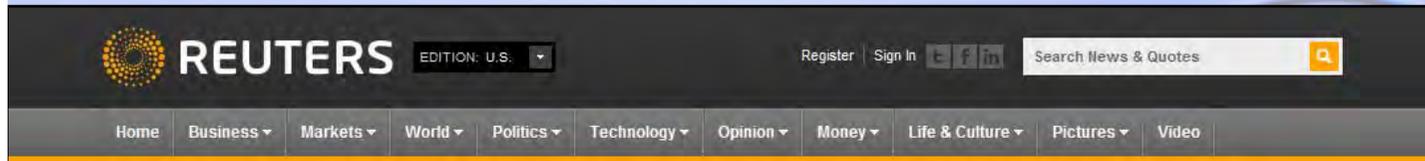
- HREE enrichment occurs in clay minerals formed by granite weathering.
- Easy extraction of REY by *in-situ* leaching.

Mineral deposits on seafloor



	Well-known mineral resources			A new mineral resource
	Hydrothermal sulfide deposit	Manganese crust	Manganese nodule	REY-rich mud
Mode of occurrence	chimny/mound (10~10 ² m)	thin coated-layer (0.1~10 cm)	spherical (2.5~25 cm)	bedded (2~70 m)
Amount	10 ⁴ ~10 ⁶ t (one site)	5x10 ¹⁰ t	5x10 ¹¹ t	> 1x10 ¹⁴ t (?)
Distribution	the open sea + EEZ	the open sea + EEZ	the open sea	the open sea + EEZ

Reported by major international news media



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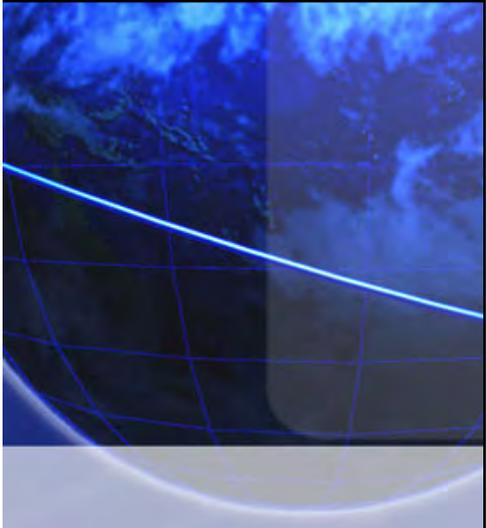
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Ocean floor muddies China's grip on '21st-century gold'

By Richard Ingham (AFP) – 1 day ago

PARIS — China's monopoly over rare-earth metals could be challenged by the discovery of massive deposits of these hi-tech minerals in mud on the Pacific floor, a study on Sunday suggests.

China accounts for 97 percent of the world's production of 17 rare-earth elements, which are essential for electric cars, flat-screen TVs, iPods, superconducting magnets, lasers, missiles, night-vision goggles, wind turbines and many other advanced products.

These elements carry exotic names such as neodymium, promethium and yttrium but in spite of their "rare-earth" tag are in fact abundant in the planet's crust.

The problem, though, is that land deposits of them are thin and scattered around, so sites which are commercially exploitable or not subject to tough environment restrictions are few.

As a result, the 17 elements have sometimes been dubbed "21st-century gold" for their rarity and value.

Production of them is almost entirely centred on China, which also has a third of the world's reserves. Another third is held together by former Soviet republics, the United States and Australia.

But a new study, published in the journal Nature Geoscience, points to an extraordinary concentration of rare-earth elements in thick mud at great depths on the Pacific floor.

Japanese geologists studied samples from 78 sites covering a major portion of the centre-eastern Pacific between 120 and 180 degrees longitude.

Drills extracted sedimentary cores to depths that in place were more than 50 metres (165 feet) below the sea bed.



A worker walks past waste being processed at a privately-owned rare earths factory in Inner Mongolia (AFP/File, Frederic J. Brown)

Map



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Tuesday, July 5, 2011 As of 12:00 AM

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2,960 Share

Japan finds rare earths in Pacific seabed

Japanese researchers say they have discovered vast deposits of rare earth minerals, used in many hi-tech appliances, in the seabed.

The geologists estimate that there are about a 100bn tons of the rare elements in the mud of the Pacific Ocean floor.

At present, China produces 97% of the world's rare earth metals.

Analysts say the Pacific discovery could challenge China's dominance, if recovering the minerals from the seabed proves commercially viable.

The **British journal Nature Geoscience reported** that a team of scientists led by Yasuhiro Kato, an associate professor of earth science at the University of Tokyo, found the minerals in sea mud at 78 locations.

"The deposits have a heavy concentration of rare earths. Just one square kilometre (0.4 square mile) of deposits will be able to provide one-fifth of the current global annual consumption," said Yasuhiro Kato, an associate professor of earth science at the University of Tokyo.



The number of seabed mining applications is a growing focus for environmentalists' concern

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Seabed mining on Pacific agenda

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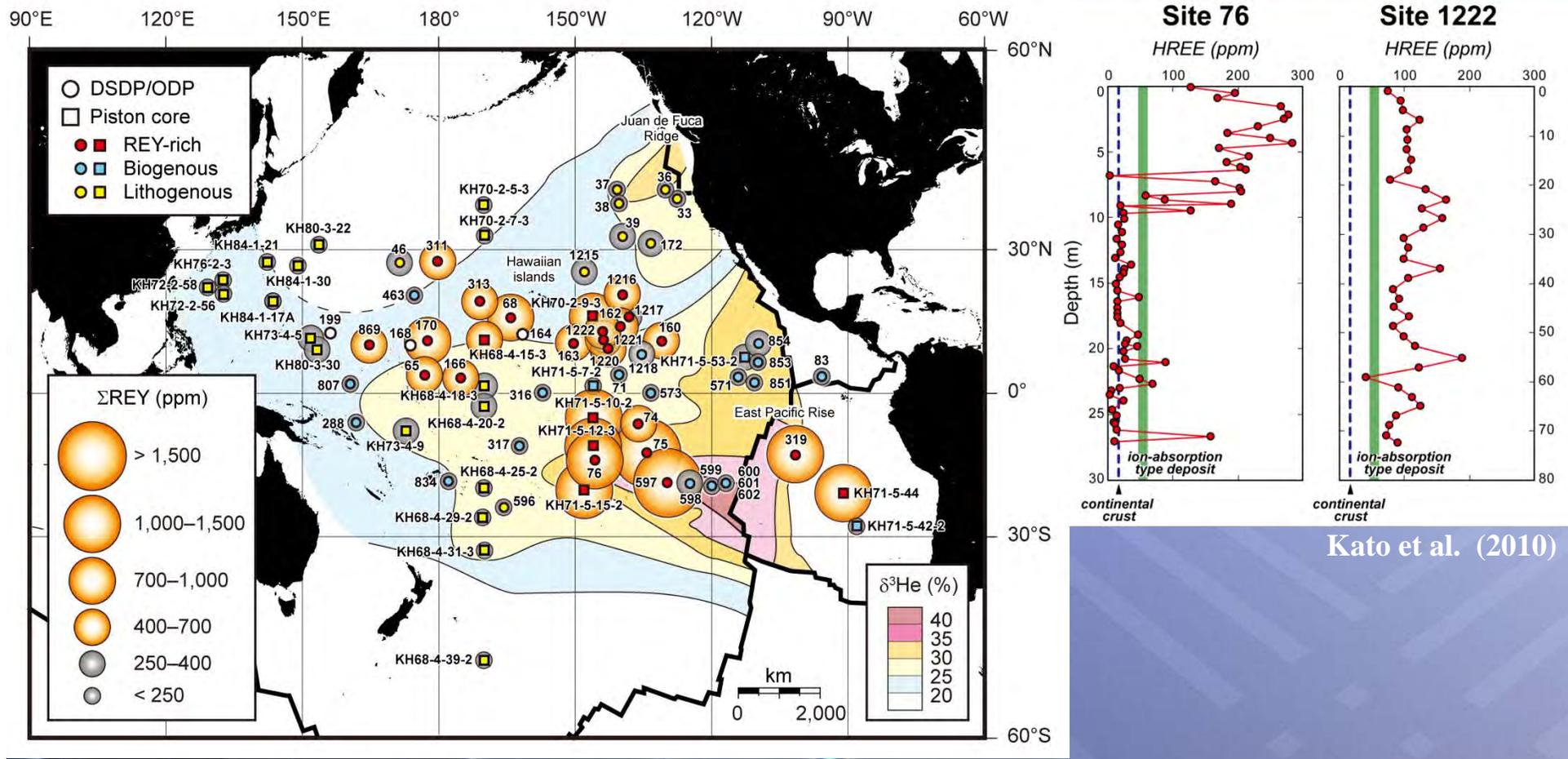


White heat

New models go on display at the Frankfurt motor show

Advantages of REY-rich mud

1. High REY (HREE) contents

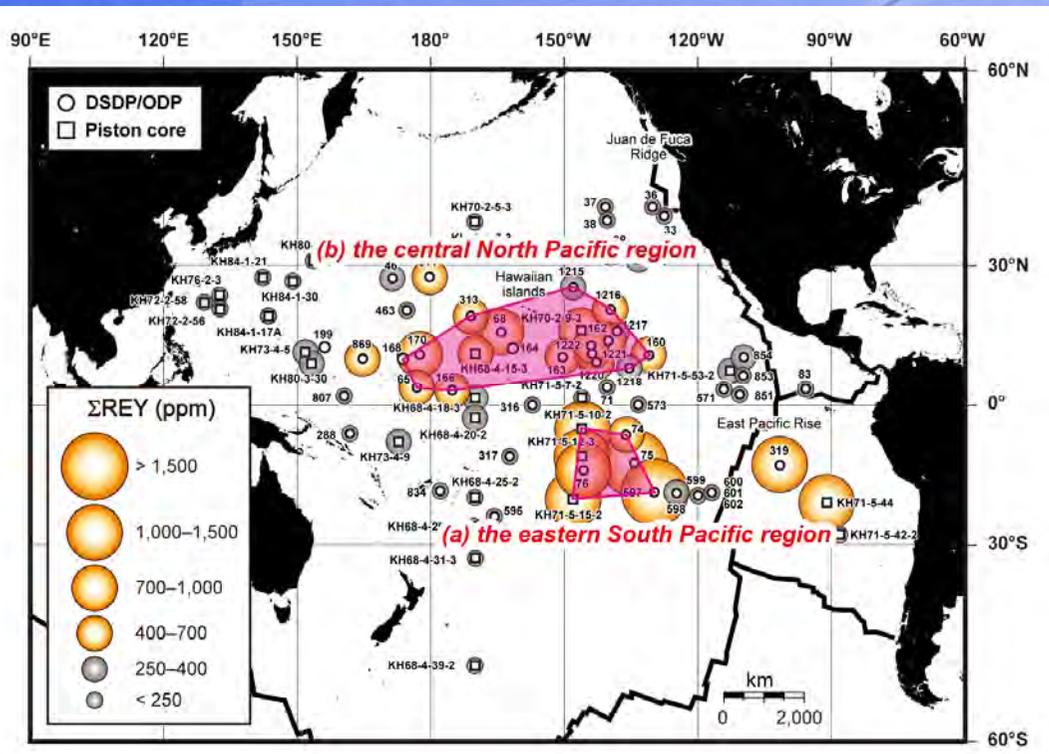


Kato et al., *Nature Geoscience* (2011)

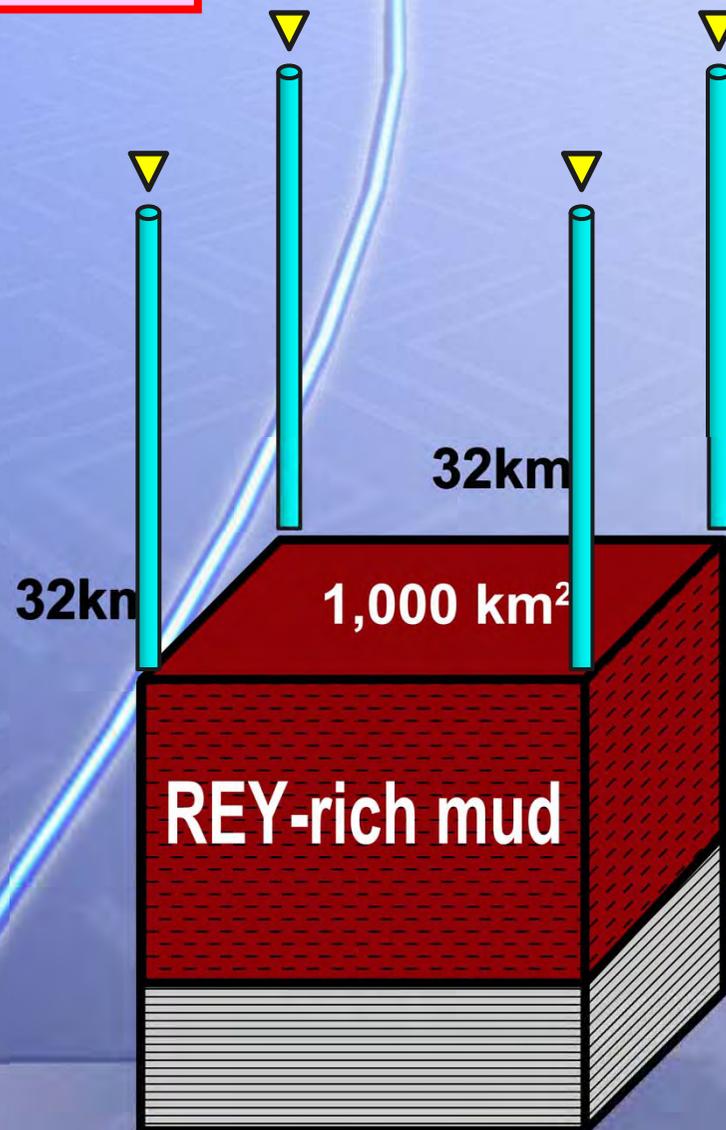
Kato et al. (2010)

Advantages of REY-rich mud

3. Easy exploration

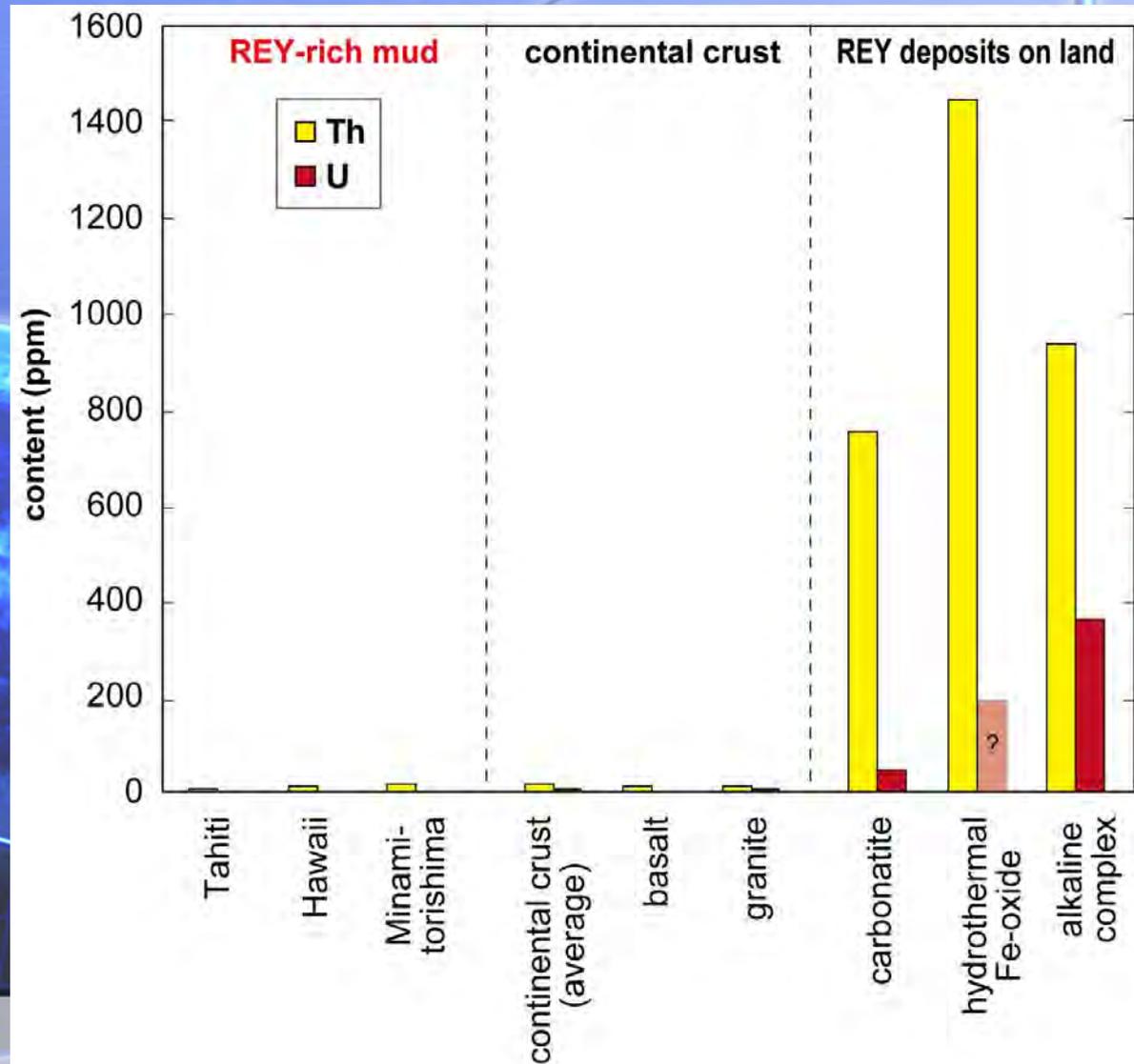


Kato et al., *Nature Geoscience* (2011)



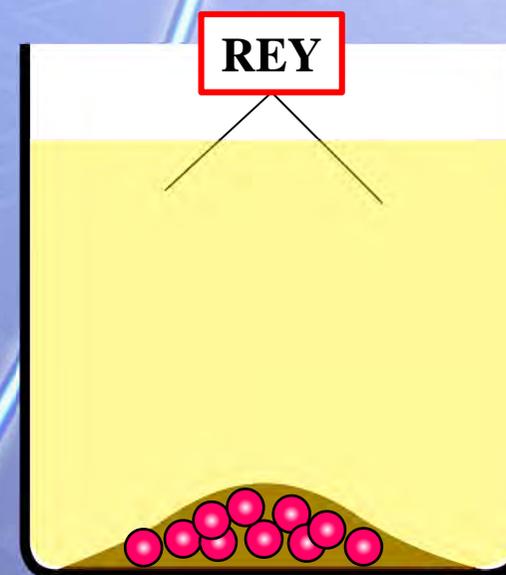
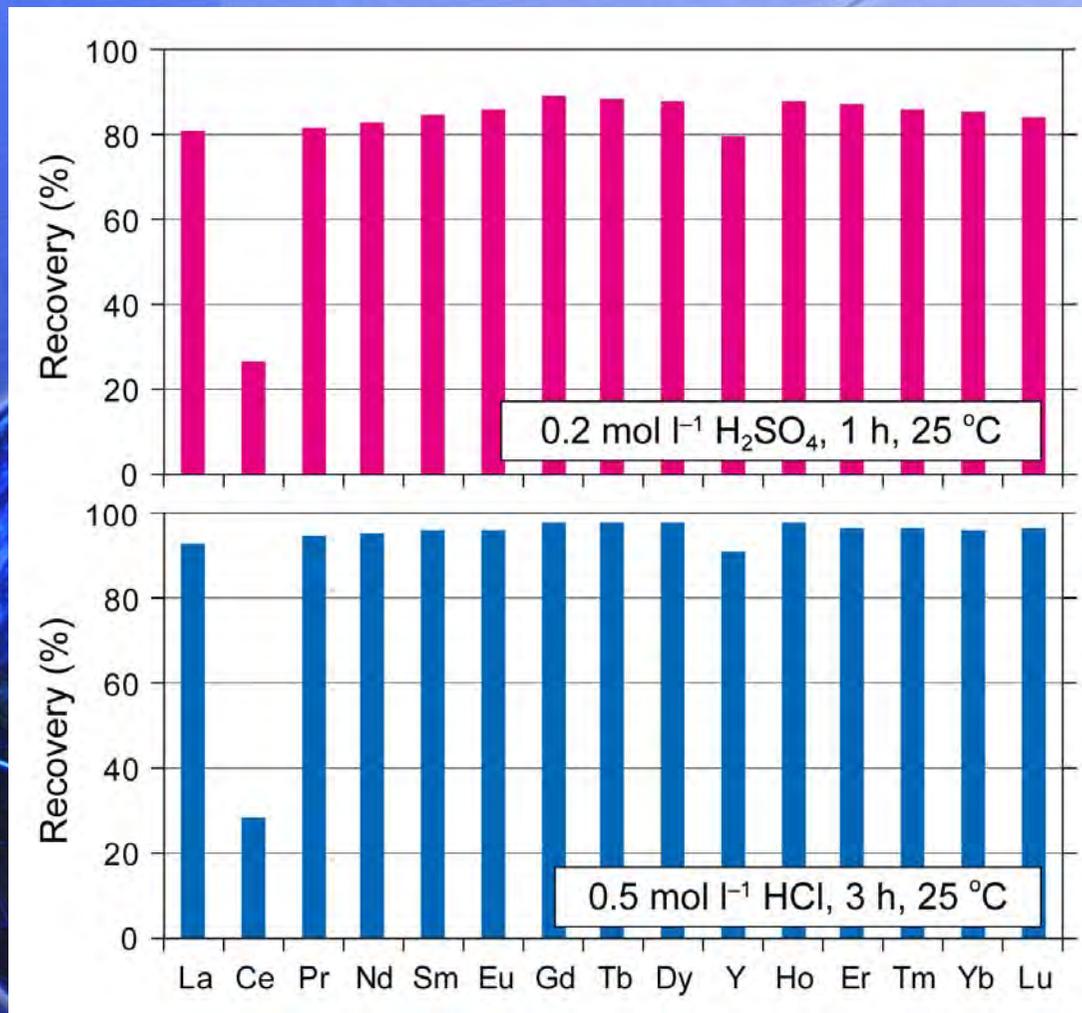
Advantages of REY-rich mud

4. Low Th and U contents



Advantages of REY-rich mud

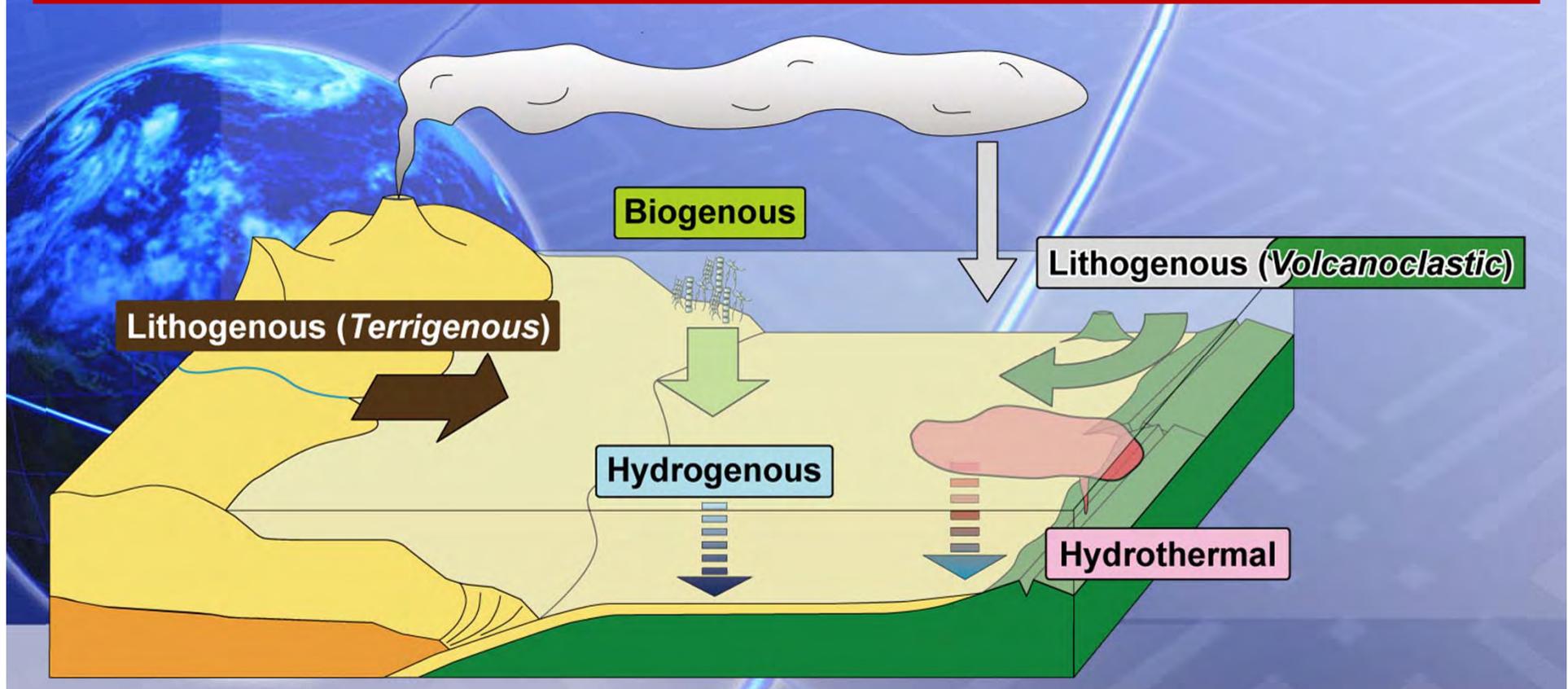
5. Easy leaching by dilute acids



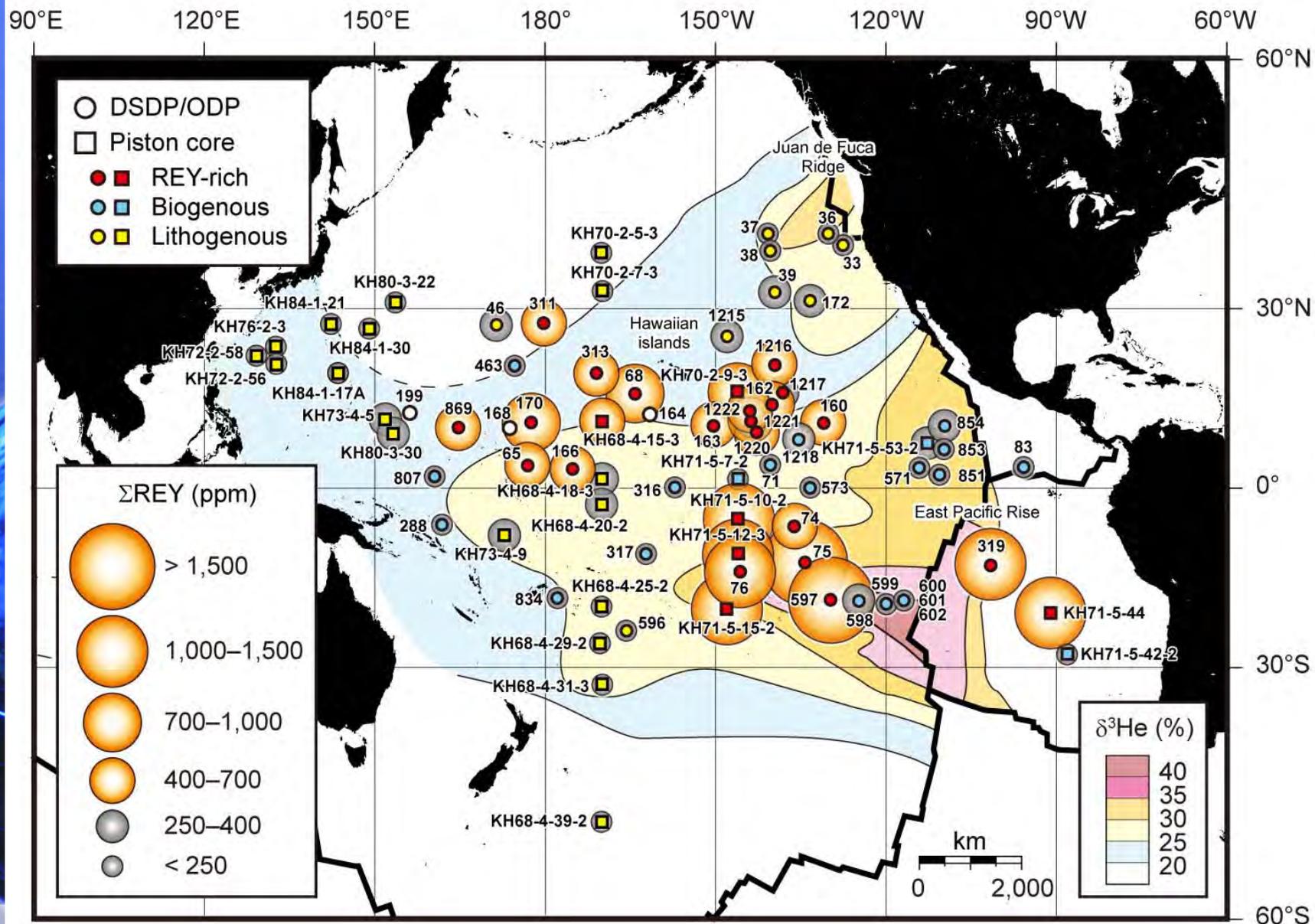
Kato et al., *Nature Geoscience* (2011)

Sources for seafloor mud

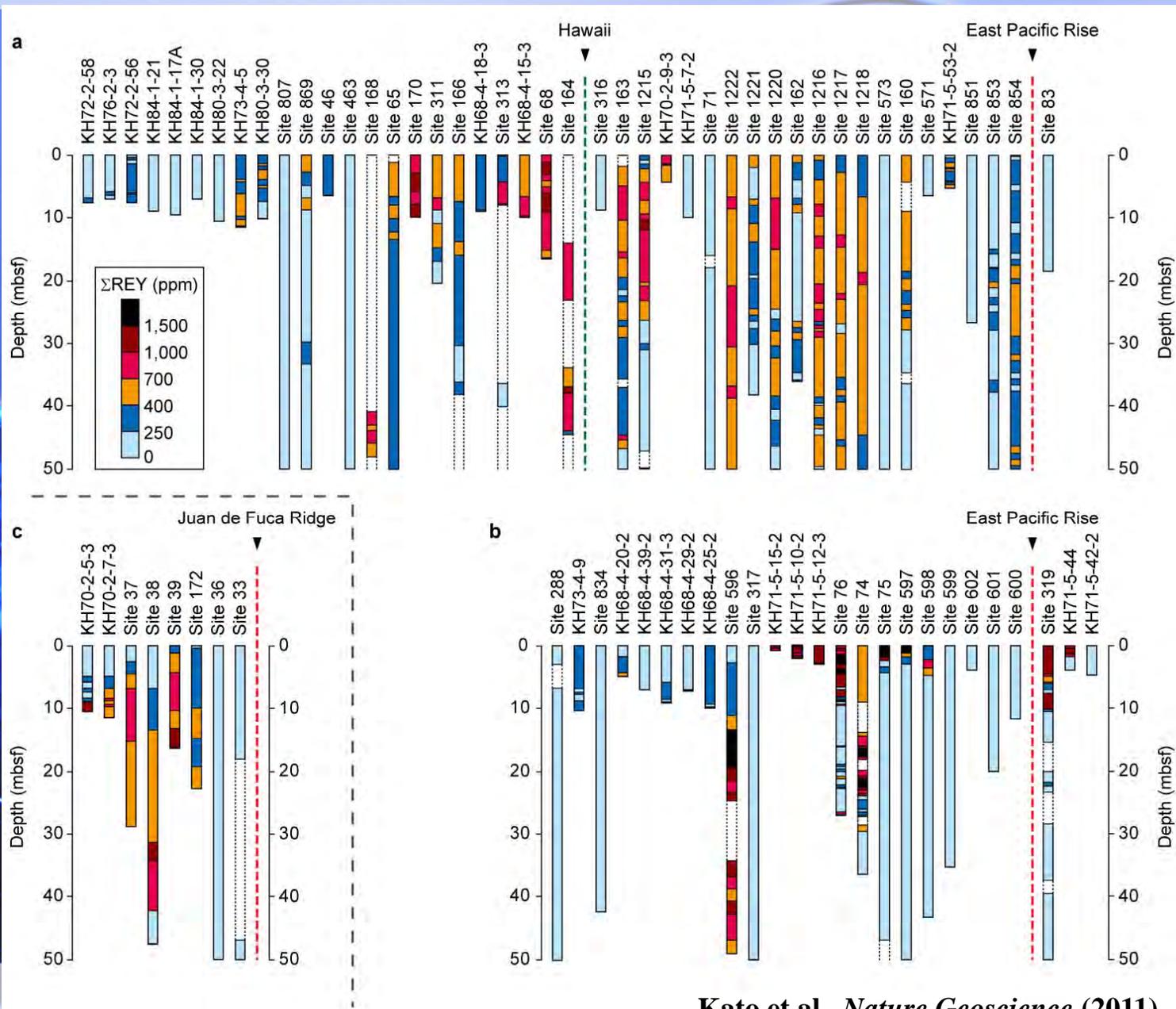
1. **Lithogenous**: Terrigenous (continental) and/or Volcanic component
2. **Biogenous**: CaCO_3 or SiO_2 shells of microorganisms
3. **Hydrogenous**: Component Inorganically precipitated from seawater
4. **Hydrothermal**: Component precipitated from hydrothermal plumes



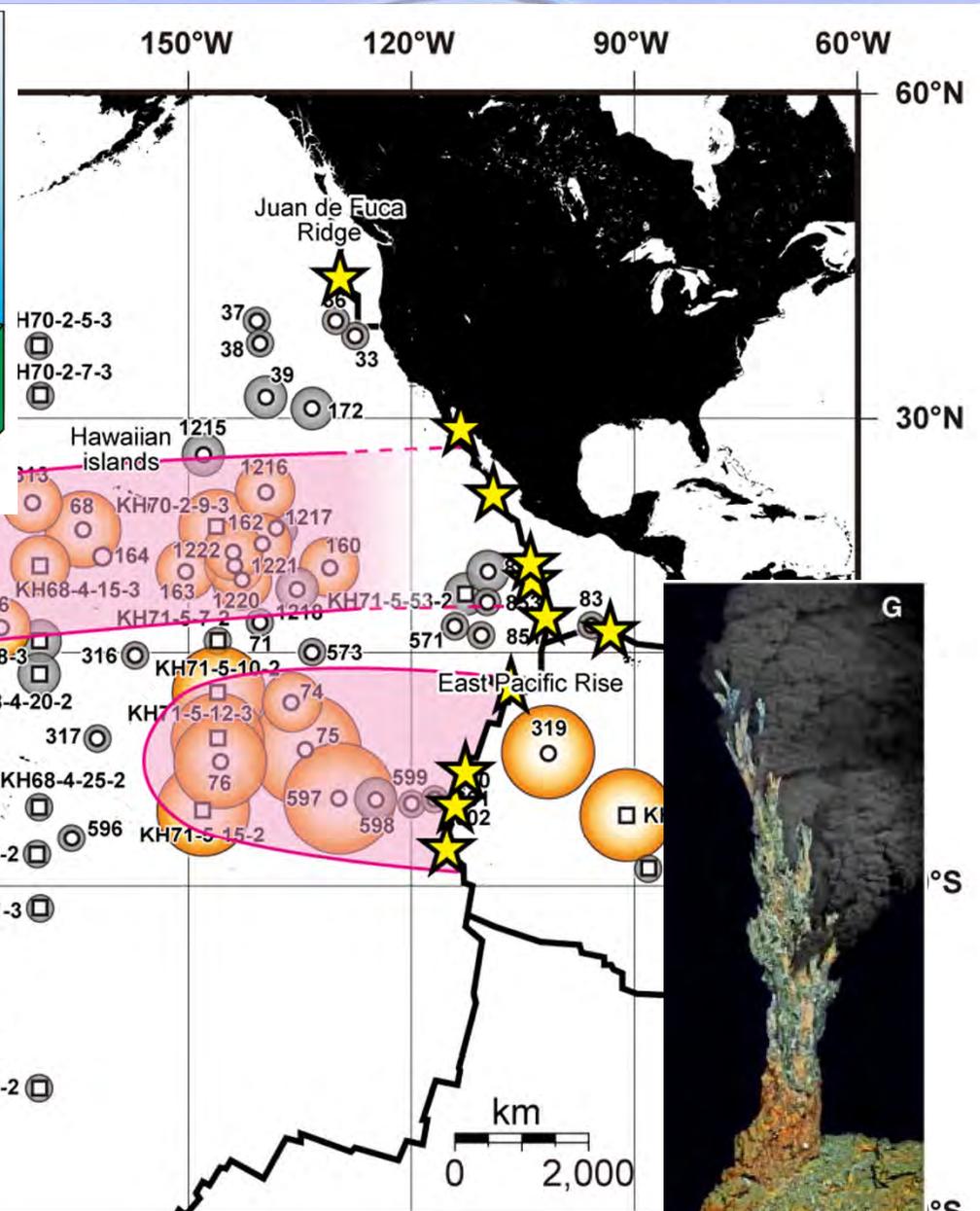
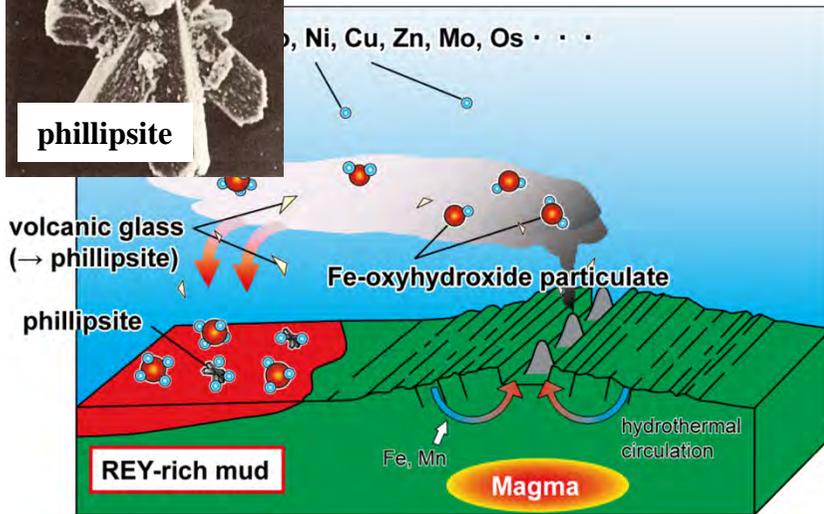
Distribution of REY-rich mud (< 2m in depth)



Depth profiles of REY-rich mud (< 50m)

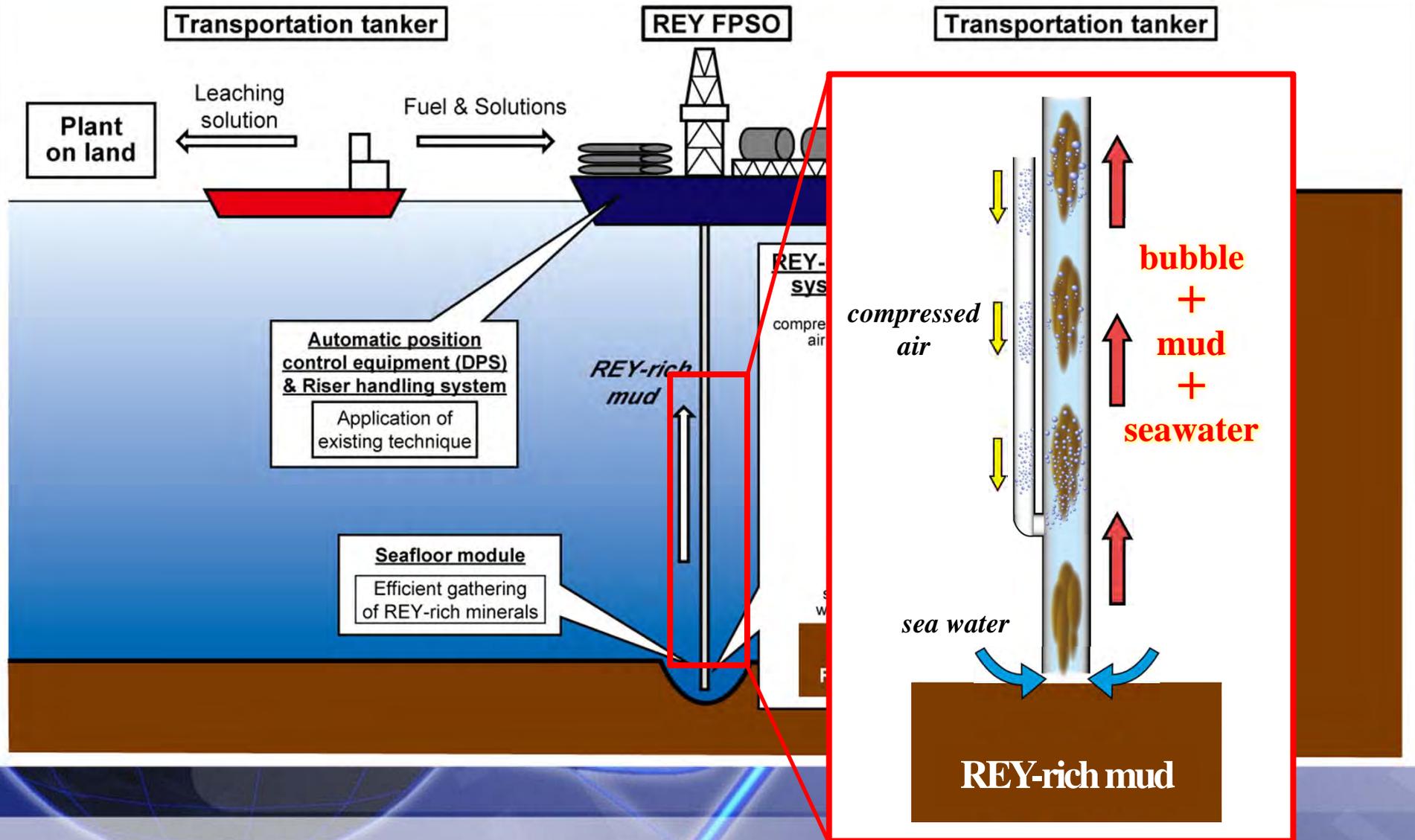


Formation of REY-rich mud



Development system of REY-rich mud

(collaboration with MODEC and Mitsui & Co., Ltd.)



Resource value of REY-rich mud at Site 76

Assuming ~3 million tons of mud lifted up
by one mining ship per a year

Amount of REY available

700 m x 700 m x 10 m x 0.66 g/cm³ x 1,178 ppm*

- Total amount of REY \doteq **3,600 t** (as oxide)
- Amount of Dy \doteq **145 t** (as metal)

(*Assuming that extraction rates of REY are 97% except for Ce (25%) and a separation efficiency of the solution from mud is 95%)

Annual REY consumption of Japan

- Total amount of REY : **30,000 t** (as oxide) \rightarrow **12 %**
- Amount of Dy : **700~800 t** (as metal) \rightarrow **18~21 %**

~1 billion US dollars in the present price**

(**Based on the prices as of April, 2012)