Artificial chemical weathering of basaltic rock under the earth surface conditions of the present and the Proterozoic era

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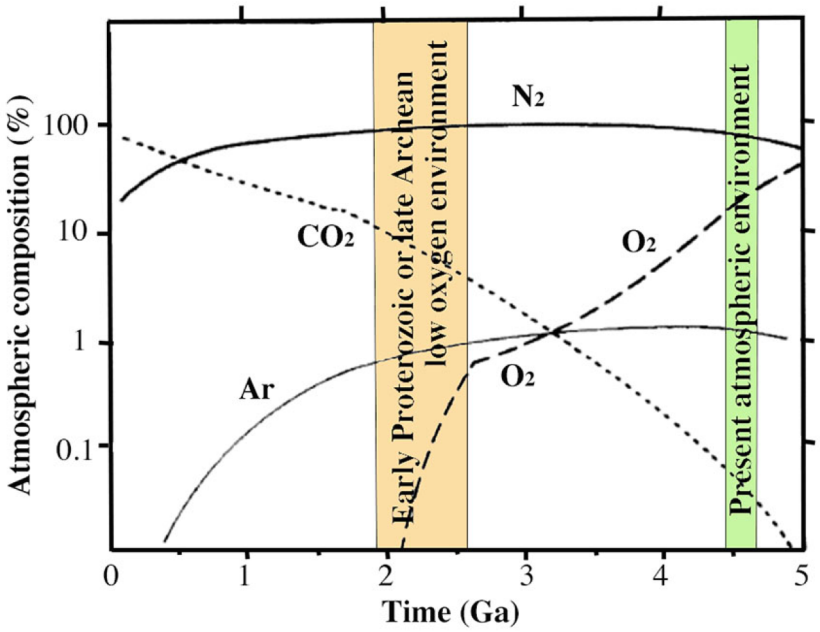
In order to compare the mineral chemical effects of acid rain on surface materials in the present oxygen level and the early Proterozoic or late Archean low oxygen before Great Oxidation Event.



The probable evolution of atmospheric O_2, CO_2, N_2 and Ar over time (modified from Tajika, E. and Matsui, T. , Pro. 25th ISAS Lunar Planet. Symposium, (1992), 178-183.).

Earth surface Environment of the early Proterozoic or late Archean

<Rock type on the crust: basaltic rock>

*Flood basalt studies (e.g. Pilbara) showed that basalt had been covered even on the early earth surface (e.g., Armstrong *et al*. Earth Planet. Sci. Lett., 101(1990), 90-106.).

<Atmospheric composition: high P_{CO2} with N_2>

*The major composition was CO_2 and N_2, and Cl, N_2 and S were also contained by influence of volcanic activity (L.A. Frankes *et al*. Cambridge Univ. Press., (1992), 274 pp., E. Tajika & T. Matsui. Lithos 30 (1993), 267-280.).

*O_2 concentration were estimated based on studies such as banded iron formation and uranium mineralization (P. Cloud. Am. Jour. Sci. 272 (1972), 537-548).

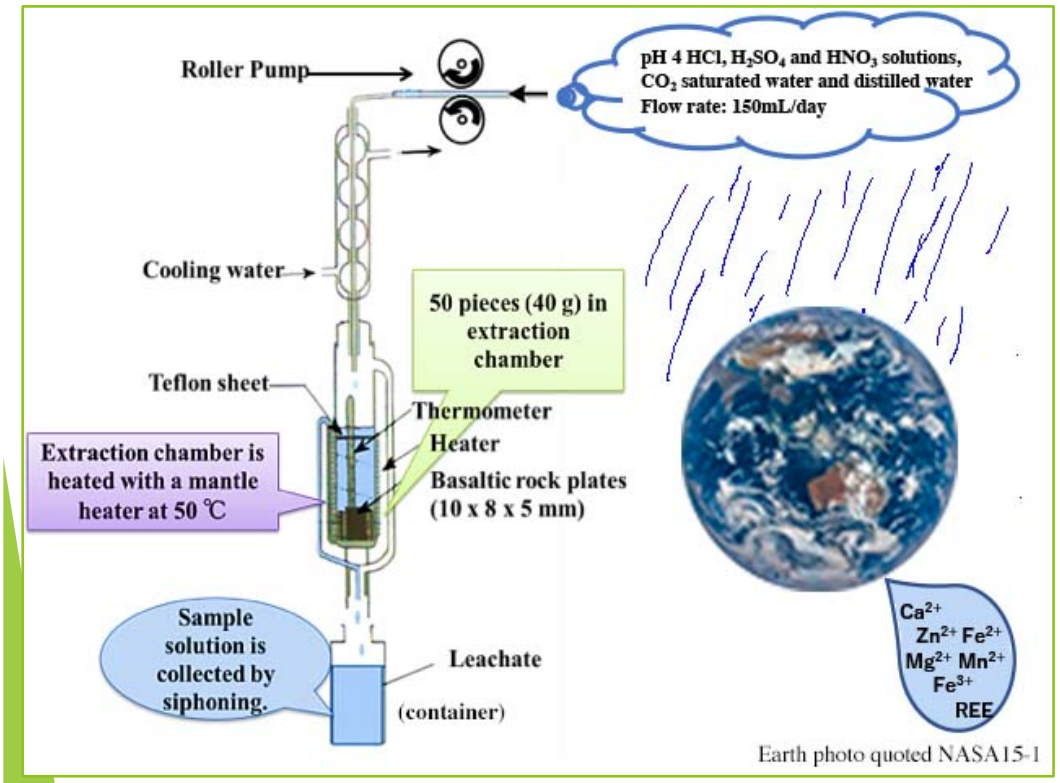
<Rain water: pH of rainwater was low >

Estimated from the atmospheric composition at the time.

Experimental methods

We have conducted experiment under **the present oxygen*** and **the low oxygen**** conditions, respectively.

Experimental image



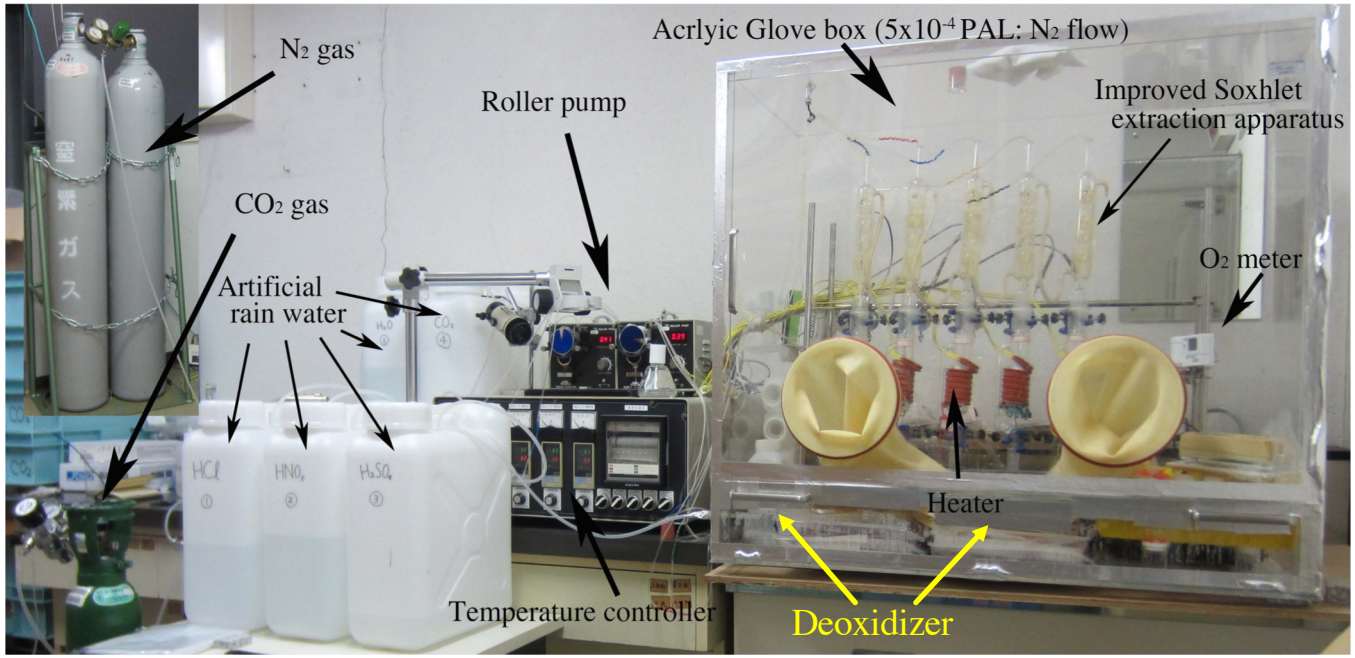
Schematic illustration of the Soxhlet extraction apparatus, which has been improved to an open system and can be imagined as rain on-and-off.

The artificial chemical weathering experiment under the present oxygen was conducted in a room environment.

The sample for the artificial weathering experiments is basalt in both experiments.

Basalt sample after 950 days reaction with pH4H_2SO_4 in the extraction chamber.

**Artificial weathering experiment under low oxygen environment

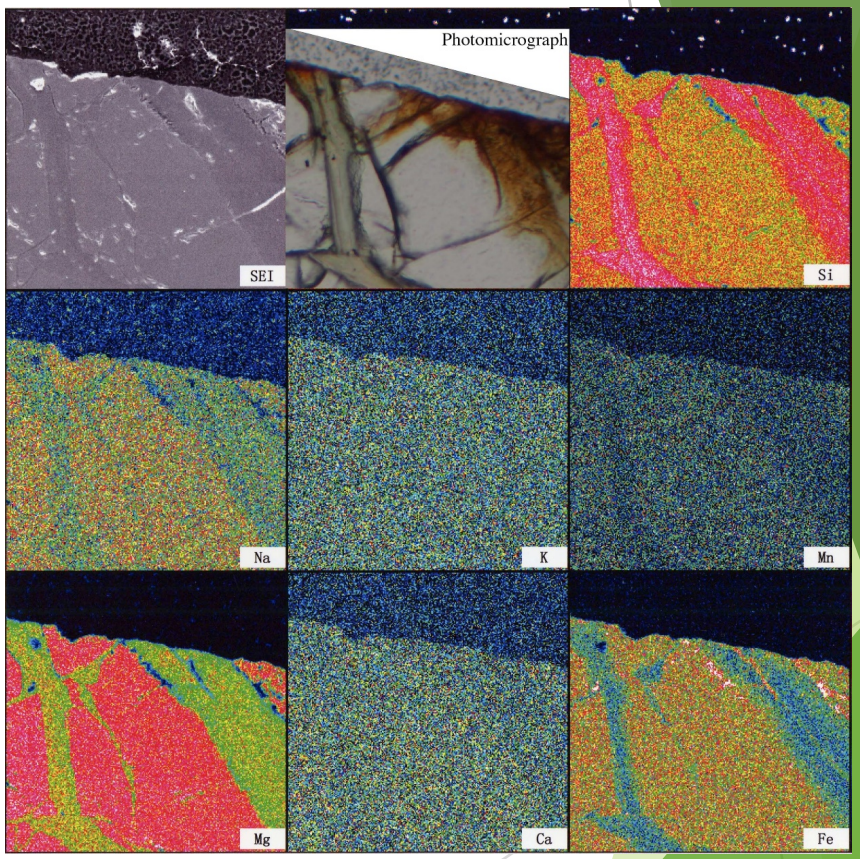


Photograph of the experimental equipment under 0.01% oxygen (<5 x 10^{-4} PAL) in N_2 atmosphere.

Apparatus: Soxhlet extractor, which can be ***imagined as rain on-and-off***, was improved to ***an open system*** with N_2 flow.
O_2 concentration: 0.01% oxygen (< 5 x 10^{-4} PAL)_with **deoxidizer**
Basalt sample: about 50 polished pieces of 10 x 8 x 5 mm size (40 g)
Artificial rain water: HNO_3, H_2SO_4 and HCl solutions at pH 4, and CO_2 saturated water, and distilled water after bubbling with N_2 gas.
Flow rate (drip amount) of the rain water: 150 mL/day
Temperature: 50 °C, **Duration**: different period of time up to 950 days

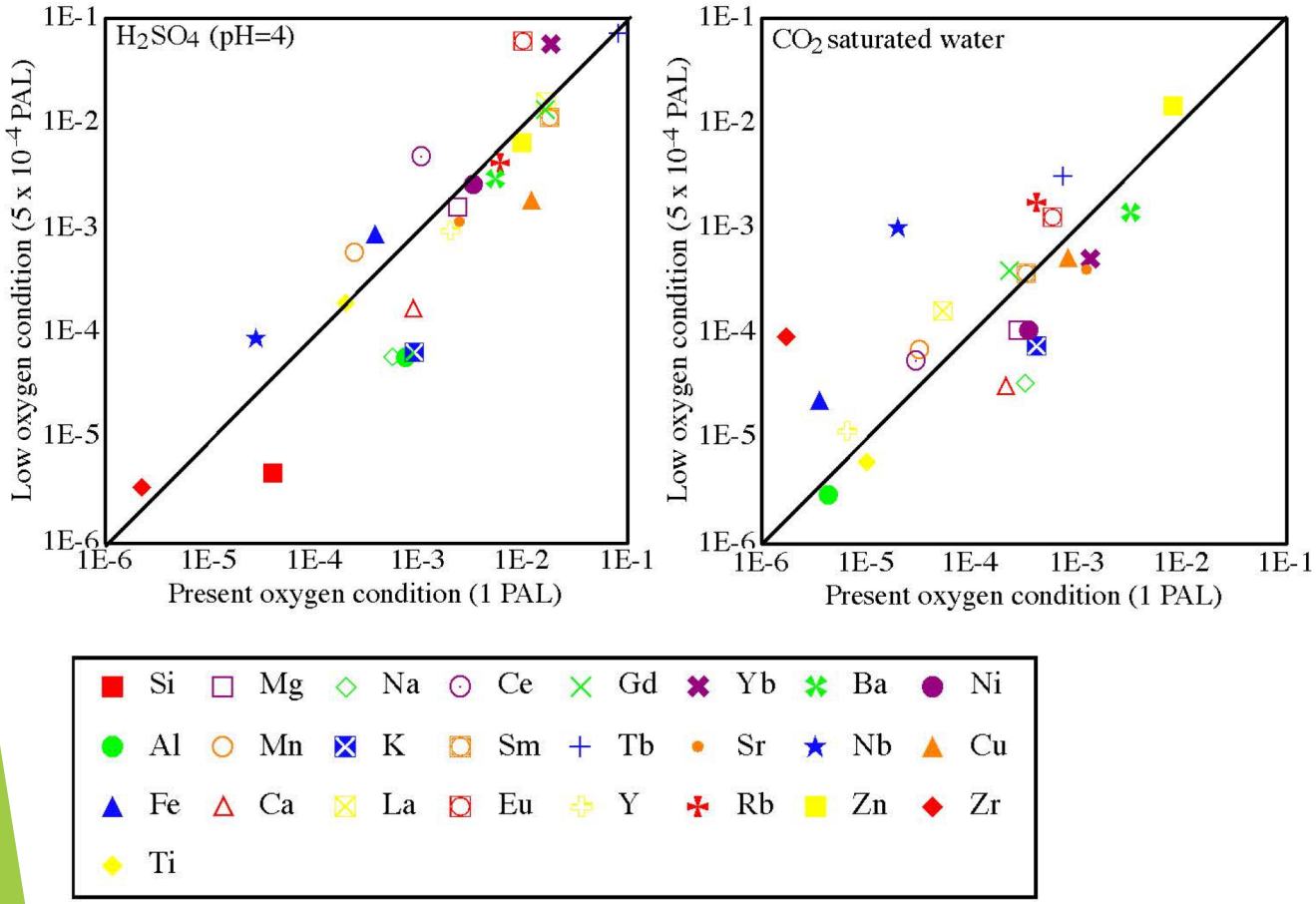
Altered products

Under the present oxygen environment, A part of olivine has changed to chlorite and akaganeite (FeO(OH)) as altered products by pH 4 H_2SO_4 treatment.



Mapping data of olivine surface after 347 days by pH4 H_2SO_4. The width of each field is 50 micrometers.

Comparison of the logarithmic molar ratios*** of extracted elements with rain water under the present oxygen and the low oxygen conditions.



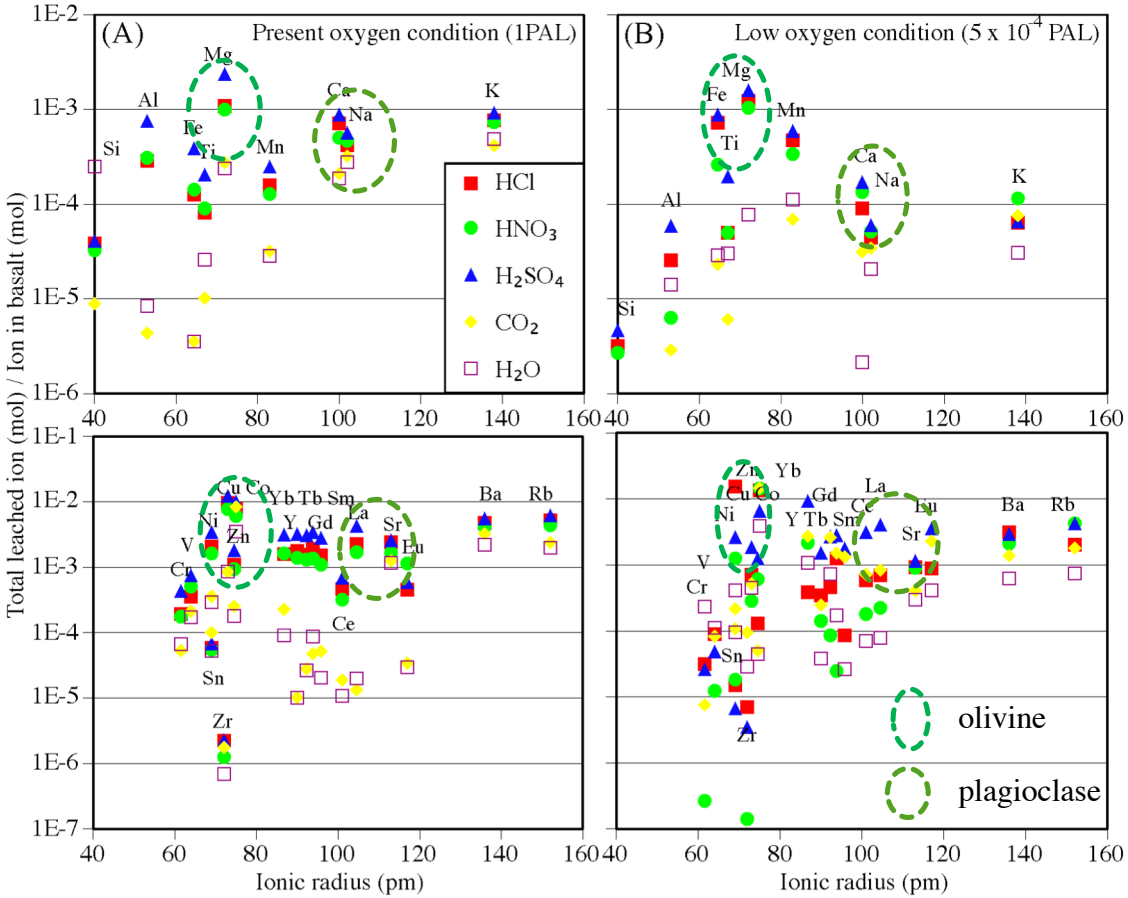
Logarithmic molar ratios of Fe and Mn are high (easy to extract) relatively under the low oxygen rather than present oxygen environment.

High field strength (HFS) elements tend to be easily extracted in any solution in the low oxygen environment. This tendency is remarkable when treated with CO_2 saturated and distilled water.

Under a low oxygen environment, Ce and Eu in REE tend to be easily extracted.

*** Molar ratio is calculated by dividing the cumulative total mole of each extracted element by the mole of individual element in the unaltered basaltic rock.

The relation between the logarithmic molar ratios and ionic radius under present (A) and low (B) oxygen environments.



In both environments, the ratios of Fe, Mg, Ni, Zn and Co near 70 pm in ionic radius are high, and reflect the dissolution from the octahedral coordination of olivine. On the other hand, mineral surface and chemical changes indicate that the extraction from CPX is low.

The high ratio of Ca, Na, Ce, La, Eu and Sr near 100-120 pm, which are occupied in the cavities within the framework, reflect the dissolution of plagioclase.

These results indicate that the first step in the weathering of basalt by acid solutions is the dissolution of olivine and plagioclase. The molar ratios of many elements indicate that the reactivity of the solution to the basalt is approximately pH 4 H_2SO_4, HCl and HNO_3, and CO_2 saturated water and distilled water.

Elements abundant in seafloor mineral resources.

Manganese nodule

周期＼族	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H <1																	He
2	Li 10	Be 2											B 25	C	N	O	F	Ne
3	Na 1	Mg 1											Al <1	Si <1	P 1	S <1	Cl <1	Ar
4	K 1	Ca <1	Sc <1	Ti 1	V 3	Cr <1	Mn 161	Fe 1	Co 90	Ni 217	Cu 378	Zn 19	Ga 1	Ge <1	As 64	Se	Br <1	Kr
5	Rb <1	Sr 1	Y 7	Zr 3	Nb 9	Mo 520	Tc	Ru 10	Rh 43	Pd 2	Ag 2	Cd 150	In <1	Sn <1	Sb 185	Te 43200	I <1	Xe
6	Cs 79	Ba 6	※1	Hf 2	Ta <1		Re	Os 37	Ir 19	Pt 97	Au <1	Hg <1	Tl 338	Pb 41	Bi 177	Po	At	Rn
7	Fr <1	Ra <1	Th 5	U 8														

※1 rantanoide	La 2	Ce 12	Pr 32	Nd 2	Pm	Sm 2	Eu 29	Gd 1	Tb 52	Dy 1	Ho 23	Er 1	Tm 71	Yb <1	Lu <1

Manganese crust

周期＼族	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H <1																	He
2	Li <1	Be 2											B 13	C	N	O	F	Ne
3	Na <1	Mg <1											Al <1	Si <1	P 8	S 5	Cl 49	Ar
4	K 1	Ca 1	Sc 1	Ti 2	V 5	Cr <1	Mn 163	Fe 2	Co 283	Ni 91	Cu 40	Zn 9	Ga 1	Ge 1	As 72	Se (3)	Br 28	Kr
5	Rb <1	Sr 3	Y 7	Zr 3	Nb 6	Mo 374	Tc	Ru 12	Rh 115	Pd 1	Ag (4)	Cd 49	In (10)	Sn 1	Sb 161	Te 8000	I <1	Xe
6	Cs (1)	Ba 4	※1	Hf 3	Ta 1	W 107	Re	Os 24	Ir 50	Pt 305	Au 1	Hg 12	Tl 378	Pb 67	Bi 177	Po	At	Rn
7	Fr <1	Ra <1	Th <1	U 8														

※1 rantanoide	La 10	Ce 25	Pr 22	Nd 8	Pm	Sm 11	Eu 9	Gd 7	Tb 13	Dy 16	Ho 9	Er 15	Tm <1	Yb 9	Lu 11

Hydrothermal sulfide ore

周期＼族	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li <1	Be <1											B <1	C	N	O	F	Ne
3	Na <1	Mg <1											Al <1	Si 1	P <1	S 879	Cl <1	Ar
4	K <1	Ca 3	Sc <1	Ti <1	V <1	Cr <1	Mn 1	Fe 5	Co 36	Ni 1	Cu 3370	Zn 4361	Ga <1	Ge <1	As 180	Se <1	Br <1	Kr
5	Rb <1	Sr 3	Y <1	Zr <1	Nb <1	Mo 118	Tc	Ru <1	Rh <1	Pd <1	Ag 3786	Cd 11075	In <1	Sn <1	Sb 1160	Te <1	I <1	Xe
6	Cs <1	Ba 200	※1	Hf <1	Ta <1	W <1	Re	Os <1	Ir <1	Pt <1	Au 3169	Hg <1	Tl <1	Pb 300	Bi <1	Po	At	Rn
7	Fr	Ra <1	Th <1	U <1														

※1 rantanoide	La <1	Ce <1	59 Pr <1	Nd <1	Pm	Sm <1	Eu <1	Gd <1	Tb <1	Dy <1	Ho <1	Er <1	Tm <1	Yb <1	Lu <1

<Numerical values show the ratio with rock on the surface.>

200	Very high
50	High
10	Slightly high

海底鉱物資源。オーム社／
Cronan(2000)/Hein(1997), Hannington(1995)/Usui,Someya(1997)

One consideration of the relationship between the extracted elements and the sea water

Material supply to the oceans is primarily thought to come from the continental and oceanic crust, the Earth's interior, and the atmosphere.
Based on the results of this study, one consideration of supply of elements is shown below, using Mn deposits on the seafloor as an example.

Mn, Mg, Cu, Zn, Ni, Co and some RE elements are shown relatively easily extracted from basalt in this research.
Among them, Mn, Ni, Co and REE are more abundant in manganese nodule and crust than in hydrothermal deposits.
This study suggests that it is important to consider the weathering of materials near the earth surface for the supply of resources.
Moreover, Fe, Mn, and Zn, which are easily extracted from basalt under the low oxygen condition.

The results of this study are expected to provide basic data for research on material supply to the ocean from the early Earth to the present.

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Hammington, M.D. & Jonasson, I.R. (1995) Seafloor Hydrothermal Systems, 115-157.
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