

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 with those in the early Proterozoic low oxygen environments, artificial chemical weathering experiments using an improved Soxhlet extraction apparatus were conducted for basalt, which had been covered even on the early earth surface. Some dozens of polished basalt plates put in the reaction chamber were reacted to HCl, H₂SO₄ and HNO₃ solutions at pH 4, and CO₂ saturated water, and distilled water at 50 °C for a different period of time up to 970 days in an open system. In the experiment under the low oxygen condition ($< 5 \times 10^{-4}$ PAL), the whole extraction apparatus was placed in the acrylic glove box, and oxygen was removed by the deoxidizer, and it was carried out in the nitrogen gas flow condition. The basalt was composed mainly of olivine as a phenocryst, and plagioclase, clinopyroxene, ilmenite and glass as a groundmass. The extracted solutions were collected, and analyzed using ICP-MS. Morphological, chemistry and altered products of each mineral surface were studied by SEM, EPMA, XRD and microscopy techniques.

Under both the low and the present oxygen conditions, SEM images showed that the dissolution of olivine surface by the H₂SO₄, HNO₃ and HCl solutions is remarkable. The (Mg + Fe) / Si on the olivine surface and (Na + Ca + K) / (Al + Si) on the plagioclase surface decreased significantly with increasing experimental period. In chemistry of the extracted solutions, molar ratios of Mg, Mn, Fe and so on were high by three kinds of acidic solutions at pH 4, and low by CO₂ saturated water and distilled water. The molar ratio is calculated from the cumulative total mole of released elements divided by the mole of individual elements in the unaltered basaltic rock. The ratio of Fe, Mg, Ni, Zn and Co near 70 pm in ionic radius is high, and reflect the dissolution from the octahedral coordination of olivine. The ratios of Ca, Na, Sm, Ce, La and Sr near 110 pm is high, and reflect the dissolution from the cavities within the framework of plagioclase. Under the low oxygen condition, major elements such as Fe and Mn, and minor one such as Zn tend to dissolve easily. Ce and Eu in REE, and Nb, Ce, Ti, Y and Zr in HFS elements are soluble in pH 4 HCl and H₂SO₄, CO₂ saturated water and distilled water under the low oxygen condition. Elements that are easily extracted under the low oxygen early Proterozoic environment were transported to the ocean, suggesting that they may have been involved in the evolution of the ocean and the formation of BIF and manganese nodules.

Keywords: artificial chemical weathering; low and present oxygen conditions; basalt.

1. Introduction

Minerals and rocks in the earth crust are altered by

dissolution, oxidization and hydration brought by contact with oxygen, carbon dioxide and rainwater under the natural environment. If the amount of oxygen in the atmosphere is constant as it is now, the alteration is controlled by climatic factors such as temperature, precipitation, chemical composition, and pH of rainwater. However, when considering the history of the earth for 4.6 billion years, the oxygen concentration was not constant.

To date, various investigations have gradually revealed the environment of the early Proterozoic era. Matsui and Tajika (1990) showed temporal changes in surface temperature based on solar luminosity, effective temperature, surface temperature assuming constant atmospheric composition (Kasting, 1987), and global carbon cycle model. Cloud (1972), Frankes et al. (1992), and Tajika and Matsui (1993) showed that compositions of the early Proterozoic atmosphere were mainly CO₂, chlorine, nitrogen and sulfur. Hart (1978) and Kasting (1987) estimated the evolution of CO₂ in the atmosphere and showed that the CO₂ content in the Proterozoic was much higher than the present. Furthermore, Tajika and Matsui (1992) showed that nitrogen has been one of the major atmospheric compositions since the early stage of Earth formation and is constant at about 1 atm.

Shikazono (2008) has summarized the evolution of oxygen concentration with geological time based on various geological data such as Detrital pyrite, Banded Iron Formation (BIF) and rhabdophane. The gradual change in the composition of volatiles added to the atmospheric-ocean system has been proposed to be the 'Great Oxidation Event (GOE)', which occurred between about 2.4 and 2.0 (Ga) in the early Proterozoic (e.g., Holland, 2002, 2006). The GOE caused a gradual increase in atmospheric oxygen concentration.

On the other hand, Armstrong et al. (1990) and Taylor and McLennan (1995) mentioned that more than 60% of the continental crust had already formed in the early Proterozoic. Enomoto (2006) also showed same mentions and summarized distribution of flood basalt at the late Archean to the early Proterozoic. Volcanic activity was prominent, as shown by the flood basalt, and that the atmosphere and seawater contained chlorine, nitrogen, sulfur and CO₂ components, as shown by Rubey (1951), Cloud (1972), Hattori et al (1983) and Shikazono (2008).

Therefore, pH of rainwater and P_{CO2} of atmosphere of the Proterozoic may be somewhat lower and higher than the present, respectively.

Many experimental studies have been known so far on the effects of weathering alteration of rocks and minerals on the global environment in the present oxygen condition (e.g. Kobayashi et al., 2005, Kobayashi et al., 2016). However, although the earth surface condition under the low oxygen condition in the Precambrian era is becoming known, there are few studies on the weathering alteration of the surface material under the low oxygen environment.

Consequently, in this study, artificial weathering experiments using HCl, H₂SO₄ and HNO₃ solutions at pH 4, CO₂ saturated water and distilled water on basalt were carried out under conditions that reproduced the so-called early Proterozoic environment, which was composed mainly of nitrogen with low oxygen. In order to clarify the influence on the formation of the global environment, the alteration process of basalt, the behavior of extracting elements and the movement of substances are examined, while comparing with the results under the present oxygen condition. Then, it was thought that this comparative study under both present and early Proterozoic environments would provide basic data to elucidate the evolution process of the global environment.

2. Material and experimental methods

Basaltic rock from Mt. Yuyama, Shizuoka Prefecture, Japan used in this study. The basaltic rock is classified as picritic basalt, which belong to ocean island basalt (Matsumoto et al., 2015). The chemical composition of the basalt was analyzed by X-ray fluorescence (XRF, Rigaku RIX-2100) and ICP-MS (Analyzed by Actlabs Co., LTD., Canada), and its main component minerals analyzed by electron microprobe analyzer (EPMA, JEOL JXA-8230) are shown in Table 1. The modal composition is approximately 70.8 % olivine (Fo₈₉Fe₁₁) as a phenocryst, and 12.0 % plagioclase (An₅₄Ab₄₅Or₁), 16.2 % clinopyroxene (En₃₄Fs₃₂Wo₃₄), 0.7 % volcanic glass with minor amounts of opaque minerals such as ilmenite in groundmass.

An improved Soxhlet extraction apparatus was used in this study to image rainfall. Fig. 1A shows a schematic illustration of the apparatus for conducting

Table 1. Chemical composition of basalt and its composed minerals

Basalt		Composed minerals in basalt			
wt%	wt%	Olivine	Plagioclase	Clinopyroxene	Glass
SiO ₂ 40.74	SiO ₂ 40.42	54.53	50.19	57.63 - 47.05	
Al ₂ O ₃ 8.61	Al ₂ O ₃ 0.05	27.00	2.10	4.20 - 6.81	
TiO ₂ 1.51	TiO ₂ 0.02	0.14	1.12	0.04 - 0.61	
Fe ₂ O ₃ 12.21	Cr ₂ O ₃ 0.13	0.00	0.05	0.00 - 0.02	
MnO 0.16	MgO 47.8	0.19	11.19	18.62 - 26.25	
MgO 20.57	CaO 0.24	11.06	15.76	0.31 - 3.64	
CaO 7.39	MnO 0.19	0.01	0.40	0.00 - 0.13	
Na ₂ O 1.18	FeO ¹⁾ 10.75	—	18.81	8.89 - 13.28	
K ₂ O 0.10	Fe ₂ O ₃ ²⁾ —	0.85	—	—	
P ₂ O ₅ 0.11	Na ₂ O 0.00	5.14	0.29	0.19 - 0.20	
Total 92.58	K ₂ O 0.03	0.23	0.05	0.24 - 0.28	
	Total 99.63	99.15	99.96		
	ppm	Atomic ratio ³⁾			
V 209.0	Ba 99.0	Si 1.000	9.996	1.933	
Cr 2070	La 8.9			15.83	2.000
Co 197.0	Ce 22	Al ^{IV}	5.833	0.066	
Ni 960.0	Sm 2.9				
Cu 130.0	Eu 1.0	Al ^{VI} 0.001		0.029	
Zn 90.0	Gd 2.9	Ti 0.000	0.019	0.032	
Ga 12.0	Tb 0.5	Mg 1.762	0.051	0.643	
Rb 5.0	Yb 1.1	Mn 0.004	0.001	0.013	
Sr 203.0	Hf 2.3	Fe 0.222	1.998	0.058	4.180
Y 13.0	Ta 7.8	Cr 0.002	0.000	0.605	1.998
Zr 95.0				0.001	
Nb 16.0		Ca 0.006	2.172	0.651	
Sn 136.0		Na 0.000	1.826	0.022	
		K 0.001	0.053	0.002	

- 1) Total Fe as FeO for olivine and clinopyroxene.
- 2) Total Fe as Fe₂O₃ for plagioclase.
- 3) O=4 for olivine, O=6 for clinopyroxene, and O=32 for plagioclase.

experiments under low oxygen condition in the early Proterozoic environment. The extraction apparatus was placed in an acrylic glove box (120 x 100 x 80 cm). Oxygen was removed by the deoxidizer, and nitrogen gas was flowed. The oxygen concentration in the box was kept at 5×10^{-4} PAL (0.01% O₂) or less and checked with an oxygen indicator during the experiment. Experiment on the present oxygen environment was conducted in room conditions. Basalt plate was cut from a fresh block with a diamond blade and polished to provide specimen. The dimensions of each plate were about 10 x 8 x 5 mm. Forty plates weighing about 40 g were put in the reaction chamber of the four apparatuses, and four other apparatuses without the plates were used as control. The reaction chamber was heated with a mantle heater at 50 °C during the experiment. HCl, HNO₃ and H₂SO₄ solutions at pH 4, and distilled water (about pH 6.5) for reference were prepared by bubbling nitrogen gas in a polyethylene reservoir tank and deoxygenating the solutions. CO₂ saturated water (pH 5.8 at about 50°C) made using carbon dioxide gas (Fig. 1B). The five fresh solutions, which were stocked in the reservoir tank, were dripped on a specimen covered by a Teflon sheet in each apparatus using a roller pump with a rate of flow of 150 mL/day.

Each solution was reacted with the platy specimen in the reaction chamber. The reactions ran until about 50 mL of solution could be collected in the reaction chamber of the apparatus. Then, the extracted solution was collected by siphoning into a container. The solution was never return to the reaction chamber. The procedure was repeated three times a day. This can be compared to natural conditions where sporadic rain can occur. Namely, the process is similar to combine flow method and batch method. The artificial chemical weathering was carried out for various times up to 951 and 970 days under low and present oxygen conditions, respectively.

Artificially weathered sample plates were taken out of each apparatus and compared with the starting material using microscope, and X-ray diffractometer (XRD) and microbeam diffractometer (PSPC-MDG, Rigaku RINT-2500V). Chemical and morphological analyses of the plate surface were performed on

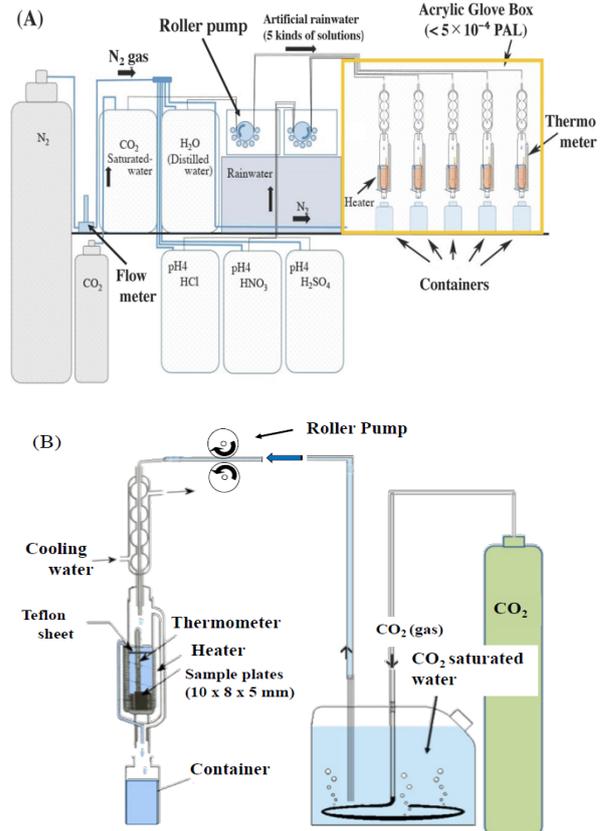


Fig. 1. Schematic illustrations of an experimental device under a low oxygen condition ($< 5 \times 10^{-4}$ PAL) using an acrylic glove box (A), and a method for preparing CO₂ saturated water, and an improved Soxhlet extraction apparatus (B). PAL, present atmospheric level.

an energy-dispersion spectrometer and scanning electron microscope (SEM-EDS system, JEOL JSM-5410LV SEM equipped with a JEOL JED-2140 EDS).

Samples of the extracted solution, which was stored in the container over a 3-day period, were collected every 3 days for the first 30 days, and then at 30-day intervals between 30 days and 150 days, and at 45- or 90-days intervals for the remaining experimental periods. Major and minor elements were analyzed by an inductively coupled plasma mass spectrometer (ICP-MS, SII, SPQ-9700). The amount of the release of elements is shown by molar ratios calculated from the cumulative total mole of

released elements divided by the mole of individual elements in the starting materials of untreated basaltic rock (see the appendix of Kobayashi et al., 2016).

3. Results

3-1 Basalt plate

A part of the basalt plates disintegrated into small fragments and individual minerals during the artificial chemical weathering experiments under the present and low oxygen conditions. The degree of dissolution of the mineral surface increases with the reaction time under the both conditions, especially olivine and plagioclase surface. As shown in the SEM images of Fig. 2, the effects of three kinds of pH 4 acidic

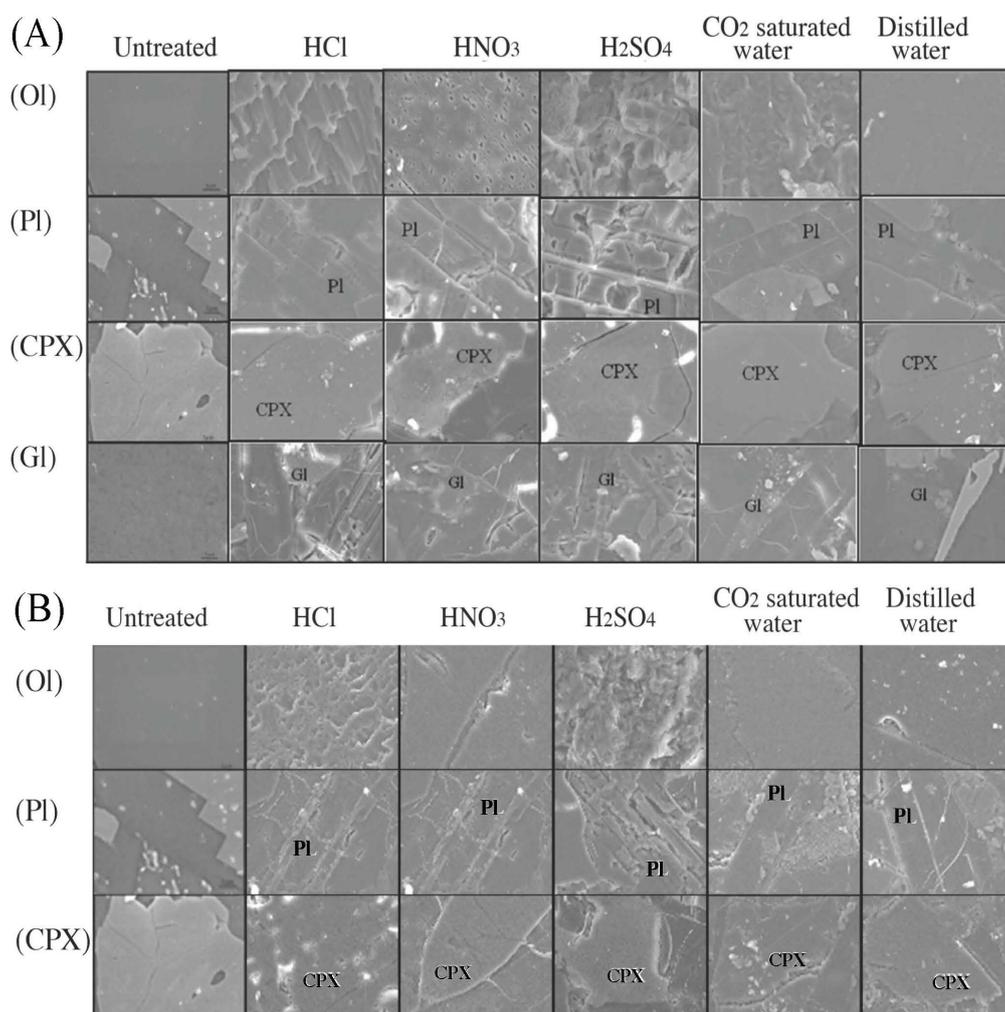


Fig. 2. SEM images of olivine (Ol), plagioclase (Pl), clinopyroxene (CPX) and volcanic glass (Gl) on basalt surface by artificial weathering using each solution. (A) After 675 days under the present oxygen condition (1 PAL). (B) After 747 days under the low oxygen condition ($< 5 \times 10^{-4}$ PAL). Each image is 40 μ m on the left and right.

solutions on olivine and plagioclase surfaces in basalt under both conditions are more remarkable with HCl and H₂SO₄ solutions than with HNO₃ solutions under the present (Fig. 2A) and low (Fig. 2B) oxygen conditions. Numerous irregular fractures forms on the olivine and plagioclase, but not shows on clinopyroxene surface. Dissolution proceeds along cleavages and cracks in the crystals. Olivine and plagioclase dissolve slightly in CO₂ saturated water and distilled water but clinopyroxene surface is hardly dissolved.

Fig. 3 show the chemical changes on the surface of each mineral as a function of reaction time, with (Mg

+ Fe) / Si (apfu) for olivine and clinopyroxene and (Ca + Na) / (Al + Si) (apfu) ratios for plagioclase. In the both present and low oxygen conditions, these ratios decrease with an increase in duration. Especially, olivine surface changed remarkable by pH 4 H₂SO₄ and HCl treatment as well as SEM image. The change of the ratio in plagioclase was initially significantly reduced by the three acid solutions in the present condition (Fig. 3A) and gradually changed in the low oxygen condition (Fig. 3B). The ratio of clinopyroxene tends to be decreased by H₂SO₄ in the present condition and by HCl in the low oxygen condition, but there is not much change.

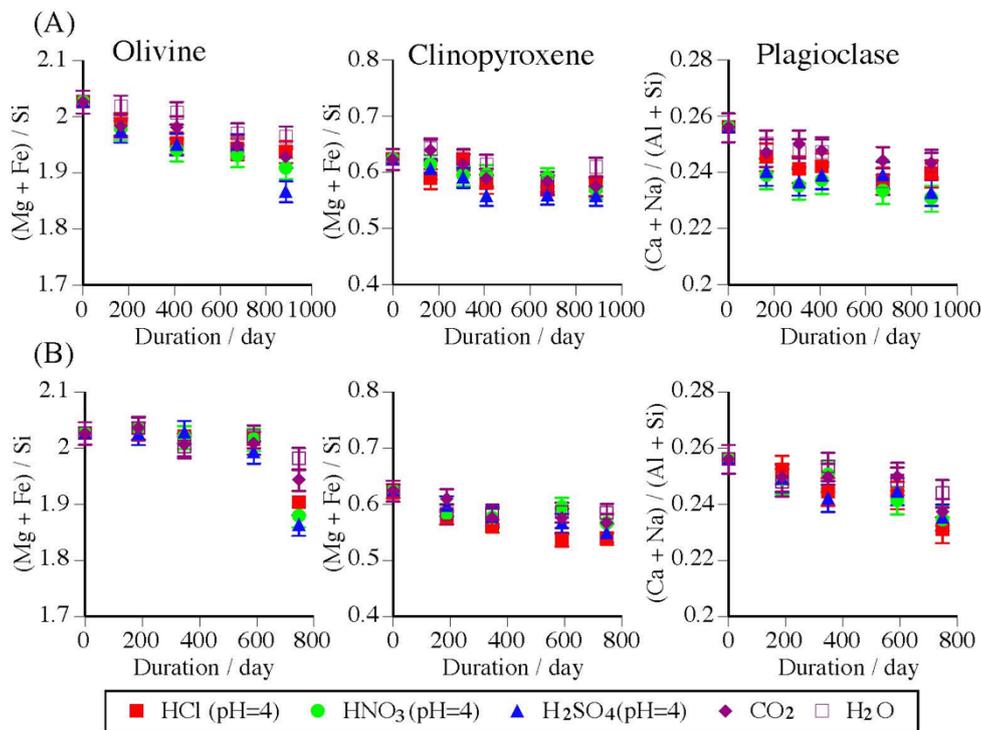


Fig. 3. Change of chemistry for olivine, clinopyroxene and plagioclase surfaces during weathering by each solution under the present (A) and low (B) oxygen conditions. Each bar shows distribution range of data.

3-2 Altered product

In the experiment with H₂SO₄ at pH 4 under the present oxygen condition, a formation of orange colored secondary mineral was confirmed on the surface of phenocryst olivine after 400 days. Experiment using a PSPC-MDG revealed that the altered minerals were mainly akaganeite and chlorite, and the chemical analysis by EPMA also showed the possibility of iron hydroxide.

Smectite was found on the groundmass. According to SEM image (Fig. 2) and chemistry (Fig. 3) on each mineral surface, plagioclase is most likely the source for smectite. On the other hand, altered product did not determine under the low oxygen condition.

3-3 Extracted chemical species

The major and minor elements released from the basalt

as a function of extracting time under the present and the low oxygen conditions are shown in Figs. 4 and 5, respectively. The release of elements is shown by the molar ratio as mentioned above. In the present oxygen condition, the elements with high molar ratios were Mg, K and Na of major element, and Cu, Zn, Rb and Ba of minor element. On the other hand, in the low oxygen condition, the molar ratios of Mg, Mn and Fe of major element, and Zn and Ni of minor element were relatively high in the reaction with three kinds of acidic solutions. In the CO₂ saturated water and distilled water, Mg, K, Mn, Zn and Rb, and Mn, Mg and Zn are relatively high, respectively. The molar ratio of Zn is relatively high in all solutions.

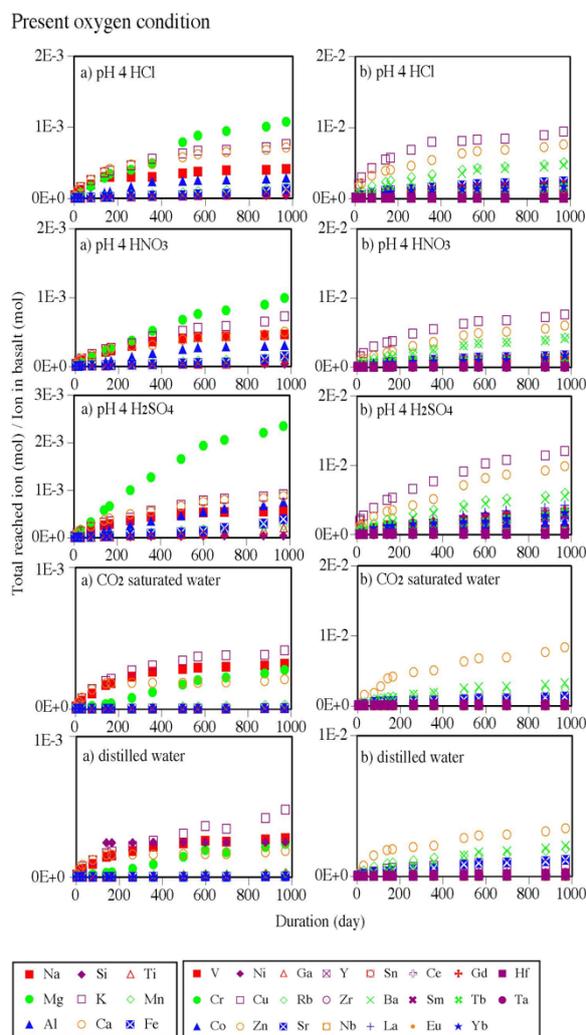


Fig. 4. Molar ratios of each element in the five kinds of extracted solutions to basalt versus duration up to 970 days under the present oxygen condition (1 PAL).

Low oxygen condition

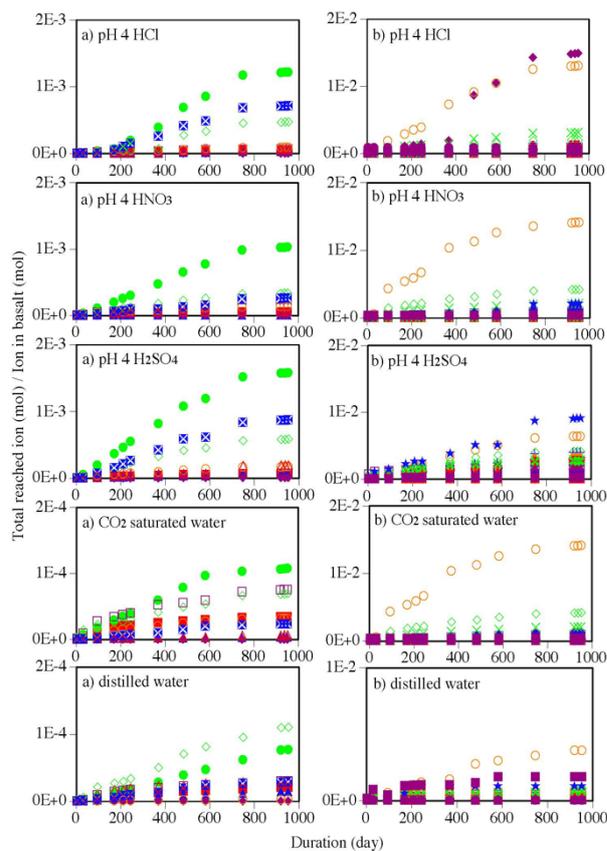


Fig. 5. Molar ratios of each element in the five kinds of extracted solutions to basalt versus duration up to 951 days under the low oxygen condition ($< 5 \times 10^{-4}$ PAL). Legend is the same as Fig. 4.

4. Discussion

The following is a comparative study of the results obtained by artificial weathering experiments under the present oxygen (1 PAL) and low oxygen ($< 5 \times 10^{-4}$ PAL) conditions.

Fig. 6 shows that the molar ratio of Fe and Mn is relatively high under the low oxygen condition rather than the present oxygen condition due to the reaction with pH 4 three kinds of acidic solutions, CO₂ saturated water and distilled water. The molar ratios used in the figures were the data at the end of the experiment on day 970 in Fig. 4 under the present oxygen condition and on 951 in Fig. 5 under the low oxygen condition, and were shown in logarithmic notation. Similarly, Fig. 7 shows that Nb, Ce, Zr, etc., which are classified as high field strength (HFS) elements among incompatible elements, tend to dissolve easily in each solution under the low oxygen condition. This tendency is remarkable when treated with carbon dioxide and distilled water. However, large-ion lithophile

(LIL) elements such as Sr, K, Rb and Ba tended to dissolve in the present oxygen condition. The relationships for elements related to marine mineral resources such as banded iron formation (BIF) and Mn nodule are also shown in Fig. 8. The Fe, Mn, and Zn tended to dissolve easily in each solution under the low oxygen condition. As shown in Fig. 9, Ce and Eu in rare-earth elements (REE) tend to dissolve easily in a low oxygen condition in all solutions except HNO₃. The molar ratio of REE under the present oxygen condition is small only for H₂SO₄ treatment among the three kinds of acid solutions. It may have been absorbed by smectite formed only under this condition.

The behavior of Fe, Mn, and Ce among the extracting elements obtained in this experiment was discussed with reference to the E_h-pH diagram in the system metal-H-O at 25°C shown by Nakada et al. (2013). Considering that the pH of the 5 kinds of solutions used in this study was in the range of 4 to 6.5, Fe precipitates in a range where the redox potential is higher than the line connecting E_h (pH) at 0.2 (6) to 0.8 (3). It is shown that Fe and Ce, and Mn, Fe and Ce are removed from the solution in a

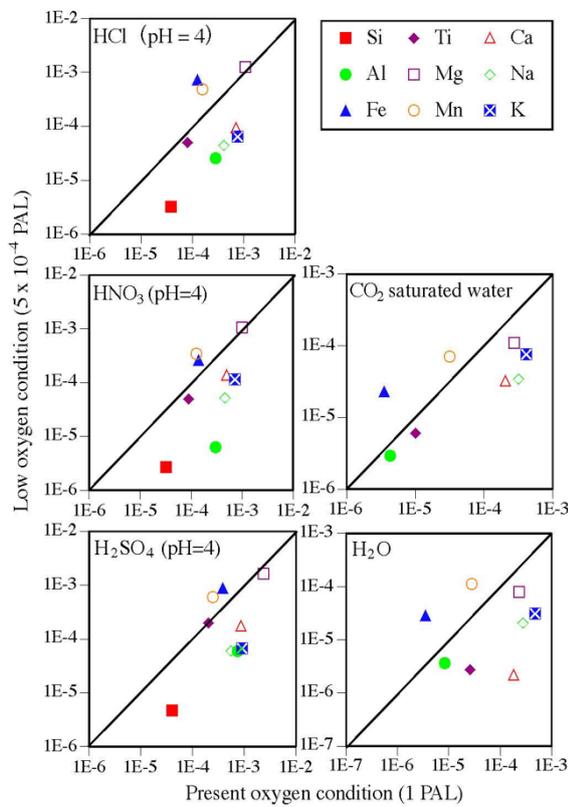


Fig. 6. Comparison of the logarithmic molar ratios of each major element extracted into five solutions under the present and the low oxygen conditions.

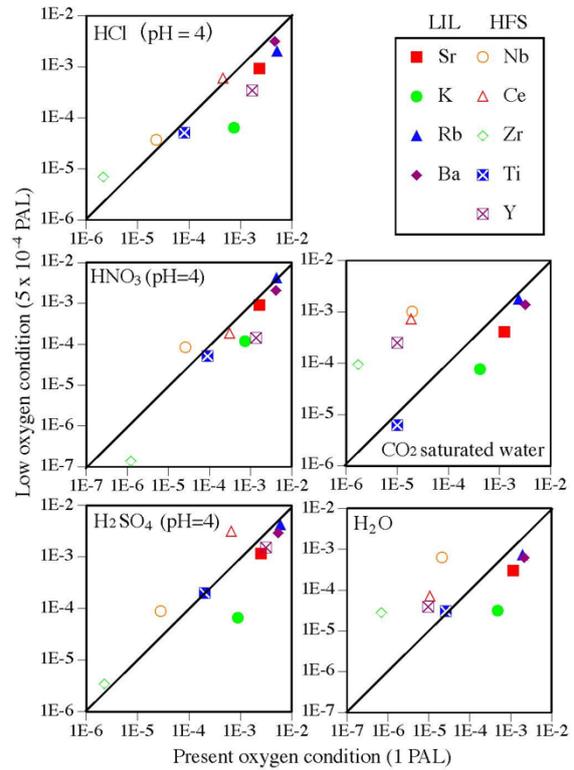


Fig. 7. Comparison of the logarithmic molar ratios of each incompatible element extracted into five solutions under the present and the low oxygen conditions.

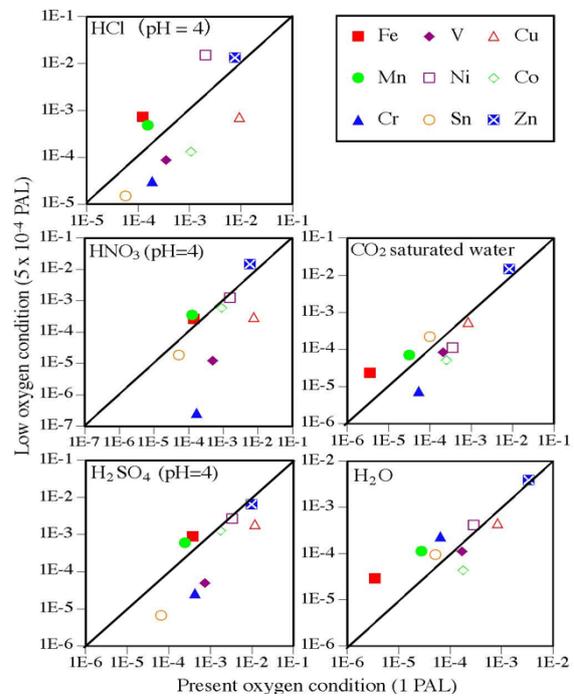


Fig. 8. Comparison of the logarithmic molar ratios of each element related to marine mineral resources extracted into five solutions under the present and the low oxygen conditions.

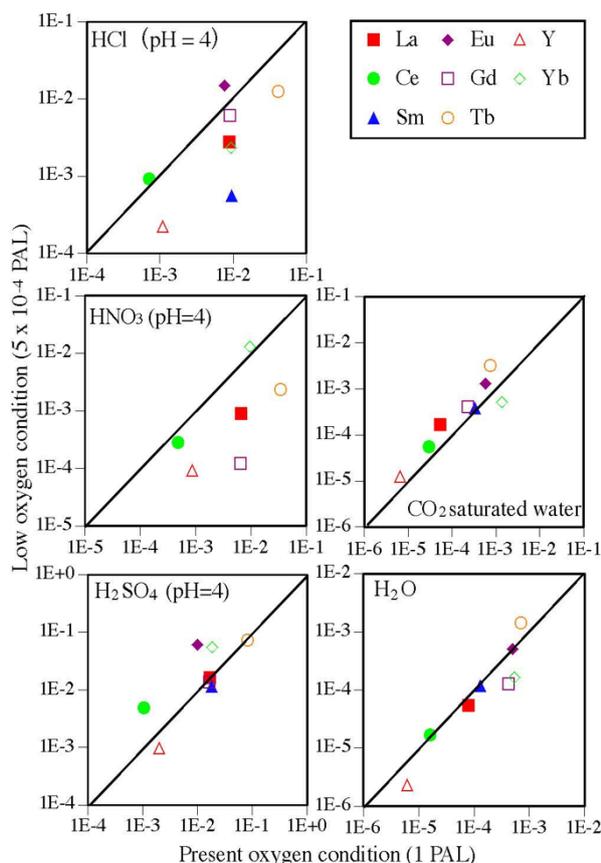


Fig. 9. Comparison of the logarithmic molar ratios of each rare earth element extracted into five solutions under the present and the low oxygen conditions

range higher than the line connecting 0.4 (6) and 0.9 (4), and the line connecting 0.7 (6) to 1.0 (4), respectively. The molar ratios of Fe, Mn, and Ce are higher in the low oxygen condition than in the present oxygen condition for any solutions. This indicates that the experiment was conducted under the low E_h condition where Fe did not precipitate, it is shown that these elements were extracted out more than under the present oxygen condition. However, the behavior of Ce in HNO_3 solution is not clear.

Akaganeite is formed on the olivine surface by H_2SO_4 treatment at pH 4 under the present oxygen condition. The crystallization of such iron hydroxide is consistent with the E_h -pH relationship diagram of Fe by Usui et al. (2015), which crystallizes in the range of E_h 0.7 to 0.9 around pH 4, and Fe extracts out when E_h is less than 0.7.

The molar ratios of elements released during reaction with the five kinds of solutions are plotted against

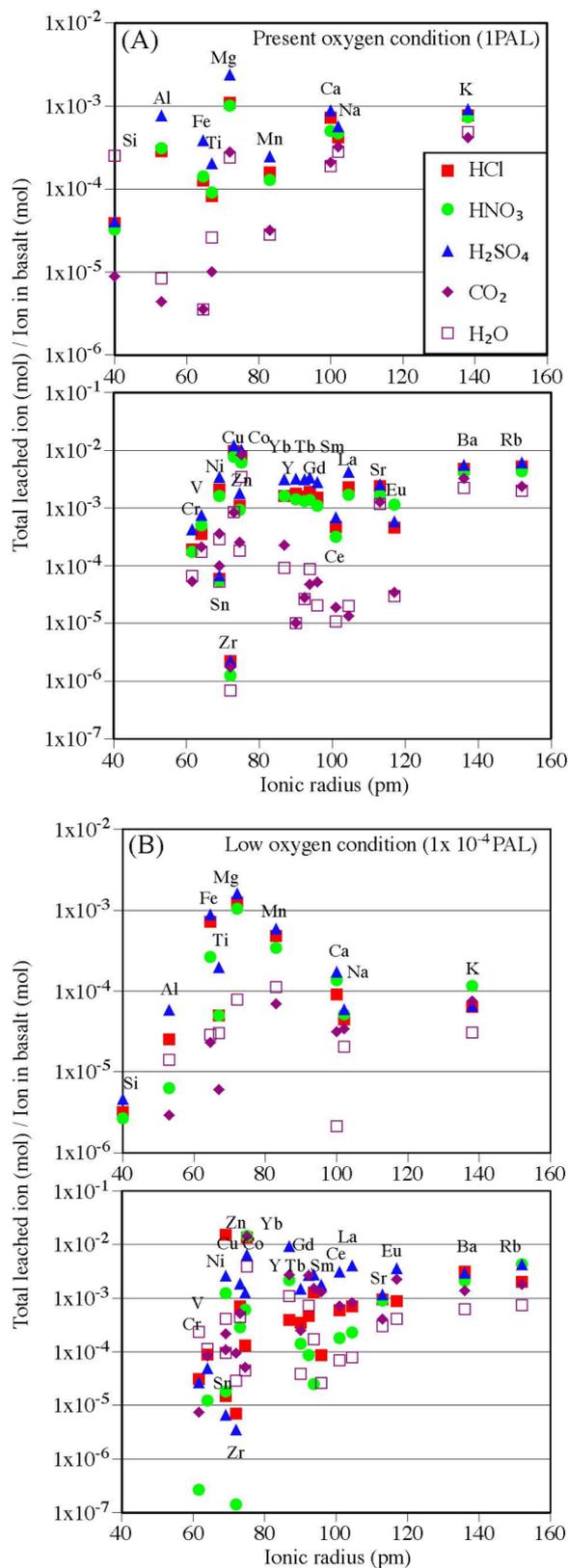


Fig. 10. The relation between the molar ratios and ionic radius under the present (A) and the low oxygen (B) conditions.

ionic radius (Fig. 10). The ratios clearly vary with the elements. The ratios having an ionic radius near 75 pm and 100 pm are relatively high for both under the present (Fig. 10A) and the low oxygen conditions (Fig. 10B). These are near the ionic radii of the main constituent elements except Si of olivine, and clinopyroxene, and Si and Al of plagioclase. The high ratios of elements such as Mg, Mn, Fe, Ni, Zn, Cu and Co near 75 pm, which dominant in the octahedral coordination, reflect the dissolution of olivine as discussed in previous reports (Kobayashi et al., 2005). Although clinopyroxene also contains these elements as the main constituents, the mineral is hardly affected chemically and morphologically by the artificial weathering. The high ratios of Ca, Na, Sr, Ce, Sm, Gd and La (i.e. near 100 pm), which are occupied in the cavities within the framework, reflect the dissolution of plagioclase (Kobayashi et al., 2016). These results indicate that the first step in the weathering of basalt by acid solutions is the dissolution of olivine and plagioclase. The ratios in Fig. 10 also indicate that the reactivity order of the solutions for olivine is pH 4 H₂SO₄, HCl and HNO₃, CO₂ saturated water and distilled water. The major elements Ca and Na of plagioclase show the order of H₂SO₄, HNO₃, HCl, CO₂ saturated water and distilled water.

Usui (2010) summarized the elements contained in manganese nodules and submarine hydrothermal sulfide ore based on the data of Cronan (2000), Hein et al. (1997), Hannington and Jonasson (1995) and Usui and Someya (1997). On the other hand, in this study, it was shown that Mg, Mn, Fe, Cu, Zn, Ni, Co, and REE (e.g., Ce, La, Tb, Eu), which tend to occupy into the structure of olivine and plagioclase in basalt, were easily extracted, although they differ somewhat depending on the oxygen concentration. This suggests that these elements were supplied to the ocean from before the early Proterozoic era. Among these elements, Mn, Ni, Co and REE are richer in manganese nodules than in hydrothermal ore deposits. In particular, Mn, which is easily soluble under the low oxygen condition, has been supplied from before the early Proterozoic. Furthermore, since Mn is hardly contained in hydrothermal sulfide deposits, it is highly probable that weathering of basalt is one of the important sources of Mn.

It was shown experimentally that Fe, Mn and Zn, which is abundant in BIF, which is one of the marine mineral resources, is extracted under low oxygen condition before the Proterozoic era rather than the

present oxygen condition. It was considered that these elements were easily extracted into seawater from basalt that covered the continent at that time under low oxygen condition and contributed to the formation of BIF with the subsequent environmental changes.

5. Conclusion

In order to investigate the effects of acid rain on basalt under the present oxygen and low oxygen conditions, artificial chemical weathering was conducted and the following results were obtained.

- 1) The SEM images of olivine and plagioclase treated with pH 4 H₂SO₄ and HCl showed that they changed from the initial stage of the reaction in both conditions. Along with this, the (Mg + Fe) / Si and (Ca + Na) / (Si + Al) molar ratios of the olivine and plagioclase surfaces also decreased.
- 2) In experiments with pH 4 H₂SO₄ under the present oxygen condition, formation of akaganeite and chlorite was observed on the olivine surface, and smectite was observed on the groundmass surface mainly composed of plagioclase.
- 3) Fe and Mn as major elements, Zn as marine mineral resource, Nb, Ce, Zr, Ti and Y as HFS elements, and Ce and Eu as rare earth elements in the basalt tend to be easily extracted by the three kinds of acid solutions under the low oxygen condition. The same tendency is shown for major elements in CO₂ saturated water and distilled water. However, the elements related to HFS and marine mineral resources are easily dissolved under the low oxygen condition. In particular, REE tended to be easily extracted by CO₂ saturated water.
- 4) It was suggested that extracted elements and alteration products from basalt influenced the evolution of the chemical composition of continental and seawater under both the present and low oxygen conditions and were involved in the formation of Mn nodules and BIF.

The results of this study are expected as basic data for research that considers the global environment.

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References

- Armstrong, R.A., Compston, W., de Wit, M.J. and Williams, I.S. (1990) The stratigraphy of the 3.5 – 3.2 Ga Barberton greenstone belt revisited: a single zircon ion microprobe study. *Earth and Planetary Science letters*, 101, 90-106.
- Cloud, P. (1972) A working model of the primitive Earth. *American Journal of Science*, 272, 537-548.
- Cronan, D.S. (2000) *Hand book of marine mineral deposits*, CRC Press.
- Enomoto, N. (2006) The oldest continental flood basalt: Aspects from geology, petrology and geochemistry of the Mount Roe Basalt and related rocks of the Pilbara craton, Western Australia, Master thesis, Tokyo Institute of Technology.
- Frankes, L.A., Francis, J.E. and Syktus, J.I. (1992) *Climate models of the phanerozoic*. Cambridge University Press, pp.274.
- Hannington, M.D. and Jonasson, I.R. (1995) Physical and chemical processes of seafloor mineralization at mid-ocean ridges. *Seafloor Hydrothermal Systems*, American Geophysical Union Geophysical Monograph, 91, 115-157.
- Hart, M.H. (1978) The evolution of the atmosphere of the Earth. *Icarus*, 33, 23-39.
- Hattori, K., Campbell, F.A. and Krouse, H.R. (1983) Sulphur isotope abundances in Amphibian clastic rocks: Implications for the coeval atmosphere. *Nature*, 302, 323-326.
- Hein, J.R., Koschinsky, A., Halbach, P., Manheim, F.T., Bäu, M., Kang, J-K. and Lubick, N. (1997) Iron and manganese oxide mineralization in the Pacific. *Manganese mineralization: Geochemistry and mineralogy of terrestrial and marine deposits* (Nicholson, K., Hein, J.R., Buhn, B. and Dasgupta, S., eds.). Geological Society, London, Special Publications, 119, 123-138.)
- Holland, H.D. (2002). "Volcanic gases, black smokers, and the great oxidation event". *Geochimica et Cosmochimica Acta*. 66, 3811–3826.
- Holland, H.D. (2006) The oxygenation of the atmosphere and oceans. *Philosophical Transactions of Royal Society*, B 361, 903-915.
- Kasting, J.F. (1987) Theoretical constraints on oxygen and carbon dioxide concentrations in the Precambrian atmosphere. *Precambrian Research*, 34, 205-229.
- Kobayashi, S., Sakamoto, T. and Yamaguchi, K. (2005) Artificial chemical weathering of gabbro under earth surface conditions -The influence of acid rain on rocks and minerals (Part 4) -. *Clay Science*, 12, 367-377.
- Kobayashi, K., Baba, Y., Kanayama, A., Naohara, J., Sakamoto, T. and Kitaoka, K. (2016) Artificial chemical weathering of plagioclase by acidic hydrothermal solutions. *Journal of Hot Spring Sciences*, 66, 89-106.
- Matsui, T. and Tajika, E. (1990) Evolution of proto- CO₂-atmosphere on the Earth, *Lunar Planet. Sci.*, XXI, pp. 740-741, Lunar and Planetary Institute, Houston.
- Matsumoto, H., Wada, H. and Kusunoki, K. (2015) Character of the Miwa-Takayama Picrite basalts with pillow lava in the Setogawa tectonic belt of Shizuoka Prefecture, central Japan. *Geoscience Reports Shizuoka Univ.*, no. 42, 51-61 (in Japanese with English abstract).
- Nakada, R., Takahashi, Y. and Tanimizu, M. (2013) Isotopic and speciation study on cerium during its solid-water distribution with implication for Ce stable isotope as a paleo-redox proxy. *Geochimica et Cosmochimica Acta*, 103, 49-62.
- Rubey, W.W. (1951) Geologic history of seawater: an attempt to state the problem, *Bulletin of the Geological Society of America*, 62, 1111-1147.
- Shikazono, N. (2008) Earth's surface environment of Archean – Carbon dioxide, oxygen and methane partial pressures -. *Japanese magazine of mineralogical and petrological sciences*, 69-77 (in Japanese with English abstract).
- Tajika, E. and Matsui, T. (1992) Evolution of the atmosphere of the Earth. *Proceeding 25th ISAS Lunar and Planetary Symposium*, 178-183.
- Tajika, E. and Matsui, T. (1993) Degassing history and carbon cycle of the Earth: From an impact-induced steam atmosphere to the present atmosphere. *Lithos*, 30, 267-280.
- Taylor, S.L. and McLennan, S.M. (1995) The geochemical evolution of continental crust. *Reviews of Geophysics*, 33, 241-265.
- Usui, A. (2010) *Kaitei kobutsu shigen*, Ohmsha, pp. 198 (in Japanese).
- Usui, A., Takahashi, Y., Ito, T., Maruyama, A. and Suzuki, K. (2015) *Geoscience of marine manganese deposits*. University of Tokyo Press, pp.246 (in Japanese).
- Usui, A. and Someya, M. (1997) Distribution and composition of marine hydrogenetic and hydrothermal manganese deposits in the northwest Pacific. *Manganese mineralization: Geochemistry and mineralogy of terrestrial and marine deposits* (Nicholson, K., Hein, J.R., Buhn, B. and Dasgupta, S., eds.). Geological Society, London, Special Publications, 119, 177-198.