MINERALOGICAL AND MORPHOLOGICAL FEATURES OF FRACTURED GRANITIC ROCK TESTED UNDER WATER-ROCK INTERACTION

Abdelrahman Abdelgawad [1], *Kunio Watanabe* [2], *and Mizuno Takashi* [3]

[1] *Department of Civil Engineering, Assiut University, Asyut, Egypt,*
E-mail: abdo_gawad2003@yahoo.com
[2] *Geosphere Research Institute, Saitama University, Saitama, Japan,*
Email: kunio@mail.saitama-u.ac.jp
[3] *Tono Geoscience Center, Japan Atomic Energy Agency, Japan,*
E-mail: mizuno.takashi@jaea.go.jp

ABSTRACT

Chemical analysis of the Water-rock interaction showed that hydrothermal altered rock contains large amount of fluoride. Considering that alteration has mainly occurred at the fractures' cleavages, the aim of this paper is to investigate the change of the mineral composition between the cleavages and other parts of the granite surfaces. Scanning electron microscope with energy-dispersive spectrometry has been used in order to identify the change in the morphology and mineralogy of the minerals crystal that occurs on the natural surface of the rock specimens due to water-rock interaction. Second sub aim is to detect the change in the mineral composition between treated and untreated altered granitic rock specimens with water-rock interaction test. However fluoride amount might be in less concentration in biotite, experiments show that the precipitation of fluoride in the cleavages occurs in biotite mineral. This phenomenon might be due to the migration of hydrothermal water causing chloritization of biotite. Scanning Electron Microscope (SEM) study of the altered fractured granitic rock indicated deposition of new minerals (fluorite) on the cleavages surfaces after water-rock interaction. One possibility might be due to dissolution of wollastonite.

Keywords: Granitic rock, water-rock interaction, fractures, mineralogy, morphology.
Received 16 April 2015.Accepted 8, February 2017
Presented in IWTC 18th

1 INTRODUCTION

Contaminated groundwater has been one of the most serious crises in the world. Contamination occurs naturally or due to human activity. In Tono area, Japan, high fluoride concentration has been observed during the construction of an Underground Research Laboratory (URL) called Mizunami Underground Research Laboratory (MIU).

Iwatsuki & Yoshida (1999) studied the mineralogy of fracture system in the deep granitic rock of the Tono area to understand the chemical evolution of groundwater. Geological studies revealed that the fracture system within the granitic rock is usually associated with hydrothermal alteration and the filling minerals are mainly chlorite-, montmorillonite-, and pegmatitic textures. The intensely fractured zones are associated with a strongly altered rock matrix, showing alteration to clay minerals such as kaolinite. Abdelgawad et al. (2009) performed water-rock interaction tests in order to understand the origin of fluoride content and it was clear that Fluoride ions mostly originated from fluoride-rich minerals like fluorite, and mica minerals. Iwatsuki et al. (2002) suggested the precipitation of fluorite in the fracture surfaces of altered Toki granite. Kim & Jeong (2005) reported that fluoride concentrations of groundwater are enriched with respect to fluorite (CaF_2) due to the removal of Ca by precipitation of calcite ($CaCO_3$). Abdelgawad et al. (2010) discussed the leaching of fluoride in groundwater from granitic aquifer within time. The correlations among fluoride, residence time, and coexisting ions have been investigated.

From the above phenomena, it is expected that fluoride rich minerals may precipitate on the cleavages of fracture surfaces of granitic rocks; however the behavior of clay minerals within the cleavages of fractures in granitic rock is not yet clearly discussed in the literature. Characterization of the fracture and its walls, whether relative to the morphology (topography, void patterns) or to the mineralogy (observation of minerals present), makes it possible to explain the fracture changes induced by water/rock interactions during the reactive percolation. Therefore, in this study we are trying to use Scanning electron microscope with energy-dispersive spectrometry (SEM-EDS) in order to investigate the fracture and cleavages surfaces of granitic rock samples before and after water rock interaction test, that might indicate deposition of new minerals on the fracture surfaces. Another objective is to investigate the changed morphology of the minerals occurs on the natural surfaces of the granitic rock specimens due to water-rock interaction test, as shown in Fig.1.

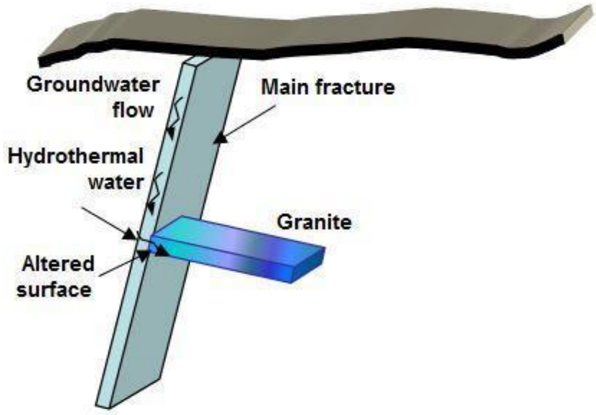


Figure 1. The effect of hydrothermal water on the fracture surfaces

2 STUDY AREA

The MIU of Japan Atomic Energy Agency has been constructing to investigate hydrochemistry of groundwater and mineralogy of crystalline rock in Mizunami city. Fig.2(a) shows the location of the MIU-site and the boreholes drilled in and around it. The MIU essentially consists of two 1000-m shafts (the main shaft and the ventilation shaft) and branch tunnels at two research levels (namely at 500 m and 1,000 m below the ground surface). To monitor the effect of shaft excavation on groundwater flow and groundwater chemistry, four shallow boreholes (MSB-1, 2, 3, and 4) and one deep inclined borehole (MIZ-1) were drilled at the site. Up to 2014 the two shafts have been excavated up to 500 m below the ground surface, as shown in Fig.2(b).

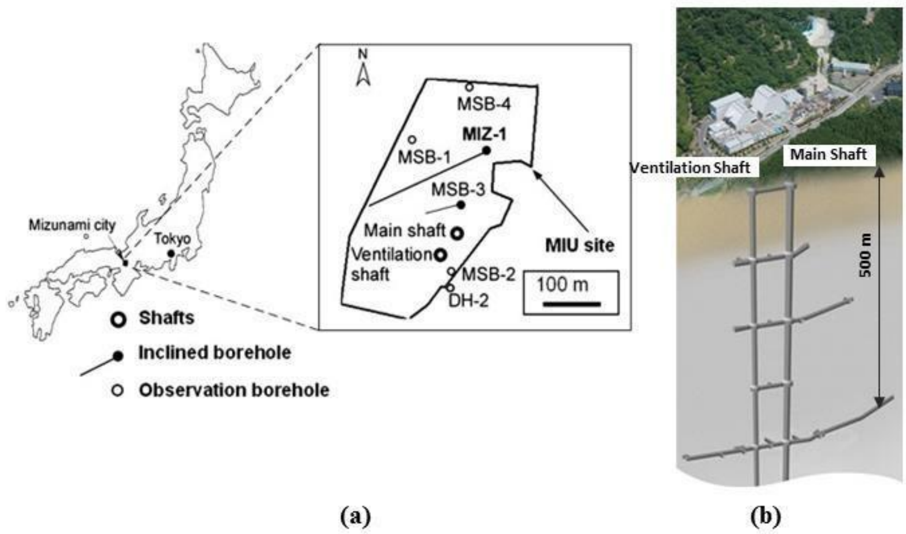


Figure 2. a) Location of the MIU site and the selected boreholes in and around the MIU construction site. b) Two Shafts excavation

2.1 Geology and hydrochemistry of the study area

The regional basement of the area around the site is mainly composed of granite called Toki Granite. The top of the Toki granite varies in elevation from 50 to 150 masl (meters above sea level) at- and around the MIU site. The basement is unconformably overlain by Tertiary sedimentary rocks with thicknesses varying from 100 to 180 m. A thin layer in the upper part of Toki granite is highly weathered and highly fractured. Geological studies revealed that the fracture system within the granitic rock is usually associated with hydrothermal alteration and it can be classified into three categories based on the degree of fracture, i.e. intact zones, moderately fractured zones, and intensely fractured zones (Iwatsuki & Yoshida 1999; Illman et al. 2009). Nakano et al. (2003) classified the structure of Toki granite based on the intensity of the fracture into two structural domains: the Upper Highly Fractured Domain (UHFD) and the Lower Sparsely Fractured Domain (LSFD). The thickness of the UHFD at the site was observed to be around 300 m.

Groundwater in granitic rock is classified as Na–(Ca)–Cl water-type and it is possibly controlled by mixing processes occurring between low salinity groundwater (Na– (Ca)–HCO3 water-type) in the sedimentary rocks and higher salinity groundwater (Na–(Ca)–Cl water-type) (Iwatsuki et al. 2005). The salinity source in the MIU area is assumed to have occurred when the region was flooded with seawater during marine transgression in the Miocene. The infiltrating rainwater has been flushing the old marinewater contained in the shallow part of granitic rock. Rainwater mainly infiltrates the area at higher altitude (recharge area) and flows down towards the area at lower altitude (discharge area). Old marine water is believed to flush more at the recharge area developing at the north of the site.

2.2 Mineralogy and morphology of granitic rock

The major minerals forming Toki granite are Quartz, feldspar, K-feldspar and biotite, associated with accessory minerals such as pyrite, ilmenite and zircon (Nakano et al. 2003). Sandström et al. (2010) found that the chloritization of biotite is one of the major mineral reactions associated with the alteration and some parts of the biotite have been replaced by clay mineral. Fig. 3(a) shows scanned photos of two granitic specimens collected from MIZ-1 borehole. One of the two specimens is slightly altered and the other one is highly altered granitic rock. Strong alteration of biotite to chlorite is observed in the tow photos. The brown- black biotite is the most dominant colors in the scanned photo. In the highly hydrothermal altered granitic specimen, green-spotted to dark green color was noticed. The green spotted is due to hydrothermal alteration of the biotite to chlorite.

Bisdom et al. (1982) stated that in the early stages of weathering, biotite often splits and opens out along cleavage planes. As in Fig.3(b) showing microscopic observations of the slightly and highly altered rocks, biotite mineral could be observed and the cleavages clearly occurred on the biotite surfaces of the altered granitic specimen. Chlorite and clay minerals are observed in the altered granite, and these minerals were generated by the interaction between rock and past hydrothermal water passing within fractured zones (Iwatsuki & Yoshida 1999).

SEM-EDS examination of the rock samples from MIU site showed that the particles mainly consist of Si, Al, S, K, Ca, and Fe. Fe-bearing aluminosilicates were a dominant mineral in the selected granitic rock specimens (Munemoto et al. 2014). The X-ray powder diffraction and EPMA analyses indicated that the carbonate minerals on the fracture surfaces are mainly calcite, enabling calcite-water isotopic fractionation relationships to be used in the interpretation (Yanagizawa et al. 1995).

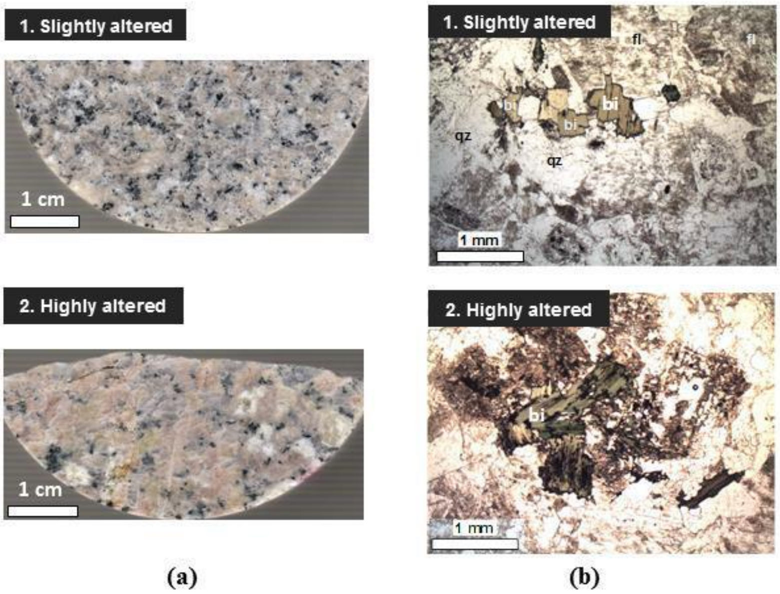


Figure 3. a) Scanning photo of rock specimens from MIZ-1 borehole. b) Optical microscopic photos of two rock specimens (Abdelgawad et al. 2009).

3 MATERIALS AND METHODS

3.1 Sampling

Three granitic rock samples were collected from the core of borehole MIZ-1; namely, MIZ1-G1, MIZ1-G2, and MIZ1-G3). Specimen MIZ1-G1 was collected from depth 131.0 meter around borehole and has been classified as slightly altered rock. Specimens MIZ1-G2 and MIZ1-G3 were collected from depth 654.5 meter around borehole and they have been classified as highly altered rock. The first specimen represents Upper highly fractured domain and the second and third specimens represent Low sparsely fracture domain of the granite aquifer.

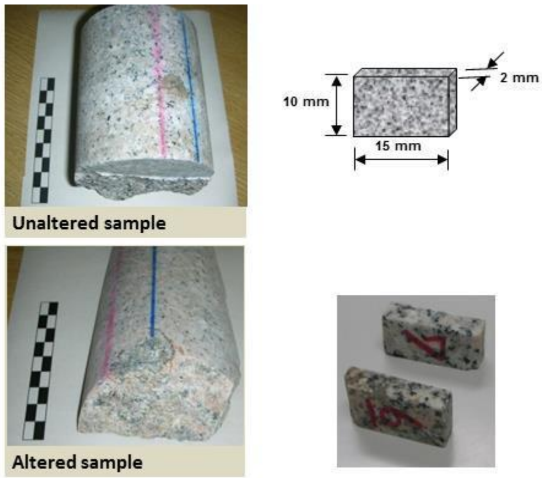
3.2 Methods

3.2.1 Samples preparation

In this study, the three core samples were prepared for the purpose of scanning electron microscopy. Firstly specimens were cut to a size similar to that illustrated in Fig. 4. A diamond wheel cutter is convenient for this process. Samples' surfaces should be polished in order to detect the distribution of different elements by SEM-EDS. Secondly, these specimens must undergo certain special preparations because the SEM utilizes vacuum conditions and uses electrons to form an image. All water must be removed from the samples because the water would evaporate in the vacuum. The surfaces should be exposed. Then surfaces should be coated with a thick layer or conducting material. This is done by using a device called a "sputter coater".

3.2.2 Water Rock Interaction test

In order to simulate the alteration and weathering that occurs to granite in nature, a Water rock interaction test was performed for an unaltered sample (MIZ1-G1) and the altered sample (MIZ1-G2). Distilled water was allowed to react with these samples for 100 days. As shown in Fig 5.



(a) (b)

Figure 4. a) Core samples. b) Prepared specimens for the experiment.

3.2.2 Scanning Electron Microscopy

The morphology and compositions of the three specimens were analyzed by scanning electron microscopy with energy-dispersive spectrometry (SEM–EDS; Jeol-JSM 5400LV). Total porosity distribution was calculated from two-dimensional images created using the SEM. Elemental compositions of the rock specimens have been calculated using EDS. SEM-EDS analysis performed for granitic rock specimens MIZ-G1 and MIZ1-G2 after 100 days interacting with purified water and for MIZ1-G3 without water-rock interaction test.

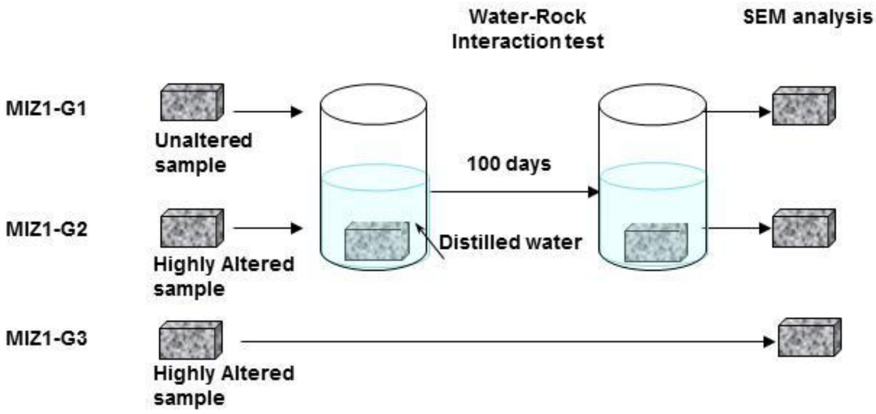


Figure 5. Schematic procedure of the experimental setup.

4 RESULTS AND DISCUSSIONS

4.1 Effect of Water Rock Interaction test

The SEM image for the unaltered sample showed that it was not influenced too much with water rock interaction test in contrast with the altered one as shown in Fig.6 (a) and (b). Sample MIZ1-G2 was an altered sample therefore the structure morphology was disturbed due to water-rock interaction test. The grains of the main minerals altered to different secondary minerals. These small size has partly been particles can be considered as an indication of weathered chlorite and major parts of chlorite replaced by clay minerals.

The results of SEM-EDS on altered granitic rock specimens before and after water rock interaction showed the change in chemical composition and structure morphology of the minerals, Fig 6 (b) and (c).

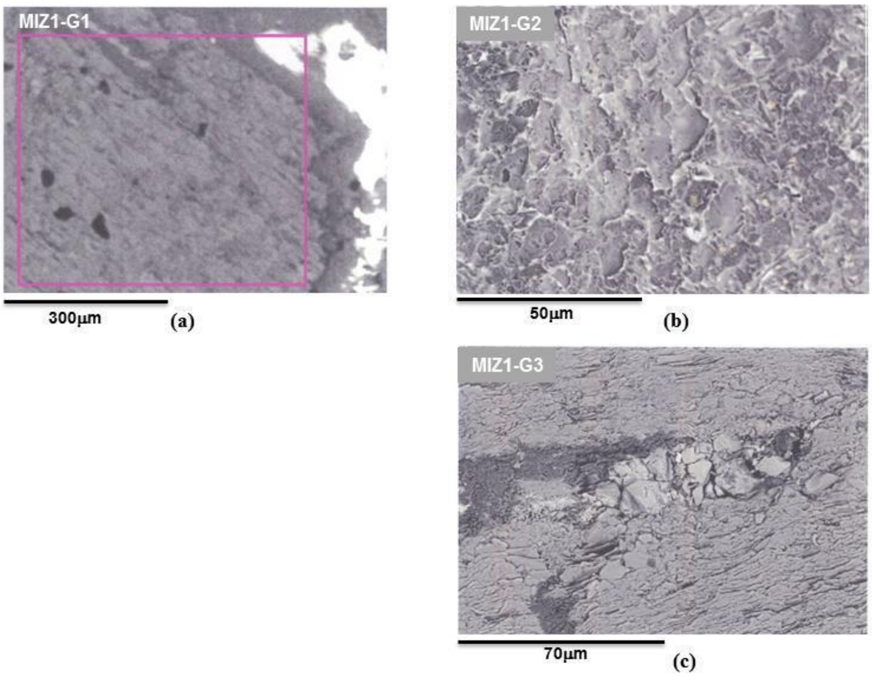


Figure 6. SEM images of granitic samples before and after water-rock interaction test a) Unaltered reacted sample b) Altered reacted sample c) Altered not reacted sample.

Table 1 shows a comparison of elemental composition between treated and untreated altered samples with water-rock interaction. The following observations have been noticed: Firstly, It was clear that fluoride bearing minerals has dissoluted into the water after water-rock interaction test. Secondly, water-rock interaction (weathering) participate in precipitation of silicate minerals which is why the silicate minerals play a vital role in chemical reaction between groundwater and rock. Usually, dissolved silica apparently shows the influences of silicate weathering on water chemistry (White & Brantley 2003). Weathered granite mainly reflects the mineralogy of aluminium-containing secondary minerals. Furthermore, Regmi et al. (2014) concluded that kaolinite ($Al_2Si_2O_5$) and chlorite ($(Mg,Fe)_3(Si,Al)_4O_{10}$) are mainly weathering products. These phenomena were clearly observed on Aluminium and Silica composition of the two samples MIZ1-G2 and MIZ1-G3, as shown in Table 1.

Table 1. Comparison between elemental composition of EDS results for treated and untreated specimens

Element	**Elemental Composition wt. %**	
	MIZ1-G3	MIZ1-G2
O	16.19	44.03
F	32.93	0.00
Na	0.24	0.00
Mg	0.35	0.81
Al	1.36	14.36
Si	3.88	24.59
K	0.19	6.67
Ca	21.78	0.00
Fe	23.08	9.54
Total	100.0	100.0

4.2 Observations in fracture surfaces

Fig.7 shows SEM-EDS results from different images at specimen MIZ1-G3. Image 2 was selected to represent the cleavages formed in fractures. Fig. 7(b) shows the spectrum of three images. Fluoride concentration was observed clearly in image 2 that was located along the cleavage. Rather than cleavage positions Fe-bearing minerals are dominant (images 1 and 3).

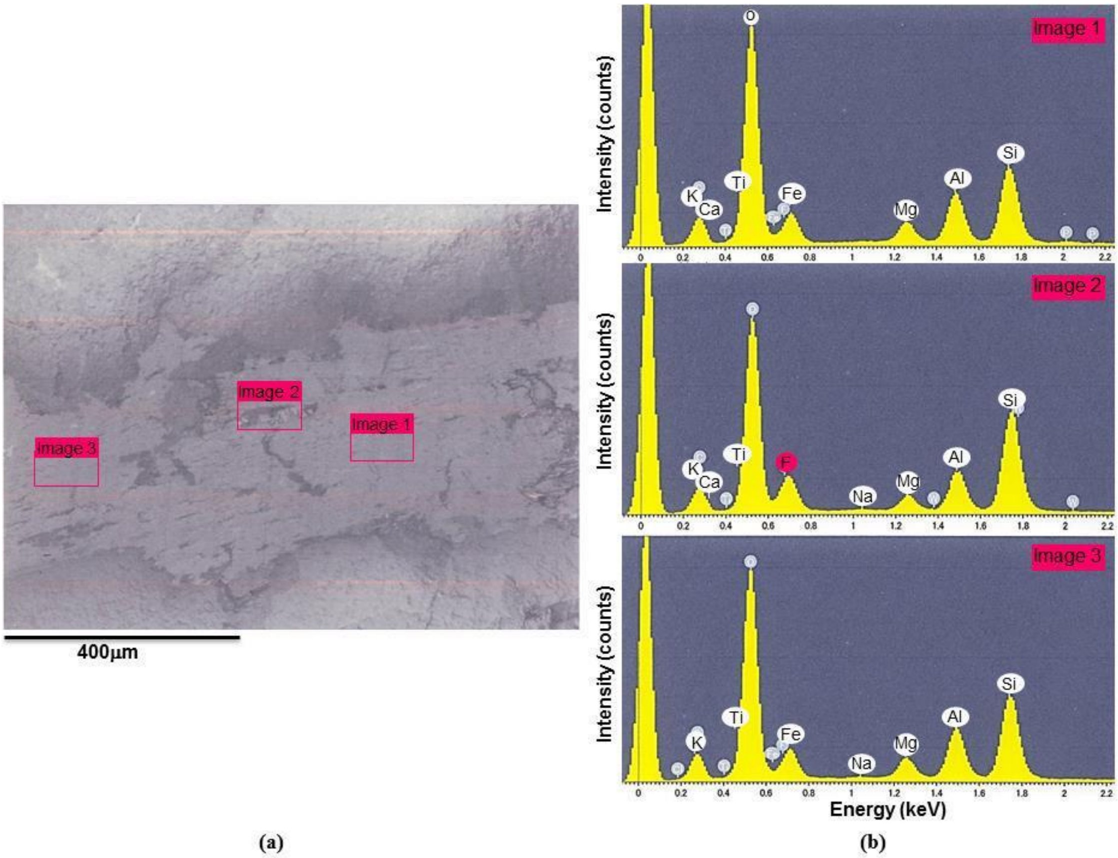


Figure 7. SEM-EDS results of an altered untreated granitic sample a) Scanning electron microscopy SEM image. b) Energy dispersive spectroscopy EDS of three different spectra

Table 2 shows the chemical composition of the three images. K-Feldspare ($KAlSi_3O_8$) is abundant in the three Images and wollastonite ($CaSiO_3$) was clearly observed at Image 2. The expected scenario is that groundwater bearing fluoride might have dissoluted wollastonite forming fluorite (CaF_2), that precipitated in the cleavages. This finding is in contrast with Kim & Jeong (2005) who reported that fluoride enriched in groundwater due to the removal of Ca^{2+} from fluorite to precipitate calcite ($CaCO_3$)

Table 2. Elemental composition of non-reacted altered sample (MIZ1-G3) 400μm

Element	Elemental Composition wt. %		
	Image 1	Image 2	Image 3
O	40.91	51.74	40.14
F	0	**11.64**	0
Na	0	0.18	0.19
Mg	2.53	2.08	2.56
Al	6.15	5.68	6.25
Si	11.1	17.06	12.43
Cl	0	0	0.19
P	0.32	0	0
K	2.41	3.46	3.52
Ca	0.75	4.97	0
Ti	1.66	1.77	1.42
Fe	34.17	0	33.3
Total	100	99.99	100

4.3 Mobilizing of fluoride in groundwater

Fig. 8 shows SEM image of the cleavage that was observed in the altered granitic rock specimen MIZ1-G3. Precipitation of some minerals inside the cleavages has been observed in image shown in Fig. 8(a). These minerals precipitation might be due to alteration process.

The EDS spectrum was obtained from a square of 150 × 100 πm. Table 3 shows the chemical compositions of the three spectra. EDS results of Spectra 1 and 2 show clearly the precipitation of fluorite (CaF_2) inside the cleavages of the fractures. K-feldspar was composed in addition to fluorite within spectra 2. That is why high fluoride concentration has been observed in groundwater within aquifer with highly altered and highly fractured granitic rock. Therefore fracture development is an important factor in the establishment of hydrothermal circulation and the facilitation of hydrothermal alteration by the interaction between fluid and rock within the granitic body. (Nishimoto & Yoshida 2010).

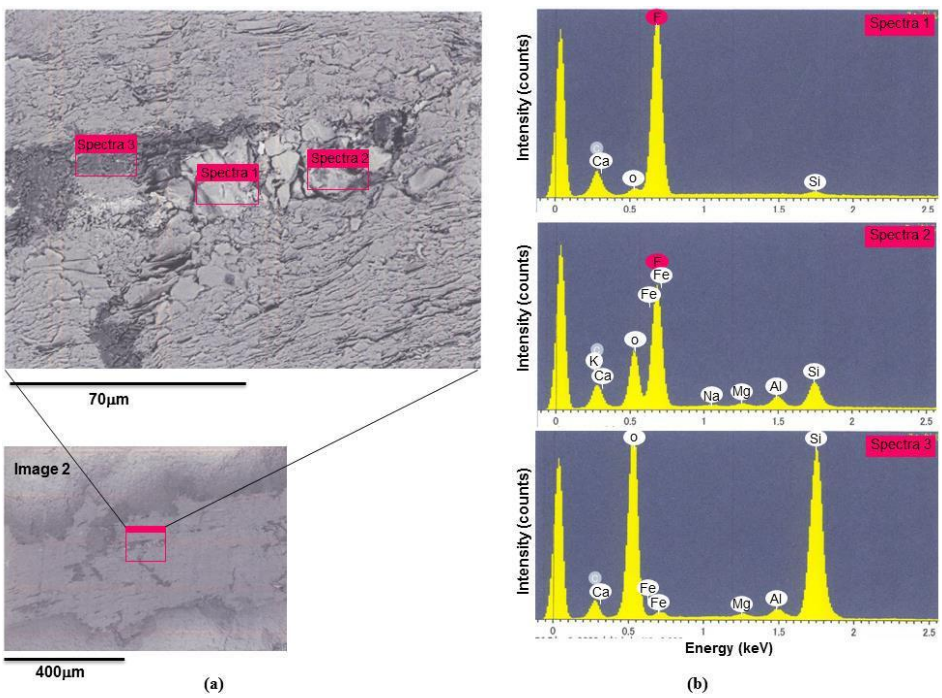


Figure 8. a) SEM image 2 of sample MIZ1-G3 b) b) Energy dispersive spectroscopy EDS of three different spectra, 70 μm.

Table 3. Elemental composition of non-reacted altered sample (MIZ1-G3), 70μm.

	Elemental Composition wt. %		
	Spectra 1	Spectra 2	Spectra 3
O	3.35	16.19	53.79
F	62.09	32.93	0
Na	0	0.24	0
Mg	0	0.35	0.53
Al	0	1.36	1.34
Si	0.57	3.88	35.72
K	0	0.19	0
Ca	33.99	21.78	0.46
Fe	0	23.08	8.14
Total	100	100	99.98

5 CONCLUSIONS

On the basis of this study, it is evident that purified water-rock interaction does not influence too much the morphology of slightly altered granitic rock. However, water rock interaction test could simulate morphologically the weathering process of highly altered granitic rock, despite some differences in mineral composition due to using purified water interacting with rock.

In the altered fractured rock, chloritization of biotite is one of the major mineral reactions that was accompanied with alteration. A possible scenario of the filling mineral in the cleavages is that Fluorite precipitated in the cleavages of the fracture due to dissolution of wollastonite. In addition to dissolution of biotite as a major source of occurrence of high fluoride concentrations in groundwater within highly altered and highly fractured granitic rock aquifer, precipitation of fluorite in the fractures' cleavages is considered also as another minor source of high fluoride concentrations in groundwater.

6 RECOMMENDATION

Advanced study is needed to study the effect of hydrothermal water on altered and weathered granite by using saline water in water-rock interaction test. SEM-EDS analysis can be done at the inner section of the reacted rock specimens with saline water in order to investigate the effect of hydrothermal water passing in the fractures on the granitic rock decompositions.

ABBREVIATIONS

URL Underground Research Laporatory

MIU Mizunami Undergroun Research Laporatory

UHFD Upper Highly Fractured Domain and

the LSFD Lower Sparsely Fractured Domain

SEM-EDS Scanning electron microscope with energy-dispersive spectrometry

REFERENCES

Abdelgawad, A. M., K. Watanabe, M. Mohammed and S. Takeuchi (2010). Estimating groundwater residence time using multiple regression model based on fluoride dissolution: an exploration of possibilities. *Environmental Earth Sciences* 60(3): 449-462

Abdelgawad, A. M., K. Watanabe, S. Takeuchi and T. Mizuno (2009). The origin of fluoride-rich groundwater in Mizunami area, Japan—Mineralogy and geochemistry implications. *Engineering Geology* 108(1): 76-85

Bisdom, E., G. Stoops, J. Delvigne, P. Curmi and H. Altemuller (1982). Micromorphology of weathering biotite and its secondary products. *Pedologie* 32(2): 225-252

Illman, W. A., X. Liu, S. Takeuchi, T.-C. J. Yeh, K. Ando and H. Saegusa (2009). Hydraulic tomography in fractured granite: Mizunami Underground Research site, Japan. *Water resources research* 45(1): W01406

Iwatsuki, T., R. Furue, H. Mie, S. Ioka and T. Mizuno (2005). Hydrochemical baseline condition of groundwater at the Mizunami underground research laboratory (MIU). *Applied geochemistry* 20(12): 2283-2302

Iwatsuki, T., H. Satake, R. Metcalfe, H. Yoshida and K. Hama (2002). Isotopic and morphological features of fracture calcite from granitic rocks of the Tono area, Japan: a promising palaeohydrogeological tool. *Applied geochemistry* 17(9): 1241-1257

Iwatsuki, T. and H. Yoshida (1999). Groundwater chemistry and fracture mineralogy in the basement granitic rock in the Tono uranium mine area, Gifu Prefecture, Japan-Groundwater composition, Eh evolution analysis by fracture filling minerals. *Geochemical Journal* 33(1): 19-32

Iwatsuki, T. and H. Yoshida (1999). Groundwater chemistry and fracture mineralogy in the basement granitic rock in the Tono uranium mine area, Gifu Prefecture, Japan—Groundwater composition, Eh evolution analysis by fracture filling minerals—. *Geochemical Journal* 33(1): 19-32

Kim, K. and G. Y. Jeong (2005). Factors influencing natural occurrence of fluoride-rich groundwaters: a case study in the southeastern part of the Korean Peninsula. *Chemosphere* 58(10): 1399-1408

Munemoto, T., K. Ohmori and T. Iwatsuki (2014). Distribution of U and REE on colloids in granitic groundwater and quality-controlled sampling at the Mizunami underground research laboratory.
Progress in Earth and Planetary Science 1(1): 1-19

Nakano, K., K. Amano, S. Takeuchi, K. Ikeda, H. Saegusa, K. Hama, N. Kumazaki, T. Iwatsuki, S. Yabuuchi and T. Sato (2003). Working program for MIZ-1 borehole investigations. *Japan Nuclear Cycle Development Institute*: 2002-2008

Nishimoto, S. and H. Yoshida (2010). Hydrothermal alteration of deep fractured granite: effects of dissolution and precipitation. *Lithos* 115(1): 153-162

Regmi, A. D., K. Yoshida, M. R. Dhital and B. Pradhan (2014). Weathering and mineralogical variation in gneissic rocks and their effect in Sangrumba Landslide, East Nepal. *Environmental Earth Sciences* 71(6): 2711-2727

Sandström, B., H. Annersten and E.-L. Tullborg (2010). Fracture-related hydrothermal alteration of metagranitic rock and associated changes in mineralogy, geochemistry and degree of oxidation: a case study at Forsmark, central Sweden. *International journal of earth sciences* 99(1): 1-25

White, A. F. and S. L. Brantley (2003). The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field? *Chemical Geology* 202(3): 479-506

Yanagizawa, K., H. Imai, K. Furuya and M. Nishigaki (1995). The effects of a shaft excavation experiment on the hydrology of the Tono research field, Japan. *Journal of hydrology* 171(1): 165-190