

## Water-Rock Interaction Study on the Occurrence of Fluoride-Rich Groundwater at Mizunami Area, Japan

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### Abstract

High fluoride concentration up to 12 mg/L was observed in the deep groundwater of Mizunami area, central Japan. Water-rock interaction tests were performed to investigate the factors affecting the fluoride concentration. Nine granitic and two sedimentary rock specimens were collected from the core of deep borehole drilled at the study area. The fluoride concentration is changed among different type of granitic rock specimens. That change may be occurred as a result of the spatial distribution of mineral composition in the granite mass. Moreover, groundwater residence time is an important factor that affects fluoride concentration. The most difficult point was the evaluation of the coexisting ions that affects on the fluoride concentration. Coexisting ions possibly related to the mineral composition in the rock specimens and chemical circumstances such as pH, groundwater type, etc.

**Keywords:** fluoride; groundwater; water-rock interaction; granitic rock; Mizunami area

### 1. Introduction

Mizunami underground research laboratory (MIU) is being constructed by Japan Atomic Energy Agency (JAEA) at the Mizunami city, Gifu prefecture, central Japan. The occurrence of fluoride-rich groundwater has been reported during the construction of MIU. The fluoride ion concentrations exceeded the Japanese environmental standard level of 0.8 mg/L and it is thought to be mainly supplied from the fluoride-rich minerals in the Toki granite that forms the basement of the area (Abdelgawad *et al.*, 2008a).

Several field studies have been carried out to understand the hydrogeochemical behavior of fluoride-rich groundwater. Apambire *et al.* (1997) studied the occurrence of fluoride in the groundwaters in the upper regions of Ghana. The authors suggested that the sources of anomalous fluoride ions in groundwater are the dissolution of fluorite and micaceous minerals. Kim and Jeong (2005) mentioned that factors regulating the occurrence of fluoride in the southeastern part of Korea are rock chemistry, groundwater age, and geologic structure. It was also difficult to investigate the correlations between fluoride and coexisting ions (Saxena and Ahmed, 2001). The difficulty mainly comes from the complexity of the geochemical processes including silicate mineral dissolution, calcite precipitation, cation exchange between minerals and some elements, and mixing among different groundwater

types. In addition, there are many other factors affecting fluoride concentration due to the inhomogeneous of granite rock. Therefore, experimental studies in combining with geochemical modeling are needed to make clear the conditions that affect the increasing of fluoride concentration in the groundwater of Mizunami area.

#### 1.1. Study area

The Mizunami Underground Research Laboratory (MIU) project began in 2002 to develop the investigation methodologies for the crystalline rock. International Atomic Energy Agency (IAEA) classified MIU as a generic URL (IAEA, 2001). Generic URLs mainly used to investigate the characteristic of rock types. The MIU consists of two 1,000 m shafts (the Main and the Ventilation Shafts) and two principal research galleries. Four shallow boreholes (MSB-1, 2, 3 and 4) and one deep inclined borehole (MIZ-1) have been drilled at the surrounding area of the MIU for monitoring the effect of shaft excavation on groundwater flow and the groundwater chemistry as shown in Fig. 1 (JNC, 2002).

In Mizunami area, Tertiary sedimentary rocks called Mizunami Group unconformably overlie the Cretaceous crystalline basement (the Toki granite). A thin layer in the upper part of the Toki granite is highly weathered. Many fractures have been identified in the Toki granite. A part of the fractured

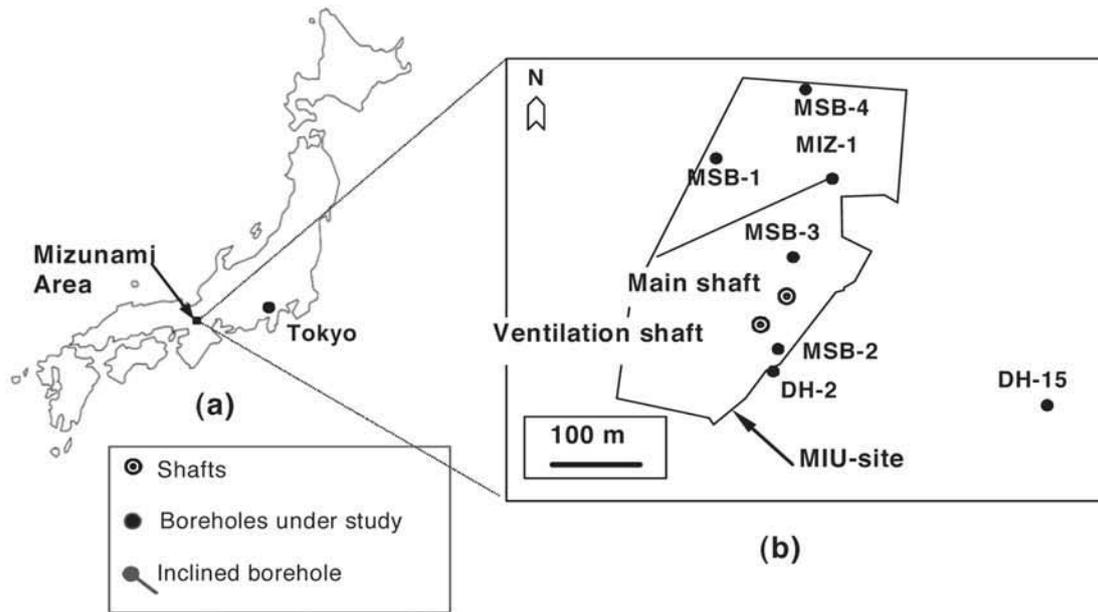


Figure 1. Location of MIU-site and the selected boreholes in and around the MIU construction site.

zones are mostly suffered by the past hydrothermal alteration and are associated with highly and extremely altered rock zones along some major fractures as shown in Fig. 2. Figure shows a hydrogeochemical conceptual model in and around the MIU site. Groundwater chemistry is mainly divided into two types. Na-(Ca)-HCO<sub>3</sub> water-type is evolved in the Akeyo Formation. In the Toki lignite-bearing formation and Toki granite the dominant groundwater is Na-Cl water-type. Iwatsuki *et al.* (2005) reported that Na-Cl water-type around MIU-site can be divided into two types i.e. the

groundwater shallower than approximately -400 masl (meter above sea level) is considered as low salinity Na-Cl water-type and the deep part of granite is dominated by a high salinity Na-(Ca)-Cl water-type. The chemical composition of the sedimentary and granitic rock were reported in Uozumi *et al.* (2005) and were summarized in Table 1.

The fluoride contents in granitic rock were measured by collecting several granitic specimens from MIZ-1 borehole (Abdelgawad *et al.*, 2008b). The results showed that the fluoride-rich minerals in granitic rock was not uniformly distributed. As

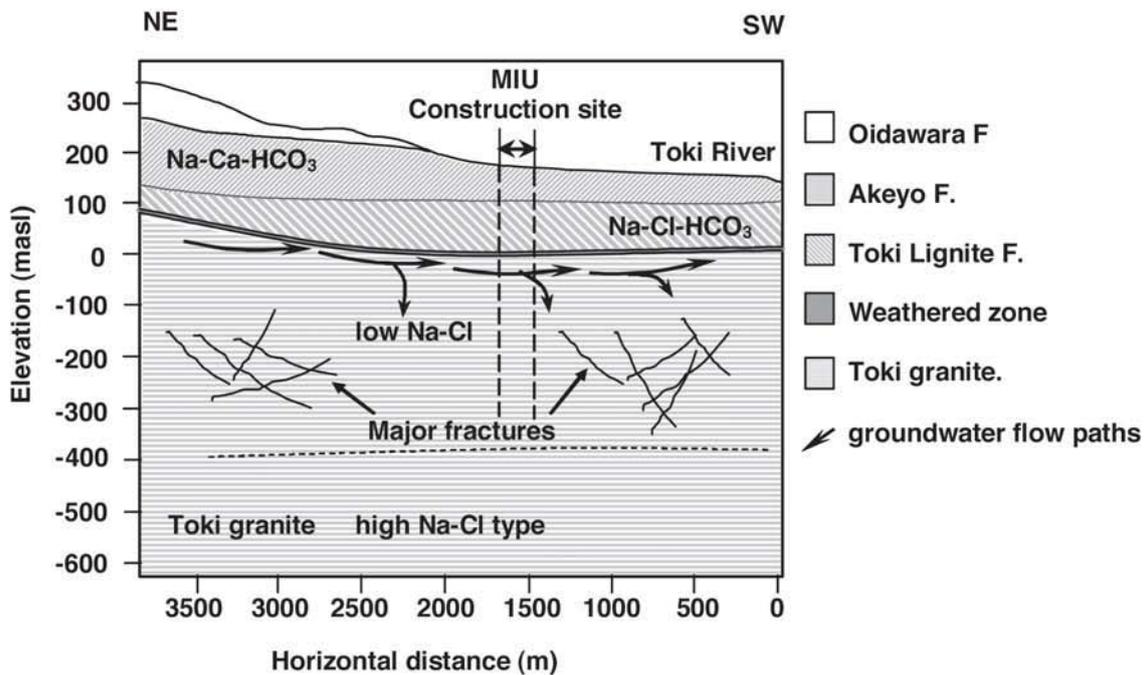


Figure 2. Schematic geological and Conceptual hydrogeochemical model in and around MIU construction site (Iwatsuki *et al.*, 2005). masl: meter above sea level

Table 1 Chemical composition of the sedimentary and granitic rock of Mizunami area (Uozumi *et al.*, 2005).

B.h. No.	Geology <sup>a</sup>	Depth m	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	CaO %	MgO %	Na <sub>2</sub> O %	K <sub>2</sub> O %	MnO %	P <sub>2</sub> O <sub>5</sub> %
MSB-1	A.	27.3	46.15	10.76	3.16	13.15	0.75	1.66	1.37	0.19	0.10
MSB-1	A.	85.8	55.29	14.30	7.44	5.99	4.80	2.65	1.01	0.18	0.13
MSB-1	T.	173.3	48.41	20.22	6.01	2.73	1.36	1.99	1.16	0.06	0.04
MSB-4	A.	34.3	60.83	10.41	2.02	10.60	0.41	2.39	3.15	0.18	0.28
MSB-4	T.	81.7	70.20	12.13	2.45	2.16	1.20	2.48	4.12	0.04	0.13
MIZ-1	G.	121.1	70.8	13.0	3.0	1.22	0.13	3.2	4.3	0.14	0.2
MIZ-1	G.	295.0	69.58	13.17	3.12	1.26	0.22	3.31	4.34	0.16	0.19
MIZ-1	G.	369.1	70.58	13.15	2.7	1.11	0.05	3.34	4.58	0.22	0.11
MIZ-1	G.	608.0	67.9	15.0	3.23	1.3	0.17	3.34	5.7	0.18	0.17
MIZ-1	G.	706.0	69.84	13.07	2.78	1.41	0.18	3.53	4.56	0.13	0.17
MIZ-1	G.	984.12	74.75	10.27	2.52	0.74	0.04	3.21	3.98	0.22	0.08
MIZ-1	G.	1180.1	71.0	12.97	2.54	0.8	0.14	2.79	5.25	0.11	0.17
MIZ-1	G.	1298.12	73.0	12.0	2.79	1.06	0.14	3.6	3.82	0.15	0.22

<sup>a</sup> A: Akeo Formation, T: Toki lignite-bearing Formation, and G: Toki granite.

example, the fluoride contents measured at several specimens collected from the depth 191.0 meter around MIZ-1 borehole (mabh) are varied between 400-1300 mg/kg as show in Fig. 3.

## 2. Material and Methods

### 2.1. Sampling and Characterization of granitic rock specimens

Two samples were collected from Akeyo and Toki lignite-bearing Formations. Nine granitic rock specimens were collected from different depths of the MIZ-1 borehole to represent different rock types. The first sample MIZ-1-G1 represents the uppermost part of the Toki granite (weathered

zone). While, other granitic rock specimens can be classified for alteration degree based on the degree of physical disintegration (Nakano *et al.*, 2003). Slightly and moderately altered granite can be noticed by clear and dull sound, respectively, when hit with a hammer. Highly and extremely altered granite fractured when hit with hammer, and clay minerals observed on a fractured plane of extremely altered granite (Table 2).

Table 3 summarized data of the major minerals compositions in granitic rock specimens that used

Table 2. Locations and characteristics of rock specimens collected from borehole MIZ-1.

Samples	depth		Weathering/ Alteration
	mabh <sup>a</sup>	layer <sup>b</sup>	
MIZ-1-A1	35.25	A	
MIZ-1-T1	80.50	T	
MIZ-1-G1	110.3	G	highly weathered
MIZ-1-G2	131.1	G	moderately altered
MIZ-1-G3	222.1	G	slightly altered
MIZ-1-G4	335.4	G	highly altered
MIZ-1-G5	542.7	G	unaltered
MIZ-1-G6	648.8	G	slightly altered
MIZ-1-G7	963.5	G	highly altered
MIZ-1-G8	35.3	G	highly altered
MIZ-1-G9	80.5	G	extremely altered

<sup>a</sup> mabh: meter around bore hole.

<sup>b</sup> A: Akeo Formation, T: Toki lignite-bearing Formation, and G: Toki granite

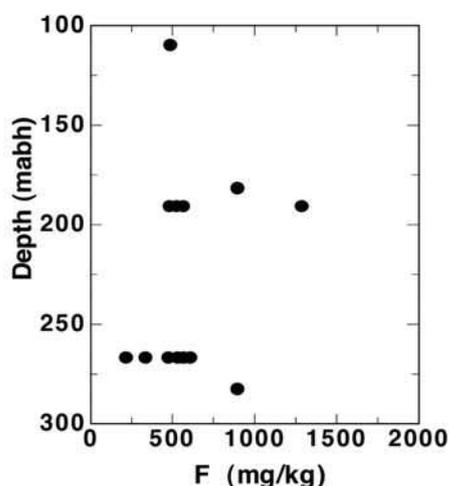


Figure 3. Fluoride content measured at specimens collected from MIZ-1 borehole mabh: meter around borehole. (Abdelgawad *et al.*, 2008b).

Table 3. Mineral compositions in granitic rock specimens, determined by X-ray diffraction analysis.

Samples		MIZ-1-G1	MIZ-1-G7	MIZ-1-G9
Mineral		I % <sup>a</sup>	I %	I %
Quartz <sup>b</sup>	SiO <sub>2</sub>	99	98	100
Albite (Plagioclase)	Na(Si <sub>3</sub> Al)O <sub>8</sub>	64	31	-
Anorthite (Plagioclase)	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	63	31	-
Sanidine (K feldspar)	K(Si <sub>3</sub> Al)O <sub>8</sub>	99	-	-
Microcline (K feldspar)	KAlSi <sub>3</sub> O <sub>8</sub>	87	15	-
Fluorite	CaF <sub>2</sub>	7	15	11
Phlogopite (biotite)	K(Mg,Fe) <sub>3</sub> (Al,Fe)Si <sub>3</sub> O <sub>10</sub> (OH,F) <sub>2</sub>	14	31	-
Annite (biotite)	KFe <sup>+2</sup> <sub>3</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	14	14	-
Muscovite	KAl <sub>2</sub> Si <sub>3</sub> AlO <sub>10</sub> (OH) <sub>2</sub>	-	-	11
Chlorite	(Mg, Al) <sub>6</sub> (Si, Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>	-	-	31
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	-	-	31

<sup>a</sup> I %: relative intensity =  $I/I_r * 100$ ,  $I_r$ : the reference standard mineral

<sup>b</sup> Quartz was chosen as the reference standard mineral ( $I_r$ ) (the most intense peak).

in water rock interaction test (Abdelgawad *et al.*, 2008b). MIZ-1-G1, MIZ-1-G7, and MIZ-G9 represent weathered, highly altered, and extremely altered granitic rock, respectively. The major observed minerals in weathered and highly altered granite are quartz, plagioclase, K-feldspar, and biotite. 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 these fractured zones (Iwatsuki and Yoshida, 1999). Minor amount of fluorite were observed in all specimens.

## 2.2. Experimental setting

The collected granitic rock specimens were crushed in a ceramic shatter box (Net stamp Mill ANS143) to make rock powder. The wet sieving technique was used to divide the powder into three sizes (0.30-0.15 mm, 0.15-0.075 mm, and smaller than 0.075 mm). After decantation to eliminate the suspended fine fraction, the powders were dried in oven of 40 °C for 7 hours. Shaking tests were performed to investigate the effect of different experimental conditions on the dissolution of fluoride-rich minerals. Shaker table (AS-ONE SRR2) used in the experiments at a constant shaking rate of 180 r.p.m. (round per minute). Table 4 shows the experimental conditions for each test.

Experiments (Run No. 1 to 25) were conducted using distilled water of pH 6.7 within tightly capped conical glass flasks at the room temperature about

20 °C. Experiments No. 1 and 2 were conducted using sedimentary rocks and continued for 30 and 60 days, respectively. Run No. 3 was conducted using powder of specimen MIZ-1-G5 with size (0.30–0.15 mm). Two sets of experiments (Run Numbers 4 to 21) were conducted under the same conditions with granitic powder size (0.15-0.075 mm) for all granitic specimens. The reaction time for the first set continued for 30 days and for the second one continued for 80 days as shown in Table 4. The size of granitic powder of run numbers 22 and 23 was <0.075 mm. Water-rock ratios were constant for all experiments (10/1) except Run numbers 24 and 25, these runs used water-rock ratio 5/1. The tests were terminated after 30 days. Run No. 26 was conducted by reacting sedimentary rock specimens (MIZ-1-A1) with distilled water for 8 days, and then the output solution was reacted with shallow granitic specimen (MIZ-1-G1) for 30 days. The purpose of this batch was to check the effect of passing water through sedimentary rock on fluoride dissolution from granitic rock.

## 2.3. Chemical analysis

The amount of the fluoride ion was roughly measured using PACK TEST and pH values were measured using a pH meter (Eutech pH 510) for all experiments at an interval time. The main purpose of PACK TEST is to know roughly the general trend of fluoride concentration. At run numbers (4, 6, 8,....20), solution samples were taken at

Table 4. Experimental conditions for shaking tests.

Run No.	Experiment ID	Solu. <sup>a</sup>	Rock type <sup>b</sup>	Time (days)	Grain size ( $\mu\text{m}$ )	W/R <sup>c</sup>	Chemical analysis <sup>d</sup>
1	MIZ-1-A1	DW	A	30	-----	10/1	ICP-IC
2	MIZ-1-T1	DW	T	60	-----	10/1	ICP-IC
3	MIZ-1-G5I	DW	G	30	300-150	10/1	P. T.
4,5	MIZ-1-30G1II	DW	G	30, 80	75-150	10/1	ICP-IC
6,7	MIZ-1-30G2II	DW	G	30, 80	75-150	10/1	ICP-IC
8,9	MIZ-1-30G3II	DW	G	30, 80	75-150	10/1	ICP-IC
10,11	MIZ-1-30G4II	DW	G	30, 80	75-150	10/1	ICP-IC
12,13	MIZ-1-30G5II	DW	G	30, 80	75-150	10/1	ICP-IC
14,15	MIZ-1-30G6II	DW	G	30, 80	75-150	10/1	ICP-IC
16,17	MIZ-1-30G7II	DW	G	30, 80	75-150	10/1	ICP-IC
18,19	MIZ-1-30G8II	DW	G	30, 80	75-150	10/1	ICP-IC
20,21	MIZ-1-30G9II	DW	G	30, 80	75-150	10/1	ICP-IC
22	MIZ-1-G1III	DW	G	30	< 75	10/1	P. T.
23	MIZ-1-G5III	DW	G	30	< 75	10/1	P. T.
24	MIZ-1-G1III-5	DW	G	30	< 75	5/1	P. T.
25	MIZ-1-G5III-5	DW	G	30	< 75	5/1	P. T.
26	MIZ-1-8A1G1	SW	G	20	< 75	10/1	ICP-IC

<sup>a</sup> Solu. (Solution): DW: distilled water, SW: used water was shaken with sedimentary rock for 8 days.

<sup>b</sup> A: Akeyo formation, T: Toki lignite-bearing formation, G: Toki Granite

<sup>c</sup> W/R: water-rock ratio.

<sup>d</sup> ICP-IC: cations and anions measured by using inductively-coupled plasma optical-emission. spectrometry for cations and fluoride and ion chromatography for anions, P.T.: fluoride measured using Pack test.

an increasing time intervals (3, 8, 12, 20 and 30 days), however for those experiments continued for 80 days, solution samples (20 mm) were taken after (40, 60 and 80 days). Samples solutions were filtered by using filter paper (Whatman No.1) and then analyzed for  $\text{F}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ , and total Fe ( $\text{Fe}^{2+/3+}$ ) using Inductively-Coupled Plasma optical-emission spectrometry (ICP-OES Varian VISTA-MPX).  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  concentrations were measured using Ion Chromatography (IC; Dionex DX-120). Water samples obtained after 80 days shaking were also used for the analyzing of the  $\text{HCO}_3^-$  concentration.

### 3. Results and Discussions

#### 3.1. Fluoride and pH measurement

Fig. 4 illustrates the results of chemical analysis of runs 4-21. The increase of fluoride concentration and the change of pH versus reaction time are presented in Figs. 4(a-b). Figure shows that the fluoride ion is continually enriched for most of the

rock specimens with increasing the reaction time even though the pH was almost stable with time. This phenomenon implies the importance of groundwater residence time in controlling fluoride concentration. Fig. 4(a) indicates the changing of fluoride concentrations among different granitic specimens. That may be due to the spatial change of fluoride-rich minerals in granite. The fluoride ion leached from sedimentary rock (MIZ-1-A1 and MIZ-1-T1) are relatively small in comparing with those of granitic specimens.

Sudden increase in  $\text{F}^-$  is associated with sudden increase in pH values up to around 9.0. The pH value decreased to 8.0 and then it became in a steady condition at 4-5 days completion of the experiment. However there is a little difference in pH trend of MIZ-1-G1 in comparing with other granitic specimens. The difference mainly noticed at approximately the first 5 days of reaction that pH suddenly increase up to about 7.5 and then kept constant at whole duration of the experiment. In contrast, sudden increase of pH up to 9.0 and then gradual decrease has been observed in pH trend of

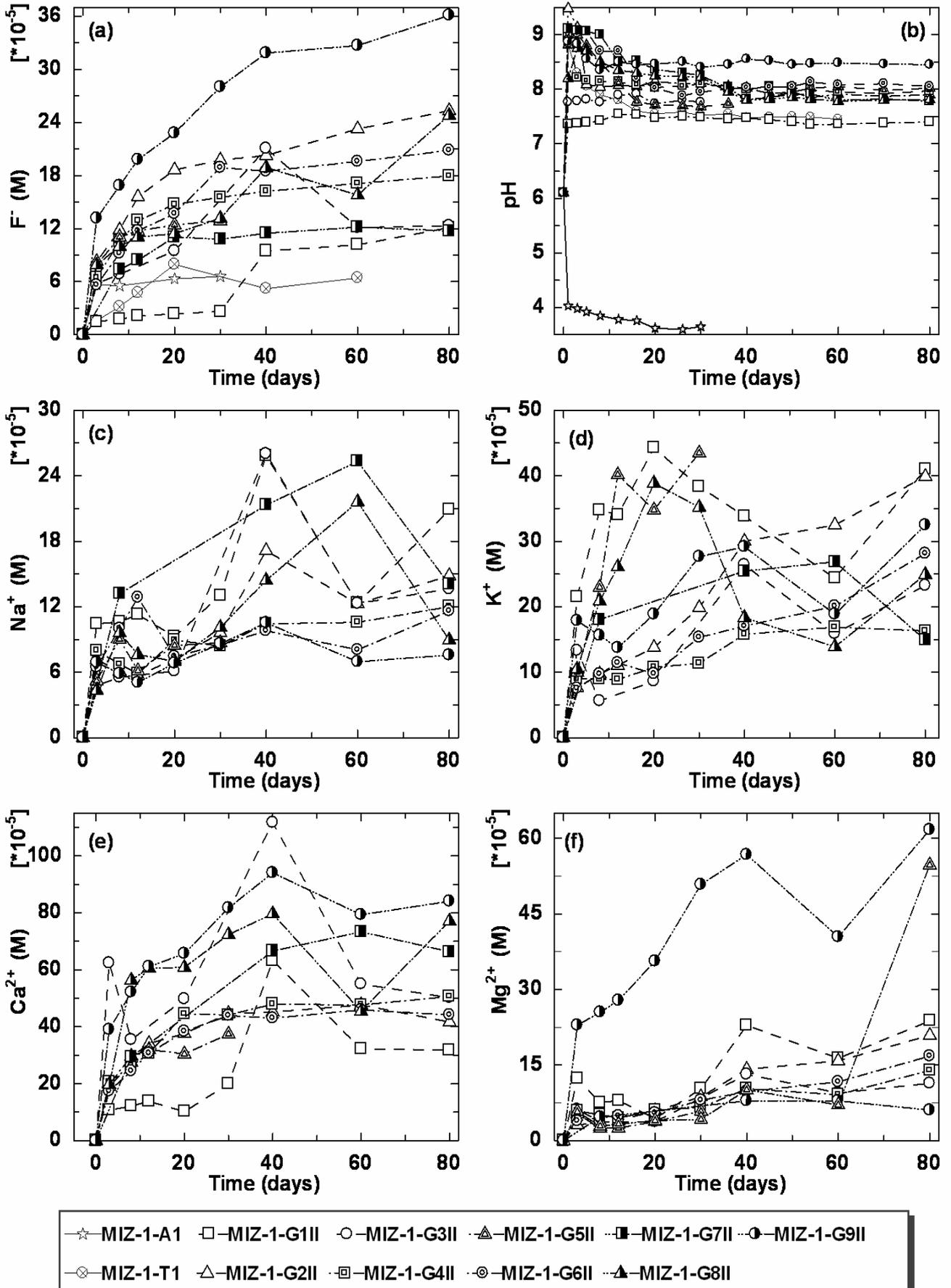


Figure 4. Time series variations of selected ions leached from granitic specimens.

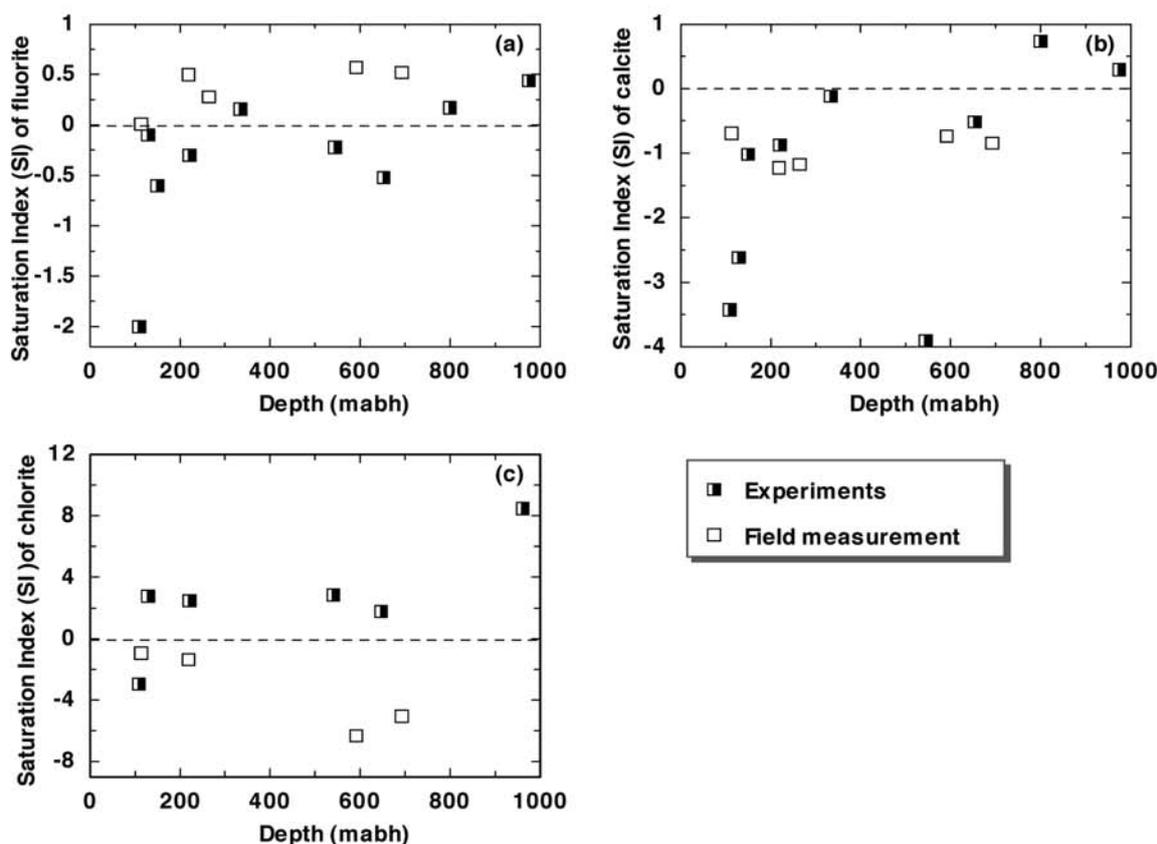


Figure 5. Saturation indices with respect to (a) fluorite, (b) calcite, and (c) chlorite.

other granitic specimens. Previous discussion explains the increasing of fluoride concentration in the alkaline solution which observed in the solution reacted with more deep granite. This result was in agreement with the finding of Gaciri and Daives (1993). On the other hand, pH value of Akeyo Formation (MIZ-1-A1) suddenly decreased and became almost constant at the end of 3 days.

### 3.2. Effect of coexisting ions

The most abundant ions were  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+/3+}$  (total Fe),  $\text{F}^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ . It was also clearly observed that among the selected ions, the  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  concentrations rapidly increased up to 10 days, as shown in Figs. 4(c-e). Gradual increase of  $\text{K}^+$  concentration suggests the dissolution of biotite ( $\text{K}(\text{Fe}, \text{Mg})_3\text{AlSi}_3\text{O}_{10}(\text{F}, \text{OH})_2$ ) and/or K-feldspar within the reaction time (Deer *et al.*, 1992). The  $\text{Ca}^{2+}$  concentration depends on several geochemical processes, including the dissolution of Ca-bearing minerals, calcite ( $\text{CaCO}_3$ ) precipitation and dissolution, adsorption and/or cation exchange (Chae *et al.*, 2006). High concentration of  $\text{F}^-$  and  $\text{Mg}^{2+}$  observed in the extremely altered specimen (MIZ-1-G9). The  $\text{F}^-$  ion is thought to be mainly supplied by biotite ( $\text{K}(\text{Fe}, \text{Mg})_3\text{AlSi}_3\text{O}_{10}(\text{F}, \text{OH})_2$ ) and/or fluorite ( $\text{CaF}_2$ ). In general, biotite changed into chlorite due to the past

hydrothermal alteration. The significant increases in the concentrations of  $\text{Mg}^{2+}$  [Fig. 4(f)] in the extremely altered granite (MIZ-1-G9) is thought as an indication of chlorite dissolution (Ganor *et al.*, 2005).

Iwatsuki *et al.* (2002) indicated the precipitation of calcite in the fracture surfaces of altered Toki granite which contains much amount of chlorite as it was evidenced by XRD results. Therefore, saturation indices of the output solutions with respect to fluorite, calcite, and chlorite have been estimated. Chemical compositions, pH, and temperature measurements of runs 4-21 were inputted into geochemical equilibrium model PHREEQC (Parkhurst and Appelo, 1999). Groundwater compositions for groundwater samples from MIZ-1 boreholes have been also used to estimate Saturation indices in the real groundwater (Iwatsuki, 2005). From Fig. 5, most of the experiments did not reach saturation with respect to fluorite and calcite. In contrast, the real groundwater is over saturated with respect to fluorite. This phenomenon emphasizes the important of groundwater residence time in fluoride concentration. Although, continuing increase of  $\text{F}^-$  was observed in the deep altered granitic samples, these samples were over saturated. This phenomenon was approved by Kim and Jeong (2005). They reported that the  $\text{F}^-$  concentrations of groundwater are enriched even after the groundwater reaches

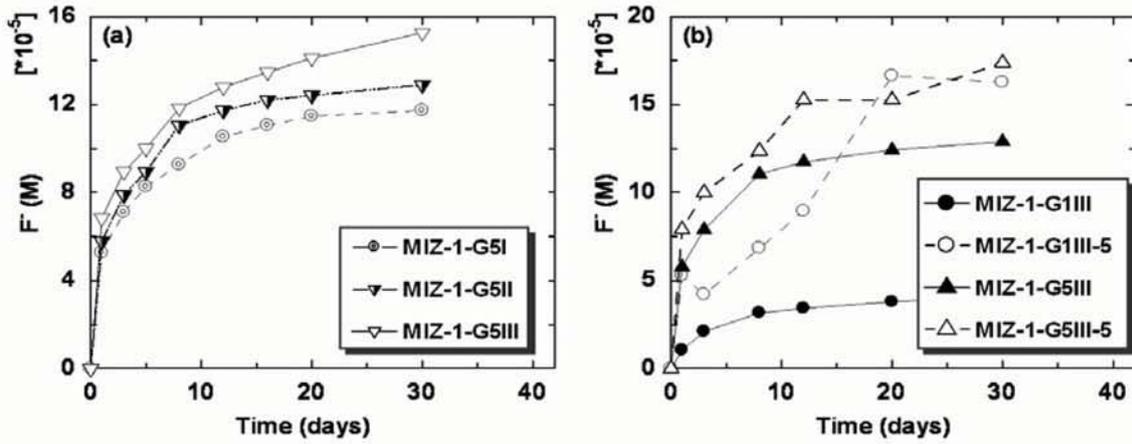
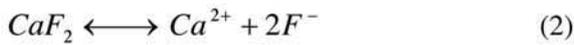
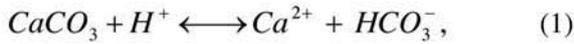


Figure 6. Experiment conditions effect on fluoride leaching (a) powder size (b) water-rock ratio.

an equilibrium state with respect to fluorite (CaF<sub>2</sub>) due to removal of Ca by precipitation of calcite (CaCO<sub>3</sub>), as shown in Eq. (1) and (2).



Saturation index with respect to chlorite indicates that it is under equilibrium at MIZ-1-G1 and near equilibrium at MIZ-1-G7, but becomes progressively oversaturated at MIZ-1-G9.

### 3.3. Effect of experimental conditions

Fig. 6(a) shows the results of MIZ-1-G5I, MIZ-1-G5II, and MIZ-1-G5III using different granitic

powder size. Figure indicates that fluoride concentration in the case of finest grain size was the highest. From the results it can be roughly said that the fluoride ion concentration decreased by about 15% when the size was doubled. This result may be relating to the fact that the finest particles have the largest surface area/volume ratio.

Fig. 6(b) shows the results of two experiments e.g. MIZ-1-G1III-5 and MIZ-1-G5III-5 that used water-rock ratio 5/1. These two experiments were compared with another two experiments MIZ-1-G1III and MIZ-1-G5III with water rock ratio 10/1. Increasing the amount of rock caused the fluoride ion concentration to increase. This figure clearly showed the high effect of water-rock ratio in the highly weathered granite (MIZ-1-G1) comparing with (MIZ-1-G5).

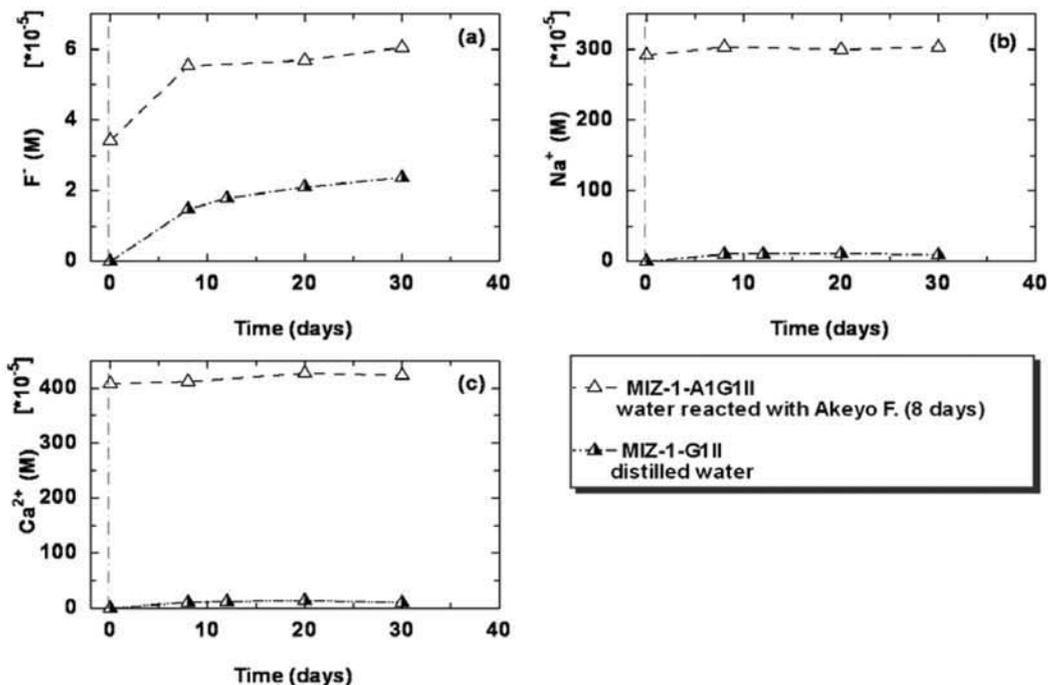


Figure 7. Effect of passing water through sedimentary rock on releasing ions from granitic rock.

### 3.4. Groundwater type Effect

Fig. 7(a) exhibited the effect of interaction between sedimentary rock and groundwater on fluoride concentration. Figure shows comparison between two fluoride leaching trends of runs MIZ-1-G1II and MIZ-1-A1G1II. Although the initial fluoride concentration is different, the difference in fluoride concentration is almost in the same trend for both tests. As illustrated in Figs. 7(b-c) concentrations of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  of MIZ-1-A1G1II are much higher than those of MIZ-1-G1II in the initial stage. This result indicates that the main source of high  $\text{Na}^+$  and  $\text{Ca}^{2+}$  in groundwater might be the sedimentary rock.

### 4. Conclusions

The granite can act as a source of fluoride ion due to the increase in the reaction time between the groundwater and the granitic rock. The spatial distribution of fluoride content in granite is one of the possible reasons for changing fluoride concentration. The significant increase of fluoride concentration was observed in the extremely altered granite. High fluoride concentration is usually associated with the high alkaline solution. Experiments did not reach to equilibrium after 80 days shaking except the deep highly altered granite. Groundwater residence time can be considered as the main factor affect fluoride concentration. Coexisting ions is an important factor in evaluation the dissolutions processes of fluoride-rich minerals.

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