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- Exchangeable cation composition of smectite-rich fault gouge was examined by wet chemical analysis
- Na^+ to Mg^{2+} exchange reaction might have progressed in the slip zone during the earthquake
- Cation exchange reaction may be intimately linked to physical aspect of smectite-bearing faults

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Exchangeable cation composition of the smectite-rich plate boundary fault at the Japan Trench

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Abstract To better understand physicochemical processes in smectite-rich fault zones, we examined exchangeable cation composition of samples from the slip zone of the 2011 Tohoku-oki earthquake (M_w9.0) recovered by the Integrated Ocean Drilling Program Expedition 343. Our chemical analyses revealed that the exchangeable Ca^{2+} and Mg^{2+} are enriched in the slip zone, while Na^+ is depleted. K^+ shows a complicated depth profile probably due to K fixation. Based on fluid chemistry data, we estimated apparent selectivity coefficients of exchange reactions in the ternary Ca^{2+}-Mg^{2+}-Na^+ system. The results suggest that the Na^+ to Mg^{2+} exchange reaction on smectite might have progressed in the slip zone. One explanation for this feature is local progress of the reaction triggered by coseismic thermogenesis during the earthquake. Considering that the frictional property of smectite gouge is dependent on the exchangeable cation composition, chemical processes as observed in this study are intimately linked to physical aspect of smectite-bearing faults.

1. Introduction

The coseismic rupture and slip of the 2011 Tohoku-oki earthquake (M_w9.0) propagated to the axis of the Japan Trench [*Ide et al*., 2011; *Fujii et al*., 2011; *Fujiwara et al*., 2011; *Kodaira et al*., 2012] and resulted in a huge tsunami along the wide area of the northeast coast of Honshu, Japan. In order to directly investigate faulting mechanisms on the tsunamigenic fault, Integrated Ocean Drilling Program (IODP) Expedition 343 (Japan Trench Fast Drilling Project (JFAST)) drilled the fault system 1 year after the earthquake [*Chester et al*., 2012] and successfully recovered core samples, including the hanging wall, footwall, and plate boundary fault (maximum thickness of 4.86 m) from ~820 m below sea floor (mbsf) [*Chester et al*., 2012, 2013; *Rowe et al*., 2013] (Figure 1). X-ray diffraction (XRD) analyses on core samples revealed that the slip zone of the Tohoku earthquake is extremely enriched in smectite (as high as 60–80 wt %) deposited far from the land [*Kameda et al*., 2015]. Laboratory experiments revealed that the slip zone materials display very low friction under various sliding conditions [*Ujiie et al*., 2013; *Ikari et al*., 2015]. Abundant smectite is likely a direct cause for such weak friction and may result in easy propagation of coseismic slip during the earthquake [*Ujiie et al*., 2013].

Smectite is a common mineral in fault zones of the shallow crust [*Vrolijk and van der Pluijm*, 1999] and is known to have several distinctive physicochemical properties including swelling, cation exchangeability, and frictional weakness. Numerous experiments have examined frictional properties of artificial or natural smectite gouges [*Moore and Lockner*, 2007, and references therein], and some work has demonstrated that friction varies in smectites saturated with different exchangeable cations [*Behnsen and Faulkner*, 2013]. Accordingly, determination of exchangeable cation composition of smectite from natural fault gouges may provide a key for better understanding of the faulting processes. However, only a few studies have analyzed exchangeable cation composition of smectite fault gouges [e.g., *Schleicher et al*., 2006], and this may be due partly to difficulty in precise determination of the composition by analytical electron microscopy [*van der Pluijm et al*., 1988].

In this study, we examine exchangeable cation compositions of the Tohoku slip zone samples by wet chemical analysis. Because of extraordinary high concentrations of smectite, the cation exchange reaction may be amplified in the slip zone, and therefore, this material is likely a suitable target for this purpose. The main objective of this study is to elucidate possible physicochemical processes in the fault zone during the large megathrust earthquakes. We address whether the process can be a temperature proxy to constrain coseismic sliding behaviors of a fault. We also briefly mention the mechanical implication of the process in the fault.

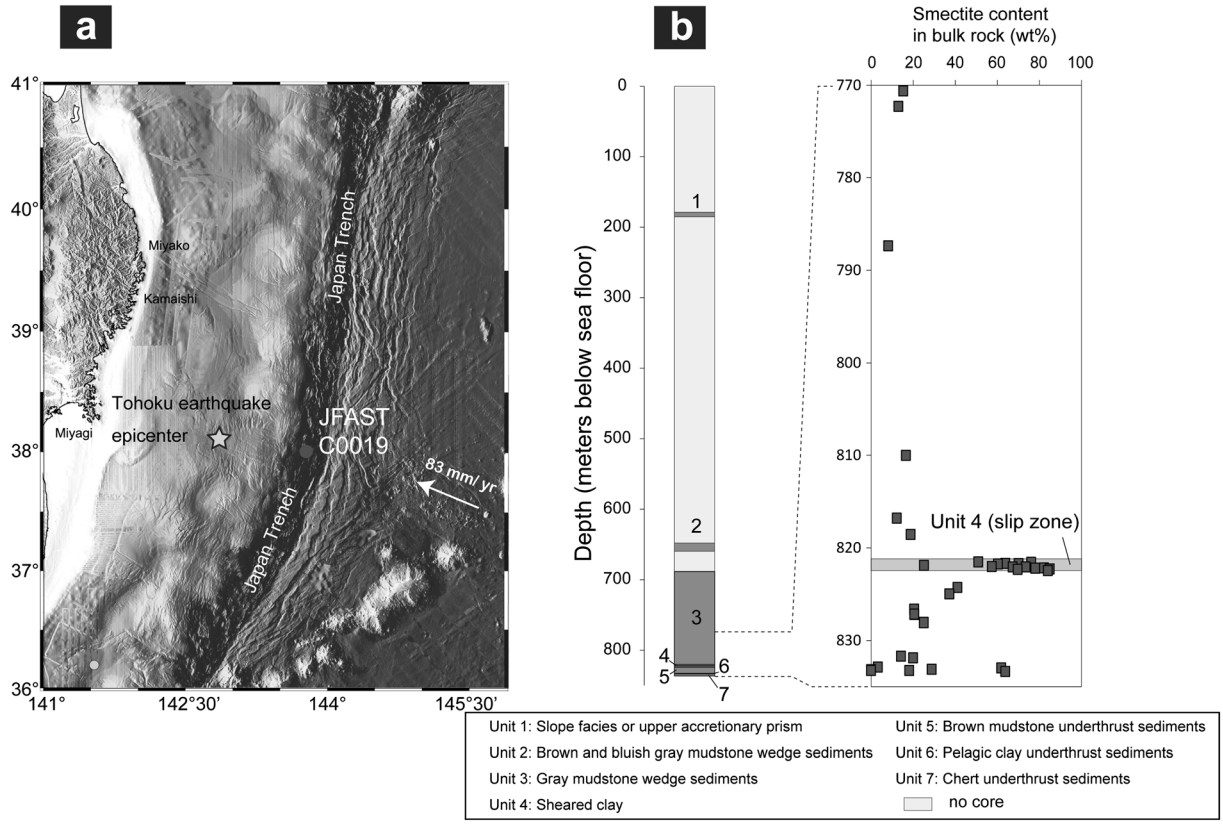

Figure 1. (a) Locations of the drill site for JFAST (Site C0019). (b) Lithologic units of the JFAST drill site and variation of smectite content in the bulk rock. Note that smectite is extremely enriched in the slip zone (Unit 4).

2. Experimental Methods

The exchangeable cation compositions (Na^+, Ca^{2+}, K^+, and Mg^{2+}) for the bulk samples were determined by two methods. Four samples including two slip zone samples (Table 1) were analyzed by extracting cations in ammonium acetate solution (Schollenberger method), and the concentrations of extracted cations in the solution were measured using an atomic absorption photometer (Z-2000; Hitachi). Other samples were analyzed by extracting cations with cobaltihexamine [*Orsini and Remy*, 1976], following standard NF X31-130 at the Institut National de Recherche Agronomique soil analysis laboratory in Arras, France.

The exchangeable cation composition in smectite is governed by the exchange reactions between smectite and dissolved cations in pore fluids, and if the exchange equilibrium is achieved between them, the equilibrium constant should be the same irrespective of the difference in lithology. Based on the mole fraction of each cation species (fractional abundance X_i where i denotes exchangeable cation species) as well as pore fluid chemistry data measured on board [*Expedition 343/343T Scientists*, 2013], we estimated the selectivity coefficient of each cation in the ternary exchange system of Ca^{2+}-Mg^{2+}-Na^+. Following the description of the ternary exchange reaction on zeolite [*Fletcher and Townsend*, 1981], the reactions can be expressed as follows:

$$4Na^+_{(c)} + Mg^{2+}_{(s)} + Ca^{2+}_{(s)} = 4Na^+_{(s)} + Mg^{2+}_{(c)} = Ca^{2+}_{(c)} \quad (1)$$

$$2Na^+_{(s)} + 2Mg^{2+}_{(c)} + Ca^{2+}_{(s)} = 2Na^+_{(c)} + 2Mg^{2+}_{(s)} + Ca^{2+}_{(c)} \quad (2)$$

$$2Na^+_{(s)} + Mg^{2+}_{(s)} + 2Ca^{2+}_{(c)} = 2Na^+_{(c)} + Mg^{2+}_{(c)} + 2Ca^{2+}_{(s)} \quad (3)$$

where subscripts s and c mean the phases in solution and crystal, respectively. The selectivity coefficients $K_{c(j)}$ of the above reactions are expressed as follows:

$$K_{c(j)} = \left(\Pi X^x_{i,j}\right) \times \left(\Pi a^x_{i,j}\right)^{-1} \quad (4)$$

Table 1. Results of Measurement of Exchangeable Cation Composition for JFAST Samples[a]

Sample	Depth (mlsf)	Ca		Mg		Na		K		Cation Exchange Capacity ($cmol_c+/kg$)
		(cmol/kg)	X_{Ca}	(cmol/kg)	X_{Mg}	(cmol/kg)	X_{Na}	(cmol/kg)	X_K	
Cobaltihexamine										
C0019E-04R-1, 94.0 cm	689.44	0.83	0.026 (0.027)	2.6	0.084 (0.087)	26.8	0.851 (0.886)	1.2	0.039	35.0
C0019E-05R-2, 95.5 cm	698.355	0.99	0.028 (0.029)	3.0	0.086 (0.090)	29.5	0.837 (0.880)	1.7	0.049	39.3
C0019E-06R-2, 14.0 cm	705.85	0.62	0.020 (0.021)	2.7	0.085 (0.090)	26.5	0.842 (0.889)	1.7	0.053	34.8
C0019E-07R-1, 59.0 cm	713.59	1.00	0.029 (0.031)	3.1	0.090 (0.095)	28.5	0.822 (0.874)	2.1	0.060	38.8
C0019E-08R-2, 0.0 cm	720.415	1.01	0.030 (0.031)	2.8	0.085 (0.089)	28.1	0.841 (0.880)	1.5	0.044	37.3
C0019E-12R-2, 76.0 cm	787.63	1.57	0.054 (0.057)	2.4	0.083 (0.088)	23.6	0.807 (0.855)	1.7	0.057	33.3
C0019E-13R-2, 45.0 cm	802.26	1.93	0.059 (0.063)	3.0	0.092 (0.098)	25.7	0.793 (0.840)	1.8	0.056	37.3
C0019E-14R-1, 74.0 cm	810.74	3.09	0.085 (0.090)	2.5	0.069 (0.073)	28.5	0.787 (0.836)	2.1	0.058	41.8
C0019E-15R-1, 0.0 cm	816.5	1.69	0.042 (0.046)	2.5	0.062 (0.067)	32.8	0.827 (0.888)	2.7	0.068	43.8
C0019E-17R-1, 99.0 cm	822.49	4.76	0.096 (0.105)	5.6	0.112 (0.123)	34.8	0.705 (0.772)	4.2	0.086	59.7
C0019E-19R-2, 102.0 cm	828.71	1.83	0.055 (0.057)	2.5	0.073 (0.077)	27.6	0.827 (0.866)	1.5	0.045	37.7
C0019E-20R-1, 45.0 cm	831.45	2.47	0.089 (0.093)	1.9	0.069 (0.072)	22.0	0.791 (0.834)	1.4	0.051	32.2
Schollenberger										
C0019E-12R-2, 48.0 cm	787.35	2.15	0.055 (0.063)	3.7	0.094 (0.107)	28.4	0.732 (0.830)	4.6	0.119	44.6
C0019E-17R-1, 67.5 cm	822.175	6.85	0.126 (0.139)	6.4	0.118 (0.130)	36.0	0.661 (0.731)	5.2	0.096	67.7
C0019E-17R-1, 70.0 cm	822.2	7.15	0.123 (0.136)	7.0	0.121 (0.133)	38.3	0.661 (0.730)	5.5	0.095	72.1
C0019E-19R-1, 69.0 cm	827.19	3.45	0.083 (0.093)	2.9	0.068 (0.077)	30.9	0.739 (0.831)	4.6	0.110	48.1

[a]Values in parentheses for X_{Ca}, X_{Mg}, and X_{Na} are X_i recalculated to be 100% without K^+.

where $a_{i,j}$ and $X_{i,j}$ are the activities and fractional concentrations of the *i*th cation species in the solution and in the crystal, respectively, in the *j*th reaction (equations (1)–(3). Because our samples also contain multiple mineral phases other than smectite, equation (4) does not strictly correspond to a thermodynamic equilibrium constant, but instead, *K* is defined as an apparent selectivity coefficient. Although the exchange reactions on smectite in the system including K^+ was examined in *Inoue* [2000], we here ignore K^+ from the reaction because we adopted the intense extraction methods, and this could have extracted even the fixed K^+ which is supposed to be unchangeable during the reaction. To check this appropriateness, the X_i values with and without K^+ (recalculated to be 100% without K^+) were tested for estimating the selectivity coefficients, but this does not significantly affect the overall trend of the results.

3. Results

Figure 2 shows the downhole variation of X_i for the interval 680–840 mbsf (Table 1). Throughout the interval, Na^+ is the most abundant cation, and X_{Na+} ranges from 0.7 to 0.85. In shallower interval (680–700 mbsf), X_{Na+} is relatively constant (~0.85) but is scattered deeper in the section with a marked negative anomaly (<0.7) at the fault zone. X_{Mg2+} and X_{Ca2+} are also constant around ~0.1 and ~0.03, respectively, in the shallower interval, but are scattered in the deeper section. In contrast to Na^+, these divalent cations show positive peaks at the slip zone. Among the cations, K^+ is also the minor species (<0.1). It is noted that the X_{K+} values determined by the different extraction methods are largely deviated outside the fault zone and show inverted trends around the fault (Figure 2). K^+ is known to be fixed strongly with the smectite interlayer [e.g., *Inoue*, 1983]. This property could explain part of the contradictory profiles in X_{K+}.

Activities of ions in the solution were estimated from onboard data of extracted pore fluids (Table 2) with Debye-Huckel

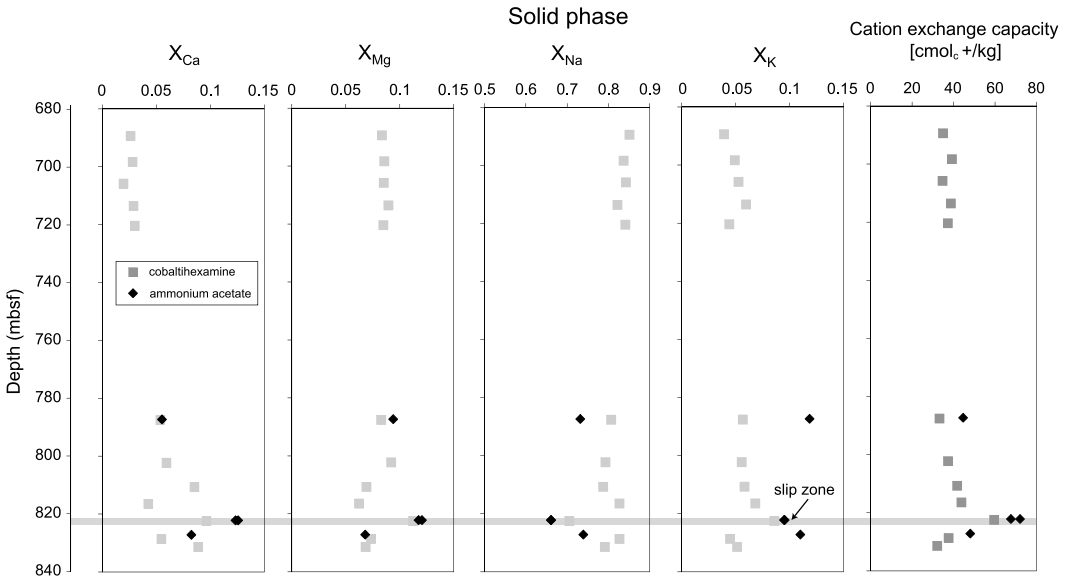

Figure 2. Downhole variations of fractional abundance of exchangeable cations X_i for the interval from 680 to 830 mbsf. Cation exchange capacity of the rock is shown in the rightmost column.

equation. Because there are no data for the slip zone sample, the ion concentration was estimated by fitting and extrapolating data from the surrounding sections with a logistic curve function (Figure 3 and Table 3). Although the depth profile of the concentration just above and below the slip zone shows a simple trend that is well fitted by a single logistic curve (Figure 3), it is noted that this extrapolation is appropriate only if the pore fluids are initially at equilibrium, and therefore, one should expect an inverse anomaly compared to the solid phase. Na^+, $K,^+$ and Mg^{2+} concentrations nearly linearly decrease from 470 m*M*, 45 m*M*, and 9 m*M* at 780 mbsf, to 450 m*M*, 35 m*M*, and 7 m*M*, respectively, to the bottom of the hole (835 mbsf). On the other hand, Ca^{2+} steadily increases from 10 m*M* to 40 m*M* over the same depth interval.

Figure 4 shows the apparent selectivity coefficient (logarithmic scale) of each ion species on smectite (equations (1)–(3)) as a function of depth, calculated from equation (4). The logK_{Mg2+} ranges from -0.6 to >0 and shows an apparent positive anomaly at the fault, indicating a greater selectivity of Mg^{2+} (i.e., deviation from the equilibrium state due to uptake of Mg^{2+}), while K_{Na+} shows a negative anomaly in the fault zone. There is no apparent anomaly in the K_{Ca2+} profile at the fault zone.

4. Discussion and Conclusions

The results of our measurement indicate that the total positive charges of exchangeable cations in a sample, namely, exchange capacity of the bulk sample, is around 2 times greater in the slip zone than the surrounding areas (Figure 2). This is consistent with the previous results that the slip zone is enriched in smectite [*Kameda*

Table 2. Shipboard Data of Major Cation Concentrations in Interstitial Fluids of JFAST Samples

Sample	Depth (mbsf)	Ca^{2+} (m*M*)	Mg^{2+} (m*M*)	Na^+ (m*M*)	K^+ (m*M*)
C0019E-04R-1, 102.5 cm	689.525	8.0	42.0	487.6	8.9
C0019E-05R-2, 90.8 cm	698.308	7.7	41.1	484.4	8.5
C0019E-06R-2, 63.5 cm	705.955	8.0	41.4	484.3	8.6
C0019E-07R-1, 46.5 cm	713.465	8.1	40.9	490.8	9.3
C0019E-08R-2, 15.0 cm	720.565	8.9	43.1	491.1	9.0
C0019E-12R-2, 69.0 cm	787.56	11.6	44.9	475.7	9.6
C0019E-13R-2, 57.5 cm	802.385	14.5	42.8	473.9	8.0
C0019E-14R-1, 64.8 cm	810.648	15.8	40.1	463.3	8.2
C0019E-15R-1, 10.5 cm	816.605	17.9	39.3	461.5	8.6
C0019E-19R-2, 85.8 cm	828.548	32.7	36.7	452.7	7.5
C0019E-20R-1, 55.0 cm	831.55	38.9	35.4	447.9	7.1

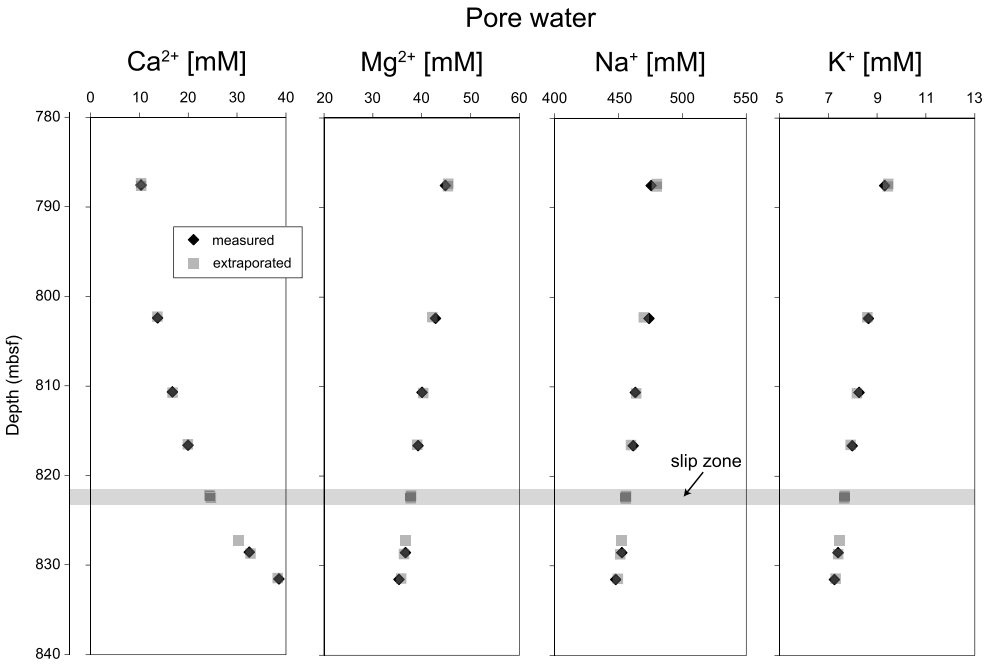

Figure 3. Major cation concentrations in interstitial fluids squeezed from the JFAST cores (gray symbols). The pore fluid chemistry in the slip zone was estimated by extrapolating from data for surrounding sediment cores (black symbols).

et al., 2015]. Although the XRD analyses also occasionally identified zeolite that also has cation exchangeability, it only occurs sporadically in trace amounts, indicating that smectite is the main exchanger of cations in the analyzed system. Therefore, the complementary anomalies between K_{Mg2+} and K_{Na+} in the slip zone suggest local progress of Na^+ to Mg^{2+} exchange reaction on smectite. As described earlier, the exact pore fluid chemistry of the fault zone was not determined from the onboard measurements, and we estimated the cation concentration by extrapolating data from the surrounding areas. This surmised value may be more appropriate for the equilibrium state before the reaction was progressed. If the fluid-rock reaction system was closed, then the selective uptake of Mg^{2+} on smectite and complementary releasing of Na^+ should result in decreasing and increasing of each cation species in the pore fluid. In this case, calculated selectivity coefficient for these cations represents a lower bound, and the anomalies may be further enlarged.

Extensive research has investigated the equilibrium constant of exchange reactions on smectite [e.g., *Benson*, 1980]. The reaction depends on factors such as valence and size of ions, but general affinity of cation to smectite interlayer is in the order of $Na^+ < K^+ < Mg^{2+} < Ca^{2+}$ [*Mitchell and Soga*, 2005]. Most of these experiments have been conducted on binary reaction system under ambient conditions, and therefore, the reaction equilibrium on temperature is not well constrained. For sedimentary core samples, *Bischoff et al*. [1970] and *Gieskes* [1973, 1974] compared cation compositions in interstitial fluids squeezed at different temperatures and demonstrated that the concentration of monovalent Na^+ and K^+ increases at higher temperature condition, while divalent Ca^{2+} and Mg^{2+} cations decrease. Moreover, the range of variation increases at higher temperature condition in Mg^{2+} than in Ca^{2+} [*Gieskes*, 1973, 1974]. This temperature dependency of fluid chemistry can be interpreted by thermodynamic properties of ion exchange reactions on smectite. In a more direct way, *Laudelout et al*. [1968] examined the thermodynamic properties of exchange reactions on montmorillonite smectite by calorimetric analyses and observed positive enthalpy changes (ΔH^0) for both Na^+ to Mg^{2+} and Na^+ to Ca^{2+} exchanges (i.e., endothermic), with the former having a lager ΔH^0. Although it is not easy to predict precisely how an equilibrium state changes at elevated temperatures in multiple-cation systems such as in natural fault zones, the earlier experimental results suggest that the Na^+ to Mg^{2+} exchange reaction is expected to be the most preferable process when temperature of a reaction system rises.

In the JFAST borehole temperature observatory by Expedition 343T, a small temperature anomaly (~0.3°C) was detected around the slip zone of the Tohoku earthquake [*Fulton et al*., 2013]. This anomaly was ascribed to a transient pulse of temperature rise caused by coseismic frictional heating, and the temperature profile

Table 3. Activities of Major Cations in Interstitial Fluids and Selectivity Coefficients of Ca, Mg, and Na on JFAST Samples

Sample	Depth (mlsf)	Ca^{2+} (m*M*)	a_{Ca} (*M*)	Mg^{2+} (mM)	a_{Mg} (*M*)	Na^{+} (m*M*)	a_{Na} (*M*)	K^{+} (m*M*)	a_{K} (*M*)	Ionic Strength	$\log K_{Ca}$	$\log K_{Mg}$	$\log K_{Na}$
Cobaltihexamine													
C0019E-04R-1, 94.0 cm[a]	689.44	8.0	0.0040	42.0	0.021	487.6	0.410	8.9	0.0075	0.647	0.381	−0.266	−0.115
C0019E-05R-2, 95.5 cm[a]	698.355	7.7	0.0039	41.1	0.021	484.4	0.407	8.5	0.0071	0.639	0.449	−0.263	−0.186
C0019E-06R-2, 14.0 cm[a]	705.85	8.0	0.0040	41.4	0.021	484.3	0.407	8.6	0.0086	0.641	0.103	−0.111	0.008
C0019E-07R-1, 59.0 cm[a]	713.59	8.1	0.0040	40.9	0.020	490.8	0.412	9.3	0.0078	0.646	0.436	−0.192	−0.243
C0019E-08R-2, 0.0 cm[a]	720.415	8.9	0.0044	43.1	0.021	491.1	0.412	9.0	0.0090	0.656	0.426	−0.272	−0.154
C0019E-12R-2, 76.0 cm	787.63	11.6	0.0058	44.9	0.022	475.7	0.399	9.6	0.0081	0.654	0.730	−0.463	−0.267
C0019E-13R-2, 45.0 cm	802.26	13.7	0.0068	42.2	0.021	469.8	0.395	8.6	0.0086	0.646	0.647	−0.306	−0.340
C0019E-14R-1, 74.0 cm	810.74	16.8	0.0083	40.3	0.022	463.9	0.389	8.2	0.0082	0.657	0.889	−0.594	−0.295
C0019E-15R-1, 0.0 cm	816.5	19.9	0.0099	39.1	0.019	459.9	0.387	7.9	0.0079	0.645	0.124	−0.342	0.218
C0019E-17R-1, 99.0 cm	822.49	24.7	0.0122	37.8	0.019	455.8	0.383	7.7	0.0077	0.650	0.516	0.054	−0.569
C0019E-19R-2, 102.0 cm	828.71	32.8	0.0162	36.4	0.018	451.5	0.378	7.4	0.0074	0.666	−0.157	−0.054	0.210
C0019E-20R-1, 45.0 cm	831.45	38.3	0.0188	35.8	0.018	449.5	0.376	7.3	0.0073	0.679	0.198	−0.216	0.018
Schollenberger													
C0019E-12R-2, 48.0 cm	787.35	10.3	0.0051	45.5	0.022	480.2	0.403	9.5	0.0095	0.657	0.904	−0.380	−0.524
C0019E-17R-1, 67.5 cm	822.175	24.4	0.0121	37.8	0.019	456.0	0.383	7.7	0.0077	0.650	0.790	0.022	−0.812
C0019E-17R-1, 70.0 cm	822.2	24.5	0.0122	37.8	0.019	455.9	0.383	7.7	0.0077	0.650	0.758	0.057	−0.815
C0019E-19R-1, 69.0 cm	827.19	30.3	0.0150	36.7	0.018	452.5	0.379	7.5	0.0075	0.661	0.365	−0.266	−0.099

[a]For calculating activities of cations for these samples, measured values from nearby samples were used.

observed was well reproduced by numerical modeling with a very small dynamic friction coefficient (0.08) [*Fulton et al.*, 2013]. The authors estimated that maximum temperature reached as high as 1250°C, assuming that the faulting was localized within a narrow slip zone (~1 mm); peak temperature was less than 100°C if the slip zone was wider than 1 m. Recently, *Schleicher et al.* [2015] analyzed hydration property of smectite in the Tohoku slip zone and concluded that the temperature did not reach 200°C because of persistent occurrence of hydrating smectite. Their observations constrain the maximum temperature experienced by the slip zone and suggest that the coseismic shearing was not as narrow as ~1 mm thick but was widespread along anastomosing shear planes [*Schleicher et al.*, 2015], and it is unclear how much the temperature was elevated during coseimic slip. The anomalous composition of the exchangeable cations found in the slip zone is likely related to a recent thermogenic event, and we infer that this may be a signature of coseismic frictional heating during the Tohoku earthquake as demonstrated by *Fulton et al.* [2013]. However, our data are compatible with the results of *Schleicher et al.* [2015], because higher exchanging capacity of the slip zone samples suggests that the extent of collapse of smectite expandability is relatively limited. Even a small temperature increase could markedly foster the exchange reaction as observed in previous research (~20°C) [*Gieskes*, 1973, 1974]. Our data are supportive of the idea that temperatures were not high during the coseismic event, but for more quantitative argument on the experienced temperature of the slip zone, experiments should be conducted to assess the equilibrium constant at elevated temperatures as well as kinetic property of the exchange reaction.

Another significant implication of our result is that the anomalous composition of exchangeable cations can potentially perturb the mechanical state of the fault. Several experiments have examined the frictional properties of cation-exchanged smectite [e.g., *Shimamoto and Logan*, 1981; *Moore and Lockner*, 2007; *Ikari et al.*, 2007; *Behnsen and Faulkner*, 2013], though most studies have focused on Ca-smectite

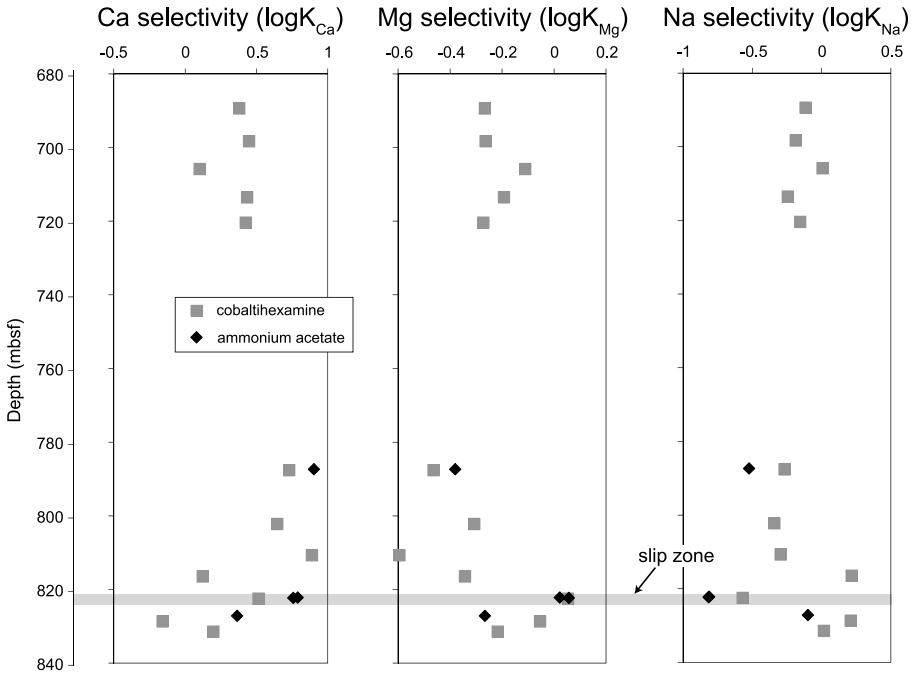

Figure 4. Downhole variations of cation selectivity (see the text for detail) in ternary exchange reaction system. Note that Na^+ and Mg^{2+} selectivities show inverted trends at the slip zone.

and Na-smectite, and Mg-smectite has been only investigated in *Behnsen and Faulkner* [2013]. The frictional coefficient of Na-smectite is higher than Mg-smectite over a wide normal stress ranges [*Behnsen and Faulkner*, 2013]. In the Tohoku slip zone, Mg^{2+} should be higher than the present value at higher temperatures, and if the forward reaction of Na^+ to Mg^{2+} substitution in smectite occurred as quickly as approximately seconds, it might cause progressive weakening of the slip zone and might help coseismic slip and rupture to propagate more easily. In the case that the reaction takes longer than seconds, this could be a weakening mechanism driving afterslip. The exchangeable cation composition in the Tohoku slip zone may be dynamic. The current state of exchangeable cation composition is likely transitional, and Mg^{2+} to Na^+ substitution will continue over time to return back to the original equilibrium state. Considering the experimental results, reestablishment of equilibrium at lower temperature can result in gradual increase of shear strength of the slip zone, which may contribute to postseimic recovery of the slip zone strength.

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