Chemical and isotopic characteristics of interstitial fluids within the Taiwan Chelungpu fault

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We determined chloride and sulfate concentrations and δD_{H2O} and $\delta^{18}O_{H2O}$ isotope ratios of interstitial fluids extracted from cores from two fault zones within the Taiwan Chelungpu fault. The fluids had higher concentrations of chloride and sulfate and higher δD_{H2O} and $\delta^{18}O_{H2O}$ values than the local meteoric water. We concluded that the higher δD_{H2O} and $\delta^{18}O_{H2O}$ values were the result of either entry of surface meteoric water at low altitude via fault zones, or isotopic fractionation by depletion at 50°C in a shallower fault zone, and at 125°C in the deeper fault zone. The high temperature in the deeper fault zone might have been earthquake-related frictional heating, which led to isotopic fractionation. However, neither of the above hypotheses explains the high concentrations of Cl⁻ and SO₄²⁻. We concluded that the high concentrations of Cl⁻ and SO₄²⁻ might have resulted from mixing with seawater and dissolution of pyrite, respectively.

Keywords: Chelungpu fault, Chi-Chi earthquake, pore fluid chemistry, isotopic fractionation, frictional heating

INTRODUCTION

Fault zones provide conduits that focus the flow of fluids and gases in the upper crust. Fluids play a critical role in a variety of faulting processes, including earthquakes. To investigate the geochemistry and origin of interstitial fluid within an active fault zone, Kharaka et al. (1999) conducted chemical and isotopic analyses of water and gases associated with the San Andreas fault system, and concluded that they might include fluids from a deep crustal source. Fluids also play a central role in the deformational, thermal, and geochemical evolution of active convergent plate margins. Kastner et al. (1991) reported that fluids in decollement zones within the Nankai and Barbados accretionary prisms were characterized by lower Cl⁻ concentrations than seawater, as a result of mixing of seawater with fluids expelled by diagenetic and metamorphic dehydration. More investigations of the geochemistry and origins of the fluid in various active fault zones are needed before the role of these fluids in fault and earthquake dynamics can be better understood.

The 2002 Taiwan Chelungpu-fault Drilling Project (TCDP) was undertaken to investigate the faulting mechanism of the 1999 Taiwan Chi-Chi earthquake. The TCDP penetrated the Chelungpu fault (Fig. 1), which slipped during the 1999 earthquake, and recovered core samples from two holes: Hole-A (total depth, 2003.00 m) and Hole-B (total depth, 1352.60 m), separated by 40 meters. In Hole-B, drilled cores were recovered only from depths between 948.42 and 1352.60 m, and three fault zones: 1136m-fault-zone (1136mFZ, 1134–1137 m), 1194mFZ (1194–1197 m), and 1243mFZ (1242–1244 m), were recognized in the core samples as a series within the Chelungpu fault (Hirono *et al.*, 2006b).

To investigate the chemistry of interstitial fluids within the Chelungpu fault, we took samples from the fault-zone cores, squeezed them to expel pore fluid, and analyzed the fluid samples for chloride and sulfate concentration, δD_{H2O} , and $\delta^{18}O_{H2O}$. In this paper, we report the results of these analyses and discuss the origin of the fluids and their relationship to the 1999 Taiwan Chi-Chi earthquake.

FLUID SAMPLING

We took core samples from 1136mFZ and 1194mFZ in Hole-B for pore fluid chemistry (Fig. 2). Core samples were quartered longitudinally, and subsampled into

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Fig. 1. Geological map of central Taiwan showing the site of the Taiwan Chelungpu-fault Drilling Project, an E-W cross section through the borehole site, and the lithological column from core samples recovered from Hole-B. CF: Chelungpu fault, FZ: fault zone.

lengths of 25 cm (1136mFZ: depth 1135.97–1136.22 m) and 20 cm (1194mFZ: depth 1194.88–1195.08 m).

We first removed the outer parts of each sample to avoid contamination by drilling water. Then the samples were squeezed to expel fluids, using procedures and equipment described by Manheim (1968). The retrieved interstitial fluids were immediately transferred to polypropylene bottles, which were refrigerated at 4°C and kept in the dark until analysis. We also tried to extract fluids from gray gouge within 1243mFZ, but were unsuccessful owing to the hardness of the sample and the low pore fluid content.

We took samples of meteoric water at the drilling site and the seeping fluid from borehole in Hole-A after casing (0-1301 m). The depth at which the latter fluid originated is unknown. Drilling water, which was contained within the drilling inner pipes adjacent to each fault-zone cores, was also sampled. River and tap water were the main sources of the drilling water.



Fig. 2. Cores from 1136mFZ and 1194mFZ used for pore fluid analyses, The white broken line shows the section of core from which fluids were extracted. BGZ: black gouge zone, GGZ: gray gouge zone.

ANALYSES

The Cl⁻ and SO₄²⁻ concentrations of the interstitial fluid samples were measured with an ion chromatograph (Tsunogai and Wakita, 1995). Analytical precision was estimated to be 0.4% for these components on the basis of five repeated measurements of the same sample, and accuracy was estimated to be 3% from the measurements of IAPSO standard ocean water.

For measurement of hydrogen isotopic composition, the interstitial water was reduced to hydrogen by using zinc (Coleman *et al.*, 1982). The obtained hydrogen was introduced into a dual inlet mass spectrometer (Finnigan MAT 252). Analytical precision was estimated to be within 1‰. Results are reported in the usual delta notation relative to standard mean ocean water (SMOW) as follows:

$$\delta D_{H2O} = \{ (D/H)_{sample} / (D/H)_{SMOW} - 1 \} \times 1000\%$$

Sample	δD (‰)	$\delta^{18} \mathrm{O}$ (‰)	Cl⁻ (mmol/kg)	SO4 ²⁻ (mmol/kg)
1136mFZ pore fluid drilling water	-32.1 -55.4	-4.9 -8.0	2.3 0.5	53.8 0.4
1194mFZ pore fluid drilling water	-36.9 -56.3	-4.6 -8.4	2.6 0.9	53.3 0.6
Seeping fluid from borehole in Hole-A Rain Seawater (as reference)	-45.4 -45.5 0	-6.8 -6.8 0	0.3 0.3 550	0.8 0.8 28

Table 1. Chloride and sulfate concentrations, δD_{H2O} , and $\delta^{18}O_{H2O}$ for pore fluids, drilling water, seeping fluid from Hole-A, and meteoric water and comparison to seawater (Berner and Berner, 1996)

Analyses of oxygen isotopic compositions of water were repeated three times with a MAT252 continuous flow isotope ratio mass spectrometer, using the technique described by Ijiri *et al.* (2003). The interstitial water was introduced into a glass vial together with solid NaHCO₃ for H₂O-CO₂ equilibration. The oxygen isotopic composition of CO₂ in the gas phase in the vial was analyzed using an isotope-ratio-monitoring gas chromatographmass spectrometer. Analytical precision was estimated to be within 0.1‰. Results are given relative to SMOW:

$$\delta^{18}O_{H2O} = \{({}^{18}O/{}^{16}O)_{sample}/({}^{18}O/{}^{16}O)_{SMOW} - 1\} \times 1000\%.$$

RESULTS

Analytical results of chemical and isotopic analyses are shown in Table 1. The relationship between δD_{H2O} and $\delta^{18}O_{H2O}$ is presented in Fig. 3. The δD_{H2O} and $\delta^{18}O_{H2O}$ values of meteoric water at the drilling site were -45.5%and -6.8%, respectively, and their relationship agreed well with the local meteoric water line in Taiwan (Shieh *et al.*, 1983), which is described by the following equation:

$$\delta D_{\rm H2O} = 8 \times \delta^{18} O_{\rm H2O} + 16.5.$$

Values of δD_{H2O} and $\delta^{18}O_{H2O}$ for the fluid found seeping from the borehole at Hole-A were -45.4% and -6.8%, respectively (Table 1). These were similar values to those of Taiwanese meteoric water, so meteoric water might have been the origin of the seeping fluid. The δD_{H2O} and $\delta^{18}O_{H2O}$ values of interstitial fluid within 1136mFZ were -32.1% and -4.9%, respectively, higher than those of the meteoric water. The δD_{H2O} and $\delta^{18}O_{H2O}$ values of interstitial fluid within 1194mFZ were -36.9% and -4.6%, respectively, and they were also higher than those of the



Fig. 3. Cross plot of δD_{H2O} and $\delta^{I8}O_{H2O}$ values for pore fluids, drilling water, seeping fluid from Hole-A, and meteoric water.

meteoric water. These interstitial fluids had notably higher concentrations of Cl^- and SO_4^{2-} (Table 1).

DISCUSSION

Altitude effect

The effects of altitude on δD_{H2O} and $\delta^{18}O_{H2O}$ were reported by Shieh *et al.* (1983) to be -0.0545%/m and -0.0062%/m, respectively. Because δD_{H2O} and $\delta^{18}O_{H2O}$ values of interstitial fluids within the fault zones were higher than those of the meteoric water, mixing with groundwater from higher altitude would reduce these values and is therefore unlikely. On the other hand, the altitude of the drilling site was approximately 205 m, and the δD_{H2O} and $\delta^{18}O_{H2O}$ values of the meteoric water at 0 m altitude were calculated to be -34.2% and -5.5%, respectively. These values are similar to those of the interstitial fluids within the fault zones, which might imply that the origin of the fluids was mainly meteoric water from lower altitude. Although surface meteoric water entering the fault zones might be a feasible explanation of the $\delta D_{\rm H2O}$ and $\delta^{18}O_{\rm H2O}$ values, its entry to the fault zones and mixing with interstitial fluids would not explain the higher concentrations of Cl⁻ and SO₄²⁻.

This hypothesis indicated that the surface meteoric water entered into deeper portions, at least 931 m under sea level. However, it may be not plausible because the hydraulic gradient would be upward in such a subduction-induced compressive setting. Even though the permeability within the fault zone is reported at most one hundred times larger than the value obtained on core samples from the host rock (Doan *et al.*, 2006), the driving force, hydraulic gradient, along the fault zone was more efficient, but it was not documented in the previous reports.

Mixing with seawater

Seawater has relatively high concentrations of Cl⁻ and SO_4^{2-} , e.g., Berner and Berner (1996) reported averaged concentrations of Cl⁻ and SO_4^{2-} in seawater of 550 mmol/kg and 28 mmol/kg, respectively. Because the host rocks were interbedded marine sandstones and shales, the interstitial fluid during early-stage diagenesis would have been seawater. During and after diagenesis, mixing with other fluids, such as water from dehydration reactions, would have taken place. Faulting might have provided fluid pathways for the entry of paleoseawater into the fault system.

Because the concentrations of Cl⁻ in pore fluids from the Chelungpu fault zones were lower than that of seawater, the origins could be explained by mixing with seawater. Because we had no fluid samples from the host rocks nearby each fault zones, we assumed the δD_{H2O} and $\delta^{18}O_{H2O}$ values of interstitial fluid within host rocks were the same as those of the fluid seeping from Hole-A. We then assumed mixing of the original interstitial fluid (the seeping fluid) with seawater, and calculated that the mixing ratios would be: 1:0.0037 (1136mFZ) and 1:0.0042 (1194mFZ) if the total amounts of Cl⁻ were to be preserved. These mixing ratios would result in slightly higher values of $\delta D_{\rm H2O}$ (-45.2% for 1136mFZ and -45.2% for 1194mFZ) and no difference in the values of $\delta^{18}O_{H2O}$ (-6.8% for 1136mFZ and -6.8% for 1194mFZ). On the other hand, the concentrations of $\mathrm{SO_4}^{2-}$ within the fault zones were approximately twice as high as that in seawater, indicating that mixing with seawater alone could not explain the observed total concentrations. The ratios of SO_4^{2-}/Cl^- (23.4 for 1136mFZ and 20.5 for 1194mFZ) were slightly higher than that of seawater (19.6). The high Cl⁻ concentrations could be explained as the result of mixing with seawater, whereas those of SO_4^{2-} could not. The mixing would not raise the values of δD_{H2O} and $\delta^{18}O_{H2O}$ efficiently.

Table 2. Isotopic discrimination coefficients (Δ) of D/H and
¹⁸ O/ ¹⁶ O under varied temperature conditions, and after inter-
action with montmorillonite, and calculated fractions of residual
fluids

Condition	Δ	Fraction of residual fluid	
		1136mFZ	1194mFZ
Depletion at 25°C			
D/H	-76‰	83.9%	89.3%
¹⁸ O/ ¹⁶ O	-9.3‰	81.6%	79.0%
Depletion at 50°C			
D/H	-27‰	78.2%	85.4%
¹⁸ O/ ¹⁶ O	-5.0‰	77.7%	74.7%
Depletion at 75°C			
D/H	-27‰	70.6%	80.0%
¹⁸ O/ ¹⁶ O	-5.0‰	73.2%	69.7%
Depletion at 100°C			
D/H	-27%	60.5%	72.5%
¹⁸ O/ ¹⁶ O	-5.0‰	68.4%	64.4%
Depletion at 125°C			
D/H	-18‰	47.1%	61.7%
¹⁸ O/ ¹⁶ O	-4.1‰	62.6%	58.2%
Depletion at 150°C			
D/H	-11%	29.9%	46.1%
¹⁸ O/ ¹⁶ O	-3.3‰	56.2%	51.3%
Interaction with mont morillonite			
D/H	-60‰	80.0%	86.6%
¹⁸ O/ ¹⁶ O	-27‰	107.3%	108.5%
•			

Isotopic fractionation between liquid and vapor phases

The high δD_{H2O} and $\delta^{18}O_{H2O}$ values in interstitial fluids from within the fault zones might be explained as a result of vaporization being accompanied by isotopic fractionation between liquid and vapor phases. The degree of depletion can be estimated from the following relationships:

$$\delta D_{\text{Fault}} - \delta D_{\text{Host}} = \Delta_D \ln f_D$$
$$\delta^{18} O_{\text{Fault}} - \delta^{18} O_{\text{Host}} = \Delta_Q \ln f_D$$

where Δ_D and Δ_O are the isotopic discrimination coefficients for D/H and ¹⁸O/¹⁶O, respectively, between liquid and vapor phases; δD_{Fault} and $\delta^{18}O_{Fault}$ are isotopic ratios in interstitial fluids within fault zones; δD_{Host} and $\delta^{18}O_{Host}$ are isotopic ratios in interstitial fluids within host rocks (seeping fluid at Hole-A); and f_D and f_O are the fractions of residual fluid. We assumed that the isotopic discrimination for δD_{Fault} and $\delta^{18}O_{Fault}$ occurred at the same time, so that f_D and f_O should have similar values. The isotopic discrimination coefficient depends more strongly on temperature than on pressure. Using the equation of Majoube (1971), we calculated Δ_D , Δ_O , f_D , and f_O at atmospheric pressure with temperatures of 25, 50, 75, 100, 125, and 150°C (Table 2).

The greatest similarity of values of f_D and f_Q were at 50°C for 1136mFZ, and at 125°C for 1194mFZ. Based on temperature measurements from borehole logging (Kano et al., 2006), the current temperature around the three fault zones encountered in Hole-A ranges from 45°C to 47°C, supporting the view that isotopic fractionation of interstitial fluid within 1136mFZ occurred at, or near, the current temperature of the borehole. However, the fractionation of fluid within 1194mFZ cannot be explained by current temperature conditions, such that two hypotheses are proposed: in-situ frictional heating induced by earthquakes affecting the amount of fractionation; or fluid of appropriate δD_{Fault} and $\delta^{18}O_{Fault}$ by isotopic fractionation at deeper depth moving shallower along the fault zone. Hirono et al. (2006a) discovered pseudotachylyte in 1194mFZ and considered it to be evidence of frictional melting, but concluded that the heating process was older than, and unrelated to, the 1999 earthquake. This leads to the conclusion that isotopic fractionation in 1194mFZ was influenced by an earlier heating process, and that the interstitial fluid within the fault gouge was in residence before the 1999 earthquake. If this was the case, it also indicates that fluid flow within the fault gouge was restricted. On the other hand, a depth of 125°C corresponds to 3.8 km when a geothermal gradient of 30°C/km is assumed. If this was the case, the fluid moved approximately 3.7 km along the fault zone (45° dip), and this seems implausible. Therefore, the isotopic fractionation of fluid within 1194mFZ was thought to result from in-situ frictional heating induced by earthquake.

We next examined whether the high concentrations of Cl⁻ and SO₄²⁻ could be explained by vaporization, thus enriching their concentrations in the aqueous phase. The fractions of residual fluid within 1136mFZ (at 50°C) were 78.2% (D/H) and 77.7% (¹⁸O/¹⁶O), which are consistent and average 78.0%. The concentrations of Cl⁻ and SO₄²⁻ in the original interstitial fluid (taken as the seeping fluid at Hole-A) became 0.4 mmol/kg and 1.0 mmol/kg, respectively. The fractions of residual fluid within 1194mFZ (at 125°C) were 61.7% (D/H) and 58.2% (¹⁸O/¹⁶O), which average 60.0%, and their concentrations became 0.5 mmol/kg and 1.3 mmol/kg, respectively. These estimations were lower than those measured, such that the isotopic fractionation does not explain the high concentrations of Cl⁻ and SO₄²⁻.

Other effects

The δD_{H2O} and $\delta^{18}O_{H2O}$ values of the drilling water in both fault zones were lower than those of meteoric water

and interstitial fluids within fault zones. Therefore, the mixing of drilling water with the interstitial fluids would not explain the higher δD_{H2O} and $\delta^{18}O_{H2O}$ values of the interstitial fluids. The lower values for drilling water might be characteristic of the river and tap water used and/or the interactions of drilling water with drilling mud. Although fractionation between water and clay minerals (e.g., montmorillonite) in the drilling mud was a possible mechanism, it was ruled out by large differences in the fractions of residual fluid calculated using isotopic discrimination coefficients of D/H and ¹⁸O/¹⁶O (Table 2).

As previously discussed, the high concentrations of Cl⁻ in pore fluids could be explained by mixing with seawater, whereas the high concentrations of SO₄²⁻ could not. Neither could be explained by the altitude effect or isotopic fractionation by depletion. We therefore speculated that a possible source of SO₄²⁻ was from the dissolution of pyrite (FeS₂). This view was supported by X-ray diffraction data (Tadai, personal communication) that showed there was less pyrite within the fault zones than elsewhere. Dissolution of pyrite is generally dependent on pH, which may be acidic owing to the reaction by faulting and producing abundant H⁺ (e.g., Kameda *et al.*, 2003).

CONCLUSION

Chemical and isotopic characteristics of the interstitial fluids within 1136mFZ and 1194mFZ were higher concentrations of chloride and sulfate, and higher δD_{H2O} and $\delta^{18}O_{H2O}$ values than those of the meteoric water. We considered five hypotheses to explain the higher δD_{H2O} and $\delta^{18}O_{H2O}$ values and concluded that the following two were most appropriate: (1) incoming surface meteoric water at low altitude along fault zones; or (2) isotopic fractionation by depletion at 50°C (1136mFZ) and 125°C (1194mFZ). However, neither of these hypotheses explains the high concentrations of Cl⁻ and SO₄²⁻, which may result from mixing with seawater and dissolution of pyrite, respectively.

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