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Geochemistry of mud volcano fluids in the Taiwan accretionary prism

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Abstract

Taiwan is located at the collision boundary between the Philippine Sea Plate and the Asian Continental Plate and is one of the most active orogenic belts in the world. Fluids sampled from 9 sub-aerial mud volcanoes distributed along two major geological structures in southwestern Taiwan, the Chishan fault and the Gutingkeng anticline, were analyzed to evaluate possible sources of water and the degree of fluid-sediment interaction at depth in an accretionary prism. Overall, the Taiwanese mud volcano fluids are characterized by high Cl contents, up to 347 mM, suggesting a marine origin from actively de-watering sedimentary pore waters along major structures on land. The fluids obtained from the Gutingkeng anticline, as well as from the Coastal Plain area, show high Cl, Na, K, Ca, Mg and NH_4, but low SO_4 and B concentrations. In contrast, the Chishan fault fluids are much less saline (1/4 seawater value), but show much heavier O isotope compositions ($\delta^{18}O = 5.1$–6.5 ‰). A simplified scenario of mixing between sedimentary pore fluids and waters affected by clay dehydration released at depth can explain several crucial observations including heavy O isotopes, radiogenic Sr contents ($^{87}Sr/^{86}Sr = 0.71136$–$0.71283$), and relatively low salinities in the Chishan fluids. Gases isolated from the mud volcanoes are predominantly CH_4 and CO_2, where the CH_4–C isotopic compositions show a thermogenic component of $\delta^{13}C = -38$ ‰. These results demonstrate that active mud volcano de-watering in Taiwan is a direct product of intense sediment accretion and plate collision in the region.

1. Introduction

Mud volcanoes are unique features in tectonically compressed areas, e.g., Taiwan, Trinidad, Indonesia, Russia, and Barbados (see Yassir, 1987; Milkov, 2000; Kopf et al., 2003; Fig. 1A). Studying the chemical characteristics of expelled fluids associated with mud volcanoes activity helps to delineate possible fluid origins and/or sediment–water interactions at depth within the accretionary prisms. Recent Ocean Drilling Program (ODP) drill holes in the Barbados ridge complex, the Peru Margin, and Nankai Trough have drawn further attention to possible impacts of the fluid expulsion fluxes on oceanic chemical budgets (Gieskes et al., 1989; Kastner et al., 1991). The first order estimated water fluxes range from 0.01 to 2 km^3/a globally based on calculations of porosity reductions or clay dehydration in worldwide convergent margins (Bray and Karig, 1985; Kastner et al., 1991). These fluids with their unique chemical compositions, are transported upward along faults, through permeable layers (Gieskes et al., 1993; Moore et al., 1988; Vrolijk et al., 1991) or through activity of mud volcanoes and, eventually, return to the ocean (Barber et al., 1986; Brown, 1990; Kopf et al.,

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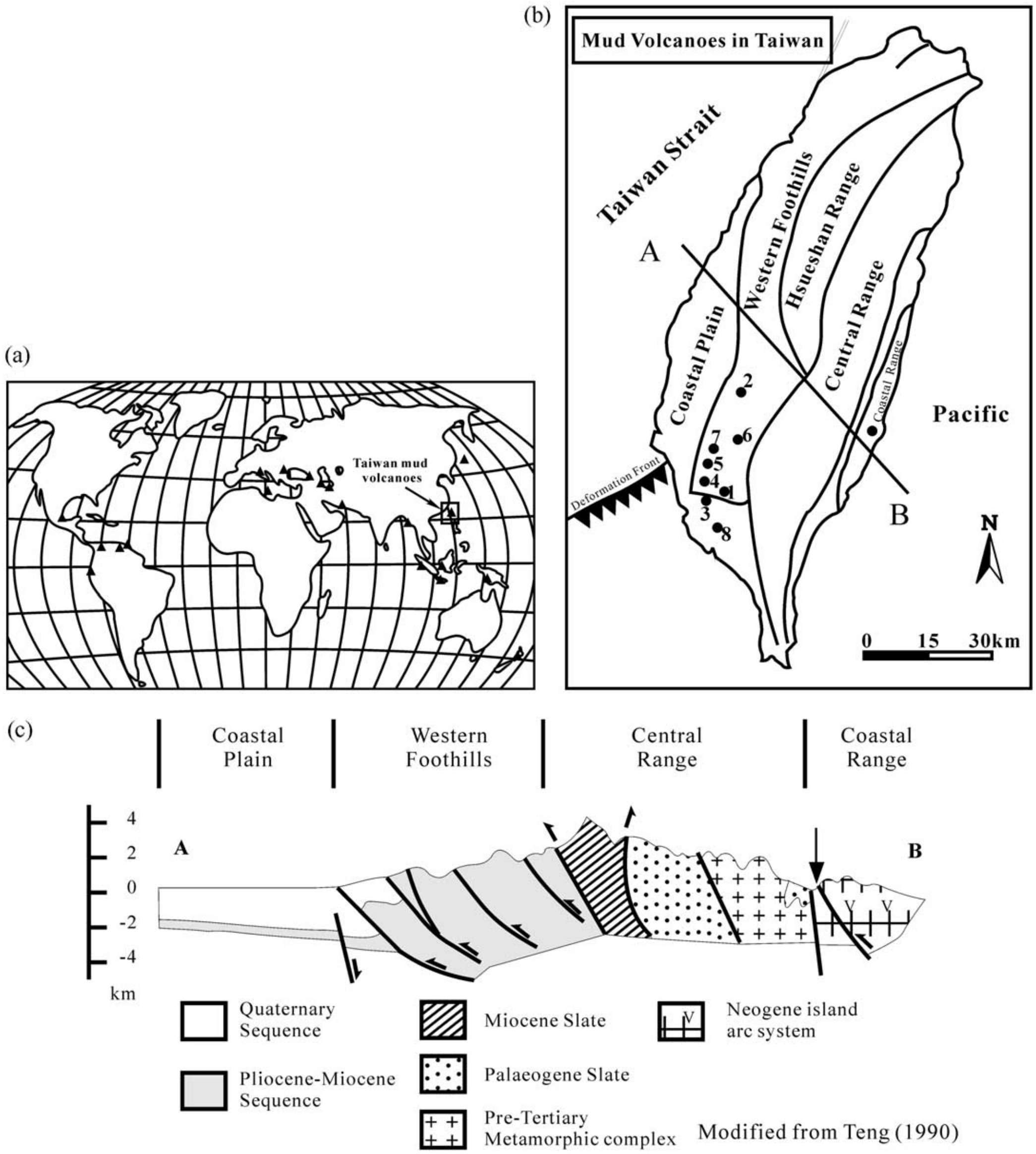

Fig 1. (a) The worldwide distribution of mud volcanoes on land (solid triangle) including Taiwan and Trinidad. Their occurrence correlates well with the locations of tectonically compressed areas globally. (b) The mud volcanoes sited on land in the southwestern Taiwan. The site numbers are labeled according to the sampling dates and the possible deformation front offshore is also described (Huang et al., 1992). Note that the majority of the mud volcanoes visited are located within the Western Foothills. Two mud volcanoes (#3 and #8) are situated in the Coastal Plain and one mud volcano is found in the Coastal Range, eastern Taiwan. (c) An east–west cross section (A–B profile) shows typical thrust fault structures at depth and on land, Taiwan (modified from Teng, 1990).

2001; Kopf and Deyhle, 2002). Active mud volcano fluid expulsion or seafloor seepage has been reported in various areas: the Japan Trench (Boulègue et al., 1987), the Nankai Trough (Gamo et al., 1992), the Oregon Margin (Kulm et al., 1986), the Barbados accretionary complex (LePichon et al., 1990; Martin et al., 1996), and the Mediterranean Sea (de Lange and Brumsack, 1998). Hitherto no direct measurements of chemical fluxes have been made. However, calculations based on progressive porosity reductions have suggested potentially large water fluxes that may have important impacts on oceanic budgets of B, δ^{11}B, Li, and Ca (Han and Suess, 1989; Martin, 1993; You et al., 1993, 1995a,b; Chan and Kastner, 2000).

Previous studies on mud volcanoes have mostly focused on structure, geomorphology, geophysics, and mineralogy (Higgins and Saunders, 1974; Barber et al., 1986; Brown, 1990). Until recently only a very limited number of chemical analyses have been conducted on fluids separated from mud diapirs. Key examples are in the Barbados area (Martin, 1993; Martin et al., 1996), in the Nankai Trough (Boulègue et al., 1987), and in the Caucasus mud volcanoes (Kopf et al., 2003). An interesting study of the chemical and isotopic composition of mud volcano fluids in Trinidad was reported recently, revealing critical information on geochemical processes at depth in convergent margins (Dia et al., 1999). In this paper, attention is focused on examining the chemical and isotopic compositions of fluids and gases from 9 sub-aerial mud volcanoes on land in southwestern Taiwan. The principal objectives are: (1) to compare the fluid chemistry from different geological settings locally, (2) to investigate the origin of fluids and associated gases, (3) to deduce possible sediment–water interactions at depth, and (4) to make a comparison with mud volcanoes from other areas globally in order to investigate common trends.

2. Methods

2.1. Geological settings

Taiwan is located at the boundary between the Philippine Sea Plate and the Eurasian Plate and constitutes a well-known arc-continent collision belt in the western Pacific (Li, 1976; Suppe, 1980). The island consists of 5 major morpho-tectonic units separated by N-S oriented major thrust faults. From west to east, there are the Coastal Plain, the Western Foothills, the Hsuehshan Range, the Central Range, and the Coastal Range (Fig. 1B). The Coastal Plain, the Western Foothills, and the Hsuehshan Range are composed of Cenozoic shallow-marine siliciclastics overlain by Quaternary alluvial deposits. The Central Range is composed of Miocene deep-marine turbidites and Mesozoic to Late Paleozoic metamorphic rock. In contrast, the Coastal Range in eastern Taiwan is composed of Miocene volcanic rocks overlain by Plio-Pleistocene turbidite deposits (Fig. 1C; Teng, 1990; Chang et al., 2000). Intense compressional tectonism has caused an extremely high rate of uplift and erosion island-wide (Liu, 1982; You et al., 1988) and consequently abundant mud volcanoes have erupted on land (Shih, 1967) and offshore (Huang et al., 1992; Liu et al., 1997) due to a focused expulsion of pore fluid.

There occur at least 17 active mud volcanoes in southwestern Taiwan, mainly located within the Western Foothills zone (Wang et al., 1988). Typical mud volcanoes on Taiwan are characterized by the flow of muddy waters accompanied by vigorous out-gassing of CH_4 and CO_2 (Shih, 1967). Among the nine sub-aerial mud volcanoes visited, Wushanting (WST#01) and Hsiaofenway (HFW#06) are located near the Chishan fault and Kunshuiping (KSP#03), Hsiaokunshui (HKS#04), Takunshui (TKS#05), Lungchuan (LC#07) and Chunglun (CL#02) are distributed along the axis of the Gutingkeng anticline (Figs. 1b and 2). Detailed morphological descriptions of these mud volcanoes are summarized in Table 1. Both structures mainly outcrop in the Western Foothills. The Liyushan (LYS#08) mud volcano is located in the Coastal Plain near Pington and Losan (LS#09) and is the only mud volcano field discovered within the Longitudinal Valley in the Coastal Range, eastern Taiwan. Thick overlying marine sediments, estimated to be over 5000 m, are present in both the Gutingkeng and the Chishan regions in southern Taiwan, and no associated igneous activity has ever been reported.

2.2. Sampling and analytical methods

Muddy waters with a range of porosities from less than 10% to greater than 90% were collected directly inside individual mud volcano craters using 50 cm^3 centrifuge tubes. The corresponding fluids were separated subsequently by filtration and/or centrifugation. Natural gases, local meteoric water, and river waters were also collected for the purpose of C, O or H isotopic analyses. A portable GC was employed in the field for continuous monitoring of gas compositions and fluxes in a few mud volcanoes. Salinity, pH, and temperature were also measured in the field. Alkalinity, Cl, Ca, Mg, NH_4, SO_4, B, Li, Na, K, Sr, and Be, as well as δ^6Li,

Table 1
Mud volcanoes visited in Southwestern Taiwan

Name and locality	Description[a]
Chishan Fault	
Wushanting (WST#01)	mud cone, inclination $>20^\circ$
Hsiaofenway (HFW#06)	small mud maar
Gutingkeng Anticline	
Kunshuiping (KSP#03)	mud shield, small cone
Hsiaokunshui (HKS#04)	mud shield, small cone
Takunshui (TKS#05)	mud basin, small cone
Lungchuan (LC#07)	small mud maar
Chunglun (CL#02)	2A: mud basin, large crater (>2m)
	2B: small mud maar
	2C: mud basin, large crater (>2m)
Coastal Plain	
Liyushan (LYS#08)	dead mud basin
Coastal Range	
Losan (LS#09)	mud maar

[a] Nomenclature from Shih (1967).

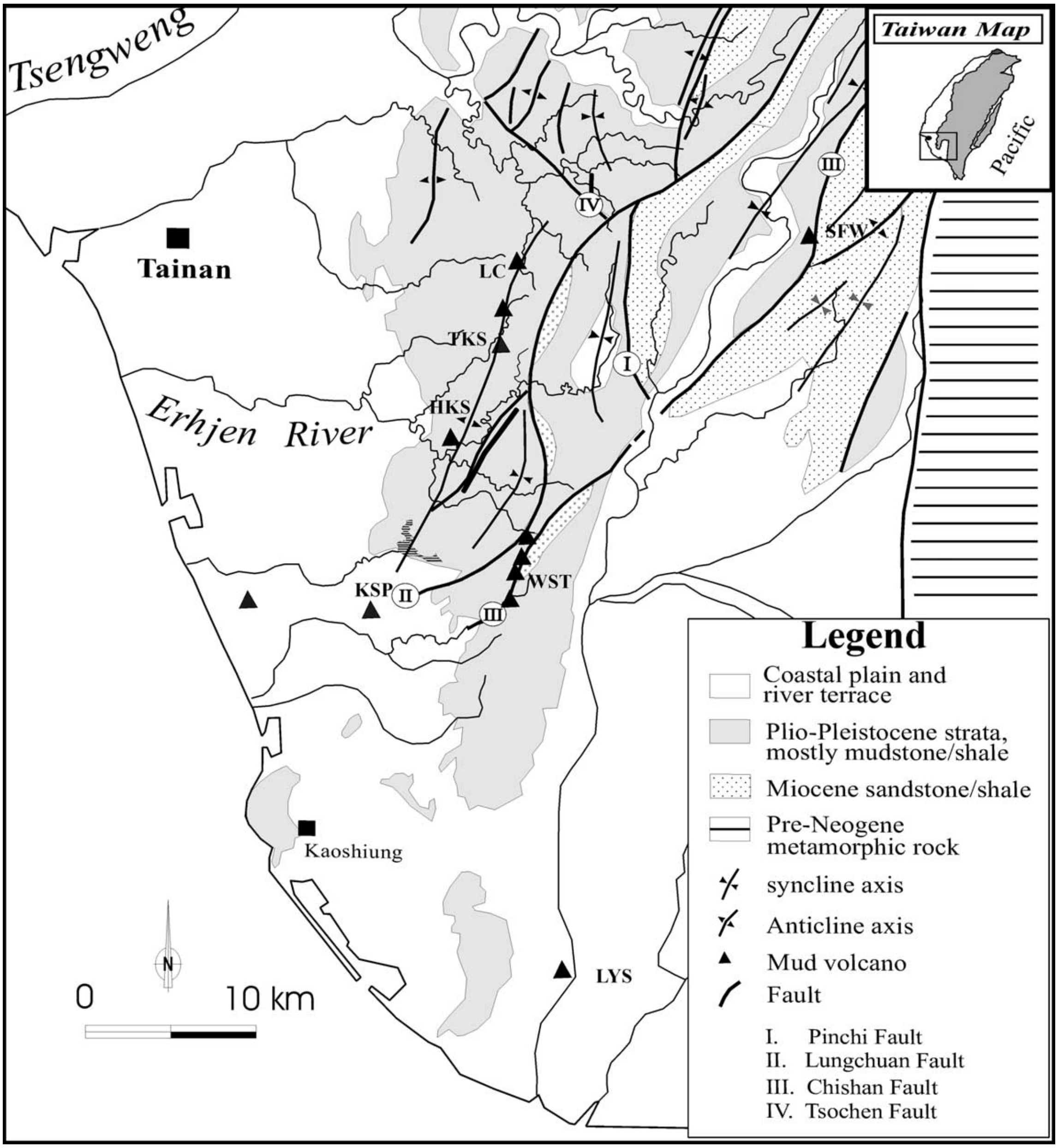

Fig. 2. A detailed geological map shows mud volcano locations, geological structures and their sedimentary stratigraphy in southwestern Taiwan. Two mud volcano fields are located near the Chishan fault (thick line with fault symbol), Wushanting (WST#01) and Hsiaofenway (HFW#06). Five mud volcano fields, Kunshuiping (KSP#03), Hsiaokunshui (HKS#04), Takunshui (TKS#05), Lungchuan (LC#07) and Chunglun (CL#02) are distributed along the axis of Gutingkeng anticline (line with an anticline symbol). Liyusan (LYS#8) is located in the Coastal Plain near Pington and Losan (LS#09) is located near the Coastal Range, eastern Taiwan. Note that CL#02A, #02B, #02C and LS#09 are located outside the range of this map. Closed triangles: mud volcanoes.

$\delta^{11}B$, and CH_4 $\delta^{13}C$ were measured at Scripps Institution of Oceanography and the department of Earth Sciences, National Cheng Kung University. The isotopic compositions of $^{87}Sr/^{86}Sr$, $\delta^{18}O$, and δD were analyzed at Institute of Earth Sciences, Academia Sinica, Taipei. The isotopic compositions of B, Li, O, D and C were calculated relative to standard reference materials SRM951, L-SVEC, SMOW, SMOW and PDB, respectively, and are expressed in terms of delta notation in per-mil (‰). Detailed sampling and analytical procedures have been presented elsewhere (Gieskes et al., 1991; You, 1994).

3. Results and discussion

The chemical and isotopic compositions of the mud volcano fluids analyzed are grouped into 3 categories according to their geological settings and are summarized in Table 2. For the purpose of separating the various mud volcano fields, plots of Cl versus alkalinity, NH_4, and SO_4 are presented in Fig. 3. From these plots it is evident that the Gutingkeng mud volcanoes are characterized by high Cl contents (roughly 65% of the average seawater concentration of 558 mM). On the other hand, the Cl contents of Chishan fault fluids are relatively low. In the anticline region, SO_4 contents are low, ranging between 0.045 and 0.13 mM. But the CL#2A and 2B and LYS#8 mud volcanoes show much higher SO_4, presumably because of contamination from surface sources including meteoric waters, local rivers and/or groundwater. High SO_4 content has been reported in local wet precipitation as a result of acid rain industrial pollution. Ammonium contents of the fluids from the Gutingkeng anticline indicate high values (up to 2.3 mM), mainly as a result of contributions from organic matter diagenesis during SO_4 reduction and CH_4 formation processes. Important observations are of note at the Chunglun mud volcano (CL#2), where linear relationships with Cl concentrations indicate possible mixing relationships or surface evaporation. This relationship also characterizes the plot of $\delta^{11}B$ vs. 1/B, where CL#2B showed a large deviation (see Fig. 7). Below the observations on the Taiwanese mud volcanoes are briefly described.

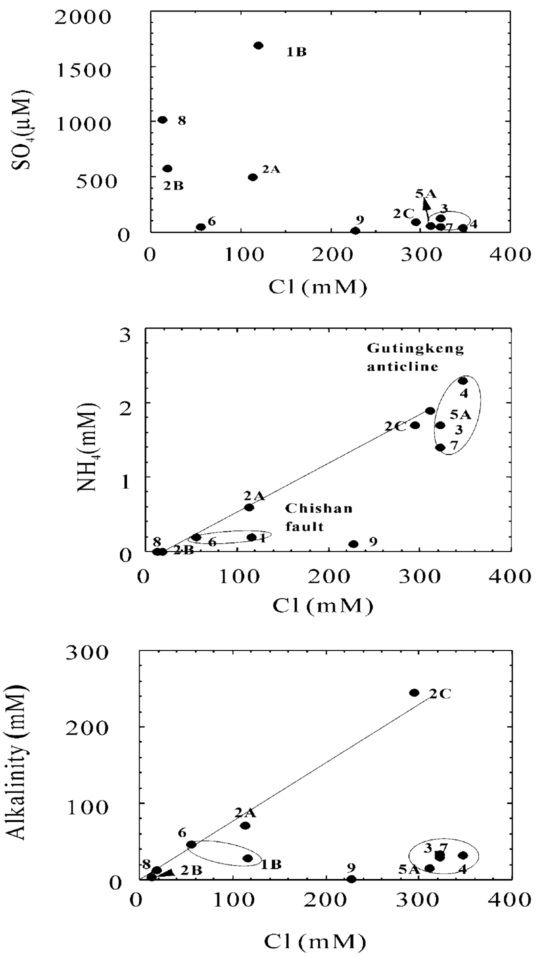

Fig. 3. Correlation plots of Cl, SO_4, NH_4 and Alkalinity in Taiwan mud volcanoes. Fluids sampled from the Chishan fault and the Gutingkeng anticline form two groups showing distinct chemical compositions.

The LS#09 mud volcano sampled from the Coastal Range in eastern Taiwan has distinctive chemical and Sr isotopic compositions compared to the others. It shows low alkalinity, NH_4, SO_4, and Na/Cl, slightly elevated Mg and Cl, high Ca, and a low $^{87}Sr/^{86}Sr$ isotopic ratio (0.70691). Gases isolated from this site are predominantly CO_2 and CH_4 (> 53%) and CH_4 shows a light C isotopic composition ($\delta^{13}C = -38.8$ ‰).

The fluids sampled from the Chishan fault area are characterized by relatively low concentrations of Cl, Na, K, Ca, Mg and NH_4 and relatively high values of alkalinity, SO_4 and B. The most striking features of the fluids associated with this fault zone are the very high $\delta^{18}O$ values (5.1–6.5 ‰) and the radiogenic Sr isotopic compositions ($^{87}Sr/^{86}Sr$ = 0.71136–0.71283). In contrast, the fluids from the Gutingkeng anticline axis and the Coastal Plain fluids are characterized by relatively high Cl contents, up to 347 mM, and a seawater-like $^{87}Sr/^{86}Sr$ ratio, 0.70982.

Three fluid samples, CL#02A, #02B and #02C, sampled from a small area in Chunglun show significant differences both in chemical and isotopic composition. The #02C sample was collected from a small pond with vigorous gas bubbling and has the highest alkalinity, Cl, Na, NH_4, Li and B, but the lowest SO_4 and Ca. The Li concentration in #02C fluids is 815 μM with a δ^6Li of −13.2 ‰. Dissolved B concentrations in most fluids analyzed are close to or higher than the seawater concentration (as much as 20 times) with large variations in $\delta^{11}B$ (~22 to 65 ‰).

Three meteoric waters, one stream water and one pond water were collected in this study. Two of these, however, deviate greatly from the average meteoric water composition (Figs. 4 and 5). SL#06 was collected during a severe thunderstorm event and SKS#03 was taken after a storm from a pool that perhaps was contaminated by mud volcano overflows.

3.1. Fluids in the coastal range

The LS#09 is the only mud volcano situated in the Coastal Range, Eastern Taiwan (see Fig. 1B) and shows distinctive fluid chemical compositions compared to the

Table 2
The chemical compositions of mud volcano fluids in Southwestern Taiwan

	The Chishan Fault		The Gutingkeng anticline and the coastal plain										CR#
	WST-01A	WST-01B	SFW-06	CL-02A	CL-02B	CL-02C	KSP-03	HKS-04	TKS-05A	TKS-05B	LC-07	LYS-08	LS-09
T(°C)	28	28	26	28.8	34.5	40	31					38	29.5
pH		5.8	8.4	7.3	7	6.4	7.8	8.1	8.3		8.1	8.2	7.3
Cl^- (mM)		116	55	113	18	294	321	347	311	296	322	13	227
Alkalinity (mM)		29	47	70.9	12.6	245.1	34.4	32.6	15.4		29.5	3.3	1
NH_4^+ (mM)	0.2	0.2	0.2	0.6	0	1.7	1.7	2.3	1.9		1.4	0	0.1
SO_4^{-2} (μM)	1440	1700	55	500	584	98	130	45	60		50	1020	20
Ca^{+2} (mM)		0.13	0.26	1.39	3.63	0.39	0.67	0.53	1.01	0.91	0.77	0.33	46.9
Mg^{+2} (mM)		0.61	0.24	2.1	0.88	1.23	1.63	1.51	1.4	1.32	0.33	0.29	2.22
K^+ (mM)		97	97	255	104	1022	183	395	146		207	97	97
Na^+ (mM)		155	106	186	40	494	366	373	318		340	10	131
Na^+ (mM)-calculated		147	101	177	23	534	349	373	320		348	17	130
B (mM)	5.46	5.62	2.72	2.32	0.28	9.95	3.04	3.74	2.26		1.03	0.16	0.93
$\delta^{11}B$ (‰)	52		65	33	22	39		46	53				35
Be (pM)		443	940	1474	258	1101	400	672	503	367	863	105	646
Sr (μM)		17.1	10			4							69.2
$^{87}Sr/^{86}Sr$		0.71136	0.71283			0.70982							0.70691
Li (μM)		14	139	367	40	817	170	50		49	128	7	20
δ^6Li (‰)					13.4								
T(°C)		38	102	99	56	130	82	54			95		32
δD (‰)	−18		−23	−33	−22	−26	−16	−18	−19		−19		−10
$\delta^{18}O$ (‰)	6.5		5.1	−2.3	−0.4	5.5	1.9	0.7	1.3		1.5		1
$\delta^{18}O$ (‰)-duplicate			−1.8	−0.1	5.3								
$\delta^{13}C$ (‰)-methane						−38.4							−38.8
Methane (%)						50							1
Meteoric waters													
δD (‰)	−43		−21	−40			−32						−56
$\delta^{18}O$ (‰)	−4.9		−0.6	−5.5			−2.1						−7.5

Isotopic compositions of B, Li, H, O, and C were calculated relative to SRM 951, L-SVEC, SMOW, SMOW, and PDB, respectively; #: The Coastal Range.

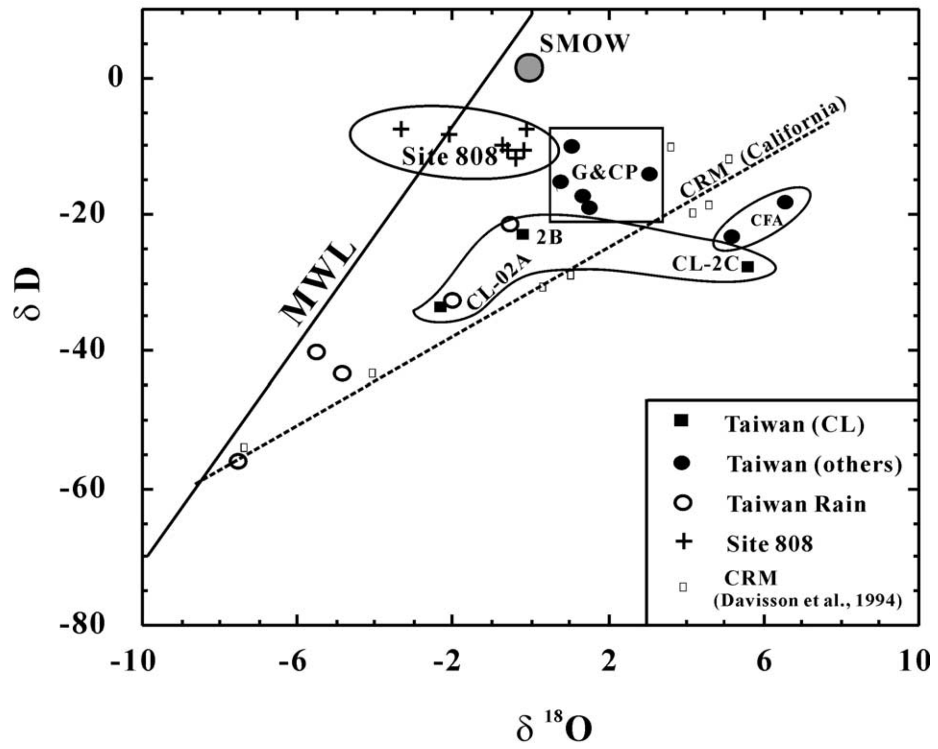

Fig. 4. The $\delta^{18}O$ and δD compositions of fluids in Taiwan mud volcanoes. Additional data from literature including mud volcano fluids of pore waters of ODP Site 808 (Kastner et al., 1993), and expelled spring fluids in Rumsey Hills, California (Davisson et al., 1994; Peters, 1993), are plotted for comparison. In addition, the average meteoric water line (MWL; Shieh et al., 1983), standard mean ocean water (SMOW), rains and river waters sampled during the mud volcano field work are also presented. Symbols: crosses, pore waters of Site 808; open squares, springs in coastal mountain range, California (CRM dashed line represents average regression results for the spring fluids); open circles, rain or river waters collected near the mud volcano fields; closed squares, fluids sampled from the CL area; closed circles, other Taiwanese mud volcano fluids; CFA, Chishan fault; G&CP, Gutingkeng anticline and Coastal Plain.

others. The low alkalinity, NH_4, SO_4 and Na/Cl, as well as the slightly elevated Mg and high Ca concentrations suggest the possible influence of the igneous basement in this region. This is particularly evident from the low (0.70691) isotopic ratio of $^{87}Sr/^{86}Sr$, which indicates a Sr contribution from adjacent young basaltic rocks. High Ca and low Sr isotope ratios have often been inferred to indicate interaction between fluids and volcanic ash or underlying basaltic basement rocks in many oceanic drill holes (e.g., Gieskes et al., 1989). Methane isolated from this site indicates a thermogenic C isotopic composition, $\delta^{13}C = -38.8$ ‰. This CH_4 $\delta^{13}C$ value is heavier than that observed in mud volcanoes in the Barbados area (Martin, 1993; Martin et al., 1996), but is comparable to those in the Caspian basin, Azerbaidzhan (Dadashev and Guliev, 1989). Similarly $\delta^{13}C$ values in CH_4 have been reported in mud volcanoes in the Caucasus (Kopf et al., 2003). Most geochemical and isotopic results obtained in LS#09 are consistent with a scenario that the mud volcano fluids have been affected by underlying basaltic basement or volcanic rocks.

3.2. Fluids in the Western Foothills and the coastal plain

Numerous active mud volcanoes occur in the Western Foothills region, mainly along the Gutingkeng anticline and the Chishan fault. The fluids from the Gutingkeng anticline axis are characterized by relatively high salinity, with Cl concentrations up to 347 mM. On the other hand, the fluids from the Chishan fault show relatively low concentrations of Cl, Na, K, Ca, Mg and NH_4, but relatively high values of SO_4 and B. Chloride is the most conservative major ion in pore waters and its distribution in mud volcano fluids provides crucial information regarding possible water sources. Previously pore waters with low Cl concentrations, as low as that of 1/3 seawater concentration, have been reported during DSDP/ODP studies of the Barbados accretionary complex (Martin, 1993; Vrolijk et al., 1991) and in the Nankai Trough (Gieskes et al., 1993). Several mechanisms have been invoked for explaining the Cl variations, including meteoric water intrusion, clay dehydration, gas-hydrate dissolution, and membrane

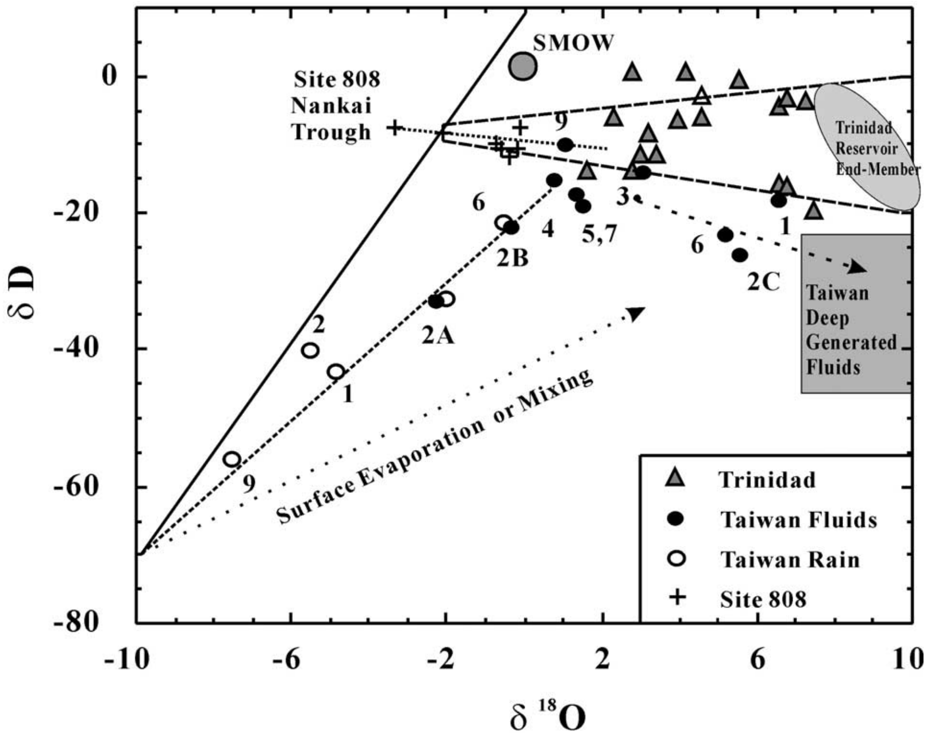

Fig. 5. A comparison of $\delta^{18}O$ and δD compositions in Taiwan and Trinidad mud volcano fluids (Dia et al., 1999).

filtration (Gieskes et al., 1989). Contributions by gas-hydrate dissolution are difficult to evaluate at this stage. Milkov (2000), however, found a close association between gas hydrate and deep-water mud volcanoes worldwide and there are extensive distributions of bottom simulating reflectors (BSR) in the continental shelf area offshore in southwestern Taiwan (Liu et al., 1997). Instability of gas-hydrate can release significant amounts of CH_4 and CO_2 gases and dilute the fluid salinity at the same time. Clay dehydration at temperatures greater than 60 °C was proposed to explain the low salinity of fluids recovered during ODP Legs 110 and 131 (Vrolijk et al., 1991; Kastner et al., 1991, 1993). Such dehydration processes are likely to have contributed to the low salinity of mud volcano fluids, but additional meteoric water dilution cannot be ruled out. Fitts and Brown (1999), however, suggest that, especially in smectite-rich sediments, clay dehydration under moderate excess pressures, even at lower temperatures, can cause dilution of the pore fluids from dehydration.

Other possible factors that may affect the fluid salinity are surface evaporation and/or subsurface groundwater mixing. To evaluate this problem, 3 fluids from the CL area, CL#02A, #02B and #02C, were collected for detailed chemical and isotopic analyses. The CL#02C fluid was collected from a small pond with vigorous gas bubbling, roughly 500 m from the major mud volcano pool where #02A and #02B were collected. In the Cl vs. element plots (see Figs. 3, 6 and 7), the major constituents of alkalinity, NH_4, SO_4, B, Li and $\delta^{11}B$ in the 3 CL fluids fall on a linear mixing trend, suggesting that mixing processes may be operative in this region. Sample #02C has the highest alkalinity, Cl, Na, NH_4, Li and B, but the lowest SO_4 and Ca. Its high Na/Cl ratio (1.4), with an excess of Na associated with a large enrichment in HCO_3, indicates possible reaction between high CO_2 solutions and sediments. Alkalinity and NH_4 data suggest enhanced HCO_3^- and NH_4^+ as a result of organic matter degradation in the CH_4 generation zone, which agrees with the low SO_4 concentrations. The slightly enhanced SO_4 in #02A and B is partly due to an addition of local meteoric water, which has [SO_4] of ~0.5 mM. These results suggest that fluids emanating from Taiwanese mud volcanoes are originally sedimentary pore waters, but mixing with meteoric water or surface evaporation may have occurred during discharge and recharge processes.

3.3. Stable isotope systematics

It is of particular interest to evaluate the data on $\delta^{18}O$ and δD in mud volcano fluids (Figs. 4 and 5). A combination of H and O isotopic results of fluids collected

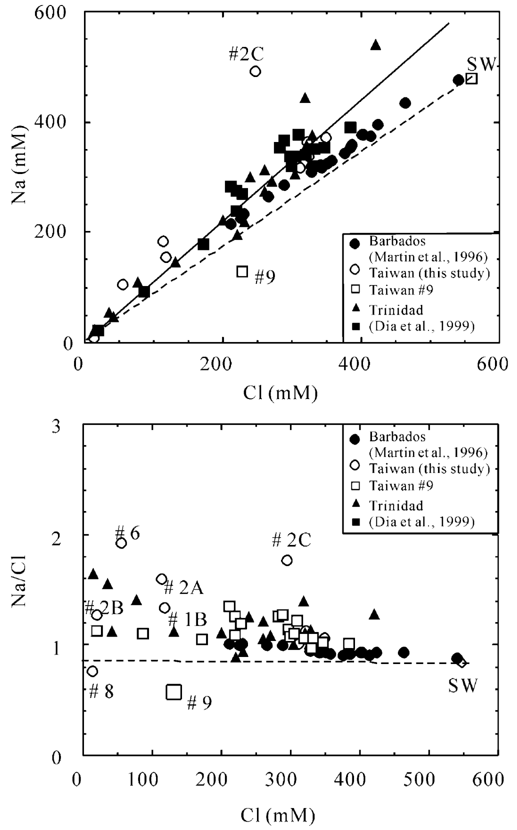

Fig. 6. A comparison of Na and Cl concentrations in Taiwan, Trinidad and Barbados mud volcanoes. The average sea water line is shown for reference. The Trinidad and Barbados results are adopted from Dia et al. (1999) and Martin et al. (1996), respectively.

from the CL#2A and #2B region, with values from the literature, indicates a line with a slope of approximately 2.5. This indicates possible surface evaporation and isotopic exchange with atmospheric moisture or water–sediment interaction at depth (Sakai and Matsubaya, 1977; Chan et al., 2000). The depletion of δD in #2C is significant, possibly due to addition of $\delta^{18}O$-enriched fluids with a low δD of −26 ‰. Such $\delta^{18}O$ and δD isotopic characteristics in fluids agree with the addition of waters derived from clay dehydration. However, more complicated humidity controlled surface evaporation and associated isotopic exchange cannot be ruled out. The associated radiogenic Sr isotopic compositions, $^{87}Sr/^{86}Sr$ = 0.71136–0.71283, compared with the modern seawater value of 0.70925, suggest intense sediment–water exchange at elevated temperatures and are consistent with the observed large Na enrichment in fluids associated with Mg and Ca depletion compared with the seawater composition. The latter chemical characteristic cannot be explained by surface evaporation alone.

As mentioned above, the Chishan fault fluids show relatively low concentrations of Cl, Na, K, Ca, Mg and NH_4 compared with the Gutingkeng anticline (Fig. 3). The most striking features of these fluids, however, are the very high $\delta^{18}O$ values (up to 6.5 ‰) associated with this fault zone (Figs. 4, 5). The observed $\delta^{18}O$ values are among the most ^{18}O enriched fluids on the Earth's surface, except those of high temperature spring waters on land (Peters, 1993; Davisson et al., 1994; Petrucci et al., 1994) or in the mud volcanoes in Trinidad (Dia et al., 1999). Submarine hydrothermal vent fluids from sedimented ridges (Campbell et al., 1994), as well as pore waters in the deeper sedimentary column in Nankai Trough ($\delta^{18}O = -4$ to 2 ‰; Kastner et al., 1993), have similar ^{18}O enriched fluids, although to a lesser degree. Clay dehydration and transformation at depth provides a mechanism for explaining both the relatively low salinity, excess Na, and the heavy $^{87}Sr/^{86}Sr$ in the Chishan samples compared with those from Gutingkeng and the Coastal plain area. Recently a systematic geochemical study of the mud volcano fluids of Trinidad has also shown high $\delta^{18}O$ values, which were explained by interaction with sediment or wall rocks (Dia et al., 1999). The Trinidad data are shown in Fig. 5 and show a similar trend as the Taiwan mud volcanoes, suggesting intense sediment/water exchange has also occurred.

The fluid–rock interaction temperatures estimated for Trinidad mud volcanoes (Dia et al., 1999) are approximately 150 °C and these fluids show similar $\delta^{18}O$ ranges as Taiwanese mud volcanoes. The $\delta^{18}O$ values in Nankai Trough pore waters fall in a range between −4 and + 2 ‰, where the in situ temperature near the décollement zone is approximately 110 °C. The Taiwanese mud volcano fluids extend the trend of Nankai Trough to higher $\delta^{18}O$ values (+ 6.5‰). This, again, is suggestive of deep fluid sources and/or intense water–sediment interactions at elevated temperatures. Alternatively, clay diagenesis leading to the release of interlayer water enriched in ^{18}O and elevated in $^{87}Sr/^{86}Sr$ (Kastner et al., 1993) can explain these observations. The Na enrichment associated with Mg and Ca depletion in Taiwanese mud volcano fluids, however, indicates influence of diagenetic effects due to modification of smectitic clays. The H and O isotopic compositions in the "andesitic waters" in convergent margins (Giggenbach, 1992; Taylor, 1992) are strikingly similar to the mud volcano fluids reported here and in Trinidad (Dia et al., 1999). This can be understood in terms of addition of slab-derived fluids, which were generated at different depths during sediment subduction at convergent margins (You et al., 1996).

The Li and B isotopic compositions in pore waters are sensitive indicators of retrograde alteration at low temperatures. The Li concentration in CL#02C fluids is 815 μM with $\delta^{6}Li$ of −13.2 ‰. Pore waters with similar

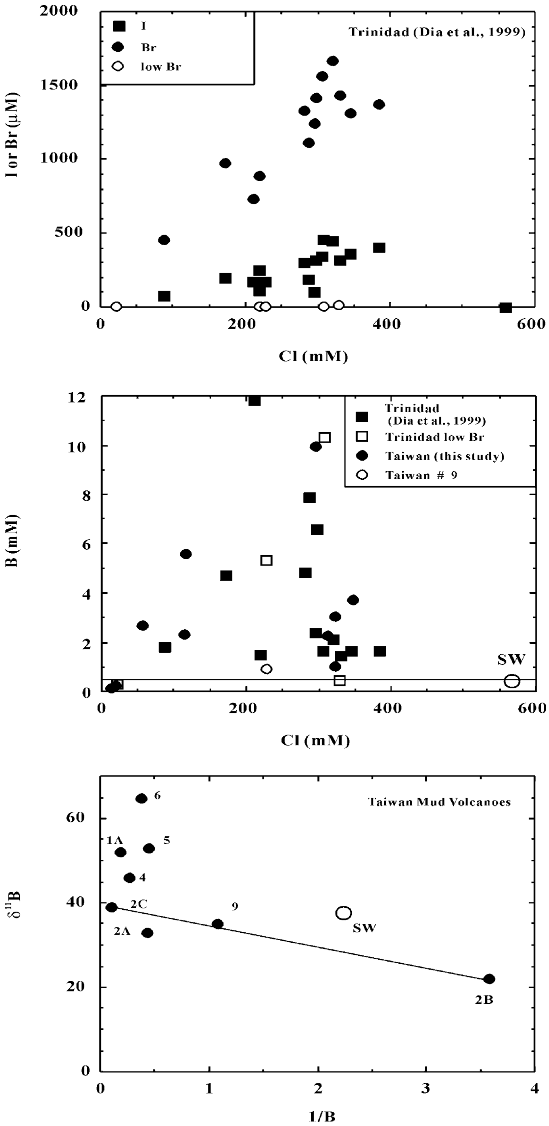

Fig. 7. A comparison of Cl, I, B and $\delta^{11}B$ in Taiwan and Trinidad mud volcano fluids. The seawater B and $\delta^{11}B$ compositions are shown for reference.

compositions have been isolated from the décollement zone in Site 808 at Nankai Trough (You et al., 1995a; Chan et al., 1994). Fluids sampled from mud diapirs on the Barbados accretionary complex display enriched Li concentration, but with seawater-like isotopic compositions ($\delta^6Li = -30$ ‰, Martin, 1993; Martin et al., 1996).

The mud volcano fluids have dissolved B concentrations far greater than that of seawater (as much as 20 times) and show large variations in $\delta^{11}B$ (~22 to 65 ‰). Similar observations were made in the mud volcano fluids of the Caucasus (Kopf et al., 2003), while $\delta^{11}B$ values in Taiwan exceed at times the seawater values (Fig. 7). Two possible processes for the extreme variation in $\delta^{11}B$ values are (1) B-bearing mineral formation with large isotope fractionation or (2) significant chemisorption at clay surfaces or preferential removal of ^{10}B in retrograde alteration reactions at low temperatures. The enhanced B concentrations in the Taiwanese mud volcano fluids, however, cannot be explained by the abovementioned mechanisms. Chemisorption leads to fluids with lower B and heavy $\delta^{11}B$, but surface evaporation or sedimentary contributions will enrich B with lighter $\delta^{11}B$ (Leeman et al., 1992; Spivack et al., 1987). Significant bulk B mobilization has been observed as a result of fluid expulsion in accretionary prisms (You et al., 1993; Kopf et al., 2003), as well as in laboratory hydrothermal water–sediment interactions (You, 1994; You and Gieskes, 2001).

Efficient sedimentary B mobilization at depth, where in situ temperatures are greater than 100 °C, and subsequent chemisorption on clays near surface when fluids discharge, can explain both B and $\delta^{11}B$ compositions observed. Assuming deep-generated fluids have a Cl concentration similar to that of seawater chlorinity (559 mM), an average end-member B in mud volcano fluids of 10 mM can be estimated. This seawater chlorinity assumption is justified as no major Cl-bearing minerals occur in marine sediments and Cl behaves conservatively in porewaters. Using the end-member fluid compositions, the mean B concentration calculated for Chihsan Fault and the Gutingken anticline is 27 and 8 mM respectively, which are comparable to those of mud volcanoes in Trinidad, [B] = 2.5–31.6 mM. A significant B return flux of 1×10^{10} mol/a to the ocean is assigned in worldwide convergent margins if B concentration is 10 mM and de-watering flux is 1 km^3 H_2O/a (Kastner et al., 1991). This flux of B is more than 1/4 of river flux estimated (LeMarchand et al., 2000), which may affect the oceanic budget of B significantly (You, 1994).

3.4. Comparison with Trinidad mud volcanoes

In the section above the similar trends in $\delta^{18}O$ and δD in the Taiwan and Trinidad fluids have already been shown. Here the data obtained for other chemical constituents in other mud volcano fluids is also compared. The contents of Na and Cl have been analyzed in a number of mud volcanoes, both on land and in the ocean. Data on mud volcanoes near the Barbados Accretionary Prism (Martin et al., 1996) and on Trinidad (Higgins and Saunders, 1974; Dia et al., 1999) have been discussed in great detail. In Fig. 6, plots are given of Na vs. Cl and the Na/Cl ratio vs. Cl, including the Taiwan data. In most instances, Na/Cl ratios are well above the seawater ratio, presumably as a result of sediment–pore water interaction. Only mud volcano LS#9 has much lower Na and Na/Cl values, as a result of Na uptake during volcanic matter alteration processes.

Boron contents of the Trinidad and the Taiwan mud volcano fluids are plotted in Fig. 7. In both cases, most fluids have increased B concentrations over those of seawater. The $\delta^{11}B$ values in Taiwanese fluids are also elevated above the seawater value. This presumably is a result of the generation of B at higher temperatures in the deep sediments (You et al., 1996).

The data on I and Br in the Trinidad mud volcanoes are plotted in Fig. 7. Though no data on NH_4 were available for these samples, both the I and Br, as well as NH_4 (see Taiwan data of Fig. 3), are the result of regeneration at depth of organic matter under CH_4 generation conditions (below the SO_4 reduction zone). This is typically observed in rapidly deposited sediments on continental margins (e.g., Martin et al., 1996).

4. Conclusions

The fluids associated with Taiwanese mud volcanoes show distinct chemical characteristics in different local geological settings. The samples distributed at the Gutingkeng anticline axis and Coastal Plain area are characterized by high Cl contents, up to 2/3 seawater, indicating a marine sedimentary pore water origin. This fluid was subsequently expelled to the surface along possible fracture zones. The fluids sampled from the Chishan fault show the lowest salinity and other chemical constituents, but with anomalously high $\delta^{18}O$ (5.1–6.5 ‰) and $^{87}Sr/^{86}Sr$ (0.71136–0.71283). A scenario involving mixing of the original sedimentary pore fluids (like the Gutingkeng fluids) and waters from sediment–water interactions released at higher temperatures with high $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ is proposed to describe the Chishan fault mud volcanoes. Overall, the Taiwanese mud volcanoes show great similarity to those in Trinidad and in the Caucasus, indicating intensive de-watering in accretionary wedges via mud diapiric structures. The high abundance of B in these fluids implies an important impact on oceanic B budgets and deserves further systematic investigation.

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