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Fluid sources and chemical processes inferred from geochemistry of pore fluids and sediments of mud volcanoes in the southern margin of the Junggar Basin, Xinjiang, northwestern China

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ABSTRACT

Understanding fluid sources, water–rock interactions and the biogeochemical processes involved in terrestrial mud volcanoes is necessary in order to predict the chemical processes most responsible for methane emissions to the atmosphere. Mud sediments ejected from the Dushanzi and Sikeshu mud volcanoes, located along the southern margin of the Junggar Basin, northwestern China, were collected by hand core sampling in order to explore whether surface and subsurface geochemical processes occur in their fluids. The ionic compositions of the pore fluids, minerals and major elements of the ejected sediments and surface sediments were analyzed. The pore fluids were mainly derived from ancient deeper sedimentary fluids which had mixed with meteoric surface water, but altered by diagenesis processes. Relative to seawater, the mud volcano pore fluids have higher ratios of Na/Cl and Li/Cl and lower ratios of K/Cl and Mg/Cl. The mud sediments are also enriched in illite, chlorite and calcite, but depleted in smectite. In addition, they are enriched in Ca and Mn, followed by Fe, Mg and P, and depleted in Si relative to the wall rocks. These chemical and mineralogical changes in the mud sediments and pore fluids are related to diagenesis processes. Clay mineral dehydration (mainly involving the conversion of smectite to illite) released large amounts of water. Ion exchange among clay minerals increased Na^+ in the pore fluid. Water–rock interaction increased Fe and Mn, but decreased Si in the mud sediments. Carbonate precipitation decreased Ca^{2+} and Mg^{2+} concentrations of the pore fluid but increased Fe, Mg and P in the mud sediments. These results indicate that the mud volcanoes system is continuously recharged from deeper sedimentary sources. The difference in fluid and sediment geochemistry of the mud volcanoes can be ascribed to the different depths of the fluid and mud sources and the different diagenesis processes during the rising of fluid and mud.

1. Introduction

Mud volcanoes are dome-shaped structures formed by the release of deep underground high-pressure mud, water and gases that rise through propagated faults and highly permeable channels (Milkov, 2000; Kopf, 2002). Mud volcanoes are a common geological phenomenon that can be found all over the world, but mainly develop in the Alps-Tethys suture zone (the Alps-Black Sea-Caspian Sea-Himalaya Range) and the Pacific belt (Dimitrov, 2002; Kholodov, 2002; Kopf, 2002; Sun et al., 2010). Many mud volcanoes are found in large petroliferous basins (e.g. Junggar Basin and Azerbaijan) (Neurauter and Bryant, 1990; Etiope et al., 2009; Mazzini, 2009). Based on the studies of more than 200 mud volcanoes, Etiope et al. (2009) showed that hydrocarbon gases released from mud volcanoes are mostly thermogenic (76%) or a mixture of thermogenic and microbial components (20%), whereas only 4% are of a microbial origin. Recently, the amount of methane emitted into the atmosphere by mud volcanoes was estimated to be 10–20 Tg per year (Etiope et al., 2011).

The geochemical study of fluids erupted from terrestrial mud volcanoes suggested multiple fluid sources and complex processes of subsurface migration. The fluids expelled at mud volcanoes may represent complex mixtures of deep and shallow waters (Planke et al., 2003), and the original chemical and isotopic composition of the fluid may be modified. The fluids may have come from sediment pore fluids and deep brine, mixed with cycling meteoric water, and been diagenetically altered by water–rock interactions

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at depth, organic matter degradation, aerobic and anaerobic methane oxidation, or chemical interactions between fluids and bedrock (Martin et al., 1996; Planke et al., 2003; Nath et al., 2008; Liu et al., 2009; Cheng et al., 2012). However, the processes ongoing during the fluid migration still remain poorly understood. So far, little is known about the geochemical process of fluid ejection associated with mud volcanoes, especially in mud volcanoes located in arid inland environments. Modern mud volcanoes associated with oil and gas fields are distributed along the southern margin of the Junggar Basin, Xinjiang, northwest China. The aim of this study is to explore the surface and subsurface geochemical processes operating on the fluids of these mud volcanoes by analyzing their ionic compositions and the mineralogical and chemical compositions of the core and surface sediments from two mud volcanoes located along the southern margin of the Junggar Basin.

2. Sampling and analytical methods

2.1. Geological setting and sampling

The mud volcanoes involved in this study are the Dushanzi (DSZ) and Sikeshu (SKS) mud volcanoes, located along the southern margin of the Junggar Basin. The DSZ mud volcanoes are located approximately 1 km south of the city of Dushanzi, at an altitude of 896 m (44°18′19.34″N, 84°50′46.45″E) (Fig. 1). This mud volcano has erupted many times, and the latest large eruption occurred in 1995 (Wang et al., 1997). At present, there are only two small vents leaking mud and gases, but numerous bubbles are visible in the water pool, which formed by the mud volcano activity. Three sediment cores (DSZ6, DSZ3, DSZ2, listed in order from center to periphery) from a water pool with an area of approximately 6.8 × 23.8 m, and six surface sediment samples around the water pool edge were collected (Fig. 2).

The Usu SKS mud volcanoes are at present the largest area of mud volcanoes in China, and are located approximately 35 km from Usu city, at an altitude of 1223 m (44°10′57.61″N, 84°23′13.86″E) (Fig. 1). The height of the mud volcanoes is several tens of meters above the surrounding landscape, and there are more than 80 vents, which are generally less than 1 m in diameter. More than 30 vents are still active and a number of these erupt intermittently. The vented materials are mainly mud with minor amounts of gas. The largest vent is oval-shaped and measures approximately 3.3 × 2.1 m. One sediment core (SKS1) from the center of the mud volcano was collected (not a transect). Pore fluids were taken from this sediment core. In addition, 11 samples of the surface sediments around 11 vents were also collected (Fig. 2).

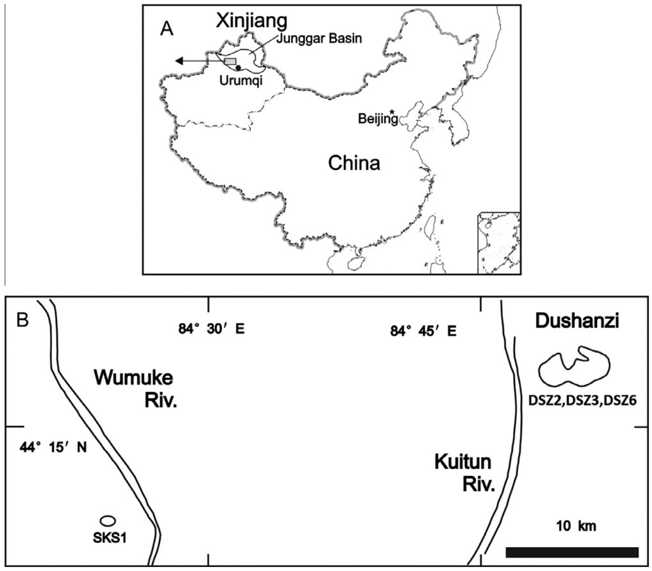

Fig. 1. Location map. Dashed line in (A) represents the border of the Xinjiang Uyghur Autonomous Region. Location of a square marked on map A is enlarged on map B (modified from Nakada et al., 2011 and Dai et al., 2012).

Three to 15 ml of pore fluid was extracted from the sediment cores at depth intervals of 3–10 cm using a Rhizon sampler, which contained a 0.2 μm membrane filter, and then $HgCl_2$ stabilizer was added. All pore water samples were preserved in ion chromatography autosampler vials produced by Thermo Fisher Scientific and stored in a refrigerator at 4 °C. Cores were cut into 2 cm sections and stored at low temperature along with the samples of pore fluids.

2.2. Analytical methods

The concentrations of the major ions (i.e., Cl^-, SO_4^{2-}, Br^-, Na^+, K^+, Li^+, Mg^{2+}, Ca^{2+} and NH_4^+) in the pore fluids were measured using a Dionex-ICS-900 ion chromatograph at the State Key Laboratory of Isotopic Geochronology and Geochemistry, Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences (CAS). The analytical precision and accuracy of the major ions was better than 5%.

The amount of total organic carbon (TOC) in the pore fluids was determined using a TOC-V CPH analyzer at the GIG, CAS. The accuracy was better than 1.5%.

The bulk mineralogy was determined via powder X-ray diffraction (XRD) using a Bruker D8 Advance at GIG, CAS. This instrument employed Cu Kα radiation filtered by a monochromatic crystal and operated at 40 kV and 40 mA. The oriented samples were scanned at an interval of 5–70° (2θ) with a step size of 0.02° and a count time of 5 s per step. Divergence, scattering and the widths of the receiving slits were 0.5°, 0.5° and 0.15 mm, respectively. The relative abundance of minerals was semiquantitatively assessed by way of a Rietveld analysis of the diffractograms using the program SIROQUANT (Taylor, 1991).

The major element compositions of the sediments were determined using a Rigaku ZSX-100e X-ray fluorescence spectrometer (XRF) (GIG, CAS). Loss on ignition (LOI) was undertaken by heating the dried powder samples in a Muffle furnace at 850 °C for 6 h. Calibration lines were generated through bivariate regression from 36 kinds of standard reference materials covering most silicate compositions. Matrix correction was performed in accordance with the Traill–Lachance procedure, and uncertainties in the analytical results were between 1% and 5% (Li et al., 2005). A detailed description of the operating procedure can be found in Li et al. (2006)

3. Results

3.1. Ionic compositions of pore fluids

The ionic compositions of the pore fluids in the cored sediments from the DSZ mud volcanoes are shown in Supplemental Table 1. Depth profiles of the concentrations of Cl^-, SO_4^{2-}, Na^+, Ca^{2+} and Mg^{2+} are presented in Fig. 3. Except for SO_4^{2-} and TOC in DSZ2, the Na^+, Ca^{2+}, Mg^{2+}, Br^-, SO_4^{2-} and TOC in all cores show trends similar to those of Cl^-. In general, these concentrations all increase with depth and then decrease, reaching a peak at about 20–40 cm.

The concentration of Cl^- in the pore fluid of the peripheral DSZ2 sediment core range from 382 to 984 mM, and exhibited a substantial increase to a depth of 28.5 cm followed by a gradual decrease with increasing depth (Fig. 3). Some samples have higher Cl^- concentrations than that of seawater (556 mM). The SO_4^{2-}, Na^+, Mg^{2+}, Ca^{2+} and TOC concentrations in the pore fluids collected from

Fig. 2. Photographs of the mud volcanoes studied. (A) Dushanzi mud volcano. (B) Sikeshu mud volcano. (C) Bubbling with oil leakage in Dushanzi mud volcano. (D) Pore fluid collection.

DSZ2 are 41.13–115.40 mM, 449–1025 mM, 0.54–44.01 mM, 1.11–24 mM and 45–101 μg/g, respectively. The variations in ion concentrations for the middle sediment core DSZ3 are similar to those in DSZ2, except that the minimum value does not appear near the surface but rather at a depth of 6 cm. The concentrations of Na^+, Cl^-, Mg^{2+} and Ca^{2+} in the DSZ6 sediment core (center of the mud volcano) reach their maximum values at a depth of 32 cm and then decrease to minimum values of 529 mM, 471 mM, 10.27 mM and 0.56 mM, respectively. Similarly, the concentrations of SO_4^{2-} and TOC reach their maximum values at a depth of 22 cm and continue to decline to 10.98 mM and 54 μg/g, respectively, showing that this core has higher concentrations of ions and TOC.

The major ion compositions in the pore fluid of the SKS mud volcanoes are Cl^- and Na^+, with the concentrations in a range from 111–170 mM to 161–223 mM, respectively, and with small amounts of Br^-, SO_4^{2-}, Li^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+} in amounts no greater than 1 mM. The concentrations of Cl^- and Na^+ gradually decrease from the top of the core to the bottom; the variation is most evident in the top 10 cm, and shows no significant change below 20 cm. Similar to the levels of Cl^- and Na^+, the concentration of TOC gradually decreases downward in the core, ranging from 318 to 586 μg/g.

3.2. Mineral and the major elements of sediments

The XRD analysis shows that the mineral assemblage of the cored sediment (DSZ6, SKS1) is similar to that of the surface sediments (Supplemental Tables 3 and 4). Both assemblages predominantly consist of chlorite, illite, quartz and albite and a small amount of K-feldspar and calcite (Supplemental Table 3). Yet individual samples contain a small amount of other minerals, such as sample D5 (white, brecciated material), which consists entirely of 30% quartz, 26.1% barite and 43.9% gypsum. In addition, in the SKS mud volcanoes, smectite is only found in surface sediments (in contrast with the sediment core SKS1), with contents ranging from 5.2% to 34.0%.

Chlorite, illite, quartz, albite, K-feldspar and calcite are all found in the sediment cores (DSZ6, SKS1) of the DSZ and SKS mud volcanoes, and the levels of calcite are as high as 6.7–12.5% in DSZ6 and 1.4–5.3% in SKS1.

Concentrations of SiO_2 (50–60.78 wt.%) and Al_2O_3 (13.46–17.2 wt.%, Supplemental Table 5) are high in all samples of the sediment cores. Compared to the sediments from the DSZ mud volcanoes, the sediment cores collected from the SKS mud volcanoes contain more Fe_2O_3 (total), MnO and P_2O_5 but less CaO. When normalized to the reported values of the reddish wall rock from a mud volcano (DSZ-00; Zheng et al., 2010), the concentrations of the major elements, except for Ca, in the cored sediments are similar to those of the wall rock (Fig. 4). Relative to the wall rock, the sediment cores are enriched in Ca and Mn, followed by Fe, Mg and P, and depleted in Si. Other elements, including K, Na, Al, and Ti are largely unchanged.

4. Discussion

4.1. Origin of pore fluid

All the pore fluids collected from the DSZ and SKS mud volcanoes are rich in Cl^- and Na^+ compared to other ions, and this is common for the mud volcanoes around the world both on land and offshore, which are usually considered to have originated from the pore fluids of marine sediments (e.g. Dia et al., 1999; You et al., 2004; Hensen et al., 2007; Liu et al., 2009; Chao et al., 2011). But the mud source of the DSZ and SKS mud volcanoes at the Junggar Basin is Mesozoic or Cenozoic shales (Nakada et al., 2011), which were possibly marine or lacustrine deposits (Carroll, 1998; Song et al., 2004; Zheng et al., 2004; Clayton et al., 1997). Although the Cl^- concentrations in some samples are higher than the seawater value, the significant correlation between Cl^- and Na^+ suggests that the fluids were derived from the same source (Fig. 5). Compared with seawater, pore fluids from the DSZ and SKS mud volcanoes have higher ratios of Na/Cl and Li/Cl and lower K/Cl

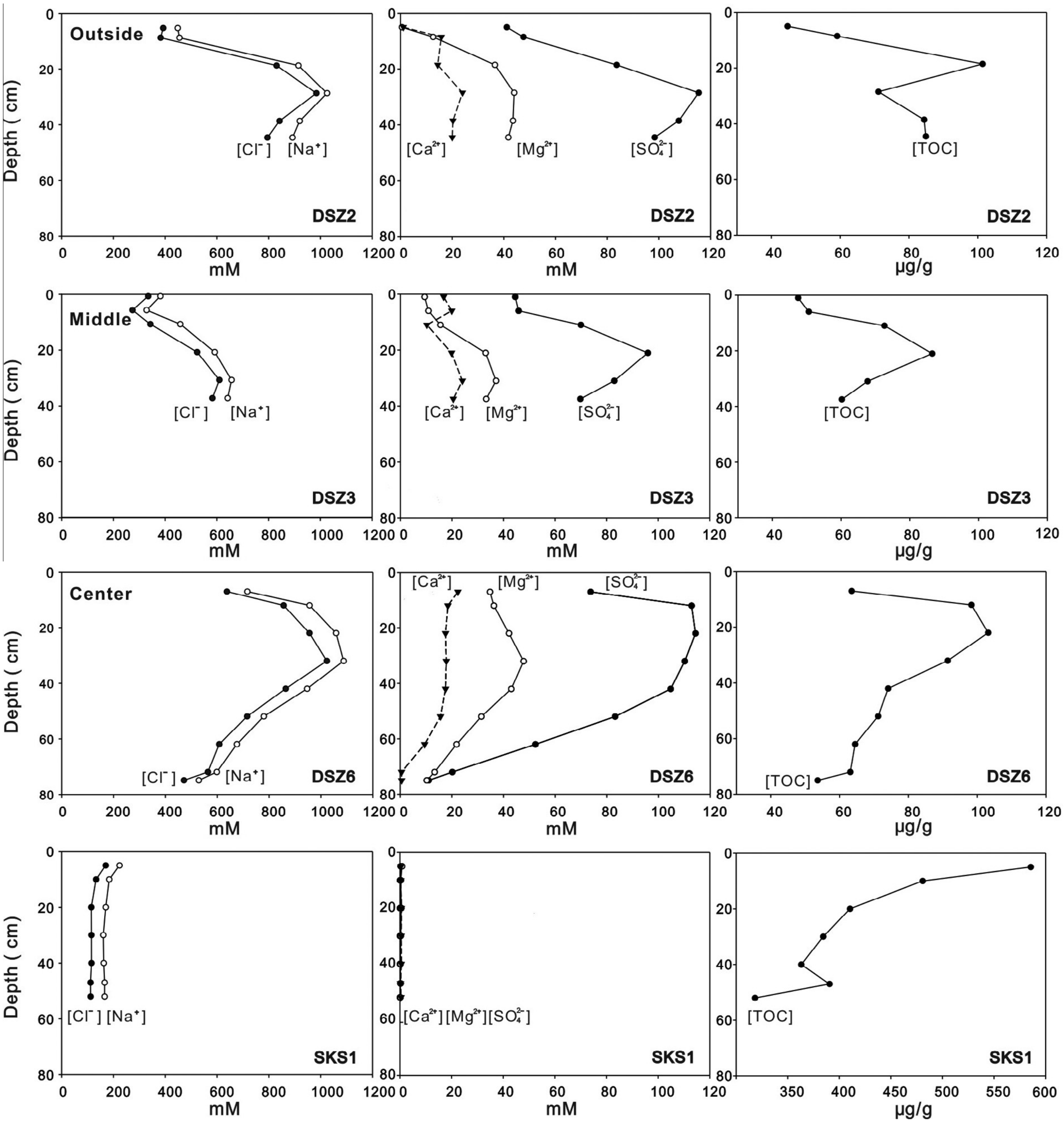

Fig. 3. Geochemical depth profiles shown for cores collected during this study. Labels DSZ2, DSZ3, DSZ6 and SKS1 marked in the diagrams indicate the respective cores.

and Mg/Cl. The ratios of Br/Cl of the SKS mud volcano are higher than those of the DSZ mud volcano, while the ratios of Ca/Cl are lower with some exceptions (Fig. 6). This may be due to different fluid sources and the water–rock interactions in the DSZ and SKS mud volcanoes.

Due to their fast ejection onto the surface, any biological and abiotic effects on the mud and fluid are expected to be weak. Moreover, chloride is the most conservative major ion (inert to most biological and abiotic reactions in such fluids), so the Cl^- concentration in the bubbling fluid may represent the composition of its source at depth. The concentrations of Cl^- in the bubbling fluid from the DSZ and SKS mud volcanoes are 72.4–180 mM and 92.3–109 mM, respectively (Nakada et al., 2011).

Several interpretations for low Cl^- concentrations in pore fluids of mud volcanoes have been proposed, including clay dehydration (e.g. Kastner et al., 1991; Dia et al., 1999; Brown et al., 2001; Dählmann and de Lange, 2003; You et al., 2004; Chao et al., 2013), membrane filtration (Gieskes et al., 1989), and meteoric water inflow (e.g. Aquilina et al., 1997; Dia et al., 1999). The study of hydrogen and oxygen isotopes in fluids collected from the DSZ and SKS mud volcanoes suggests an input of meteoric water (Nakada et al., 2011). The low salinity of fluids obtained from Ocean Drilling Program Legs 110 and 131 was attributed to clay dehydration at temperatures higher than 60 °C (Vrolijk et al., 1991; Kastner et al., 1991, 1993). In addition, the alteration of smectite to illite not only reduces the pore fluid salinity but also releases Na^+ from smectite interlayers and removes K^+. Mimic experiments showed that marine sediments will release Li^+ and B^+ at 50 °C during this alteration (Chan et al., 1994; You et al., 1996; James et al., 2003).

The low Cl^- in mud volcano fluids is partly due to a fresh water contribution derived from clay dehydration. Sediment cores (DSZ6

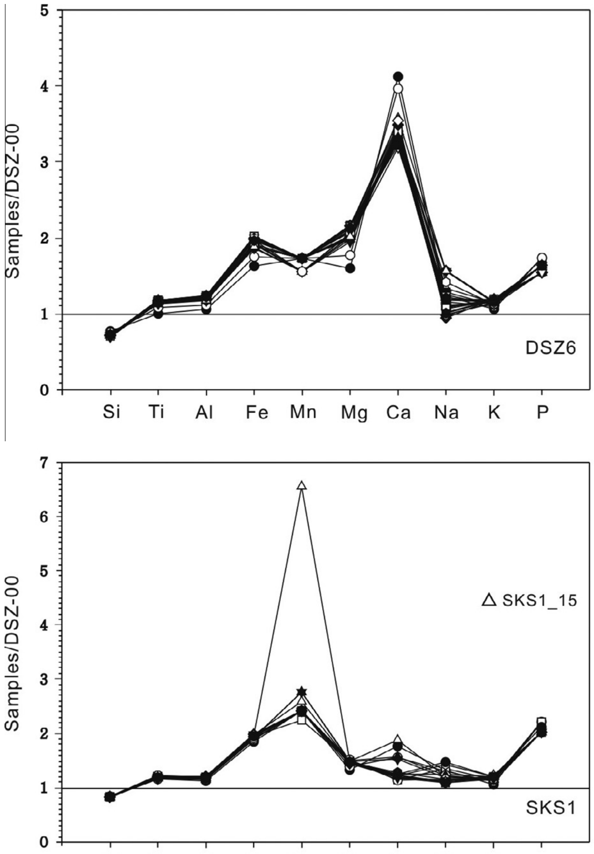

Fig. 4. Major-element distribution of DSZ6 and SKS1 normalized with the wall rock (DSZ-00), the horizontal line represents the same major element composition of DSZ-00.

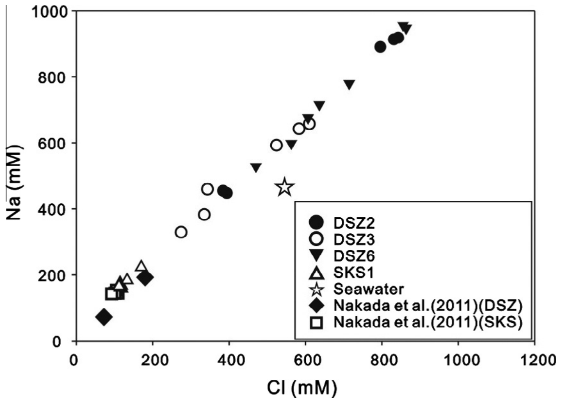

Fig. 5. Plot of Na vs. Cl in DSZ and SKS mud volcanoes.

and SKS1) collected from the mud volcano areas contain large amounts of illite and chlorite, while the wall rocks around the mud volcanoes that are not affected by mud volcano activity contain smectite (Supplemental Table 4). Nakada et al. (2011) used oxygen isotope fractionation between water and calcite to calculate an equilibrium temperature. The calculated temperatures for the DSZ and SKS sites deeper than 3670 ± 200 m were 81 and 95 °C, respectively, which are in the range for smectite dehydration and its alteration to illite. This calculation supports smectite dehydration (including the release of interlayer water) and its alteration to illite by elevated temperatures at depth, yielding low salinity pore fluids. In addition to the influences of clay mineral dehydration and meteoric water, the mud volcano fluids may also be modified by the degradation of organic matter. The Br/Cl and NH_4/Cl ratios in the pore fluids of the SKS site are higher than those of the DSZ mud volcano (Supplemental Table 2). Br^- and NH_4^+ in pore fluids mainly originate from the recycling of organic matter by the effects of sulfate reduction and methanogenesis (Martin et al., 1996; Lein et al., 1999).

4.2. Water–rock interaction

The Na/Cl ratios for SKS are between 1.31 and 1.50 (Supplemental Table 2), which is significantly higher than that of seawater (0.86), indicating the release of Na^+ deep within the mud volcano. In addition, the significant correlation between Na^+ and Cl^- suggests that the release of Na^+ occurred at depth prior to the eruption of the mud volcano. Excess Na^+ can develop due to mineral alteration (alteration of smectite to illite), the dissolution of minerals containing Na^+ (such as Na-feldspar), and ion exchange between layers of clay minerals (Hower et al., 1976; Dia et al., 1999; You et al., 2004). The release of interlayer ions from smectite could be triggered by an increase in the concentration of NH_4^+ due to the decomposition of organic matter. In the case of the SKS mud volcano (Supplemental Table 1), the higher concentration of NH_4^+ in the pore fluids relative to the DSZ mud volcano indicates that the high Na/Cl ratio is due to the release of Na^+ in smectite interlayers and there is a strong water–rock interaction at depth in the mud volcano.

Moreover, according to the calculation by Nakada et al. (2011), the mean temperature of water–rock interactions within the SKS mud volcano is higher than that of the DSZ mud volcano, suggesting that the reaction between fluids and minerals (i.e., carbonates and silicates) at the SKS site is stronger than for the DSZ site. At the same time, the sediment cores from SKS have higher contents of Fe_2O_3 (total) and MnO, and lower CaO than those from DSZ (Fig. 4), suggesting a difference in the source rocks or extensive water–rock interactions. In addition, relative to the wall rocks of the mud volcanoes, sediments from the DSZ and SKS mud volcanoes are depleted in Si and enriched in Fe and Mn, supporting water–rock interactions.

4.3. Fluid processes and evaporation

Based on the chemical compositions of the mud, water and gases of both mud volcanoes, it is suggested that the gas released from the mud volcanoes is mainly methane, and its reservoir depth may be approximately 3600 m (Nakada et al., 2011). Simultaneously, secondary methanogenesis may occur with oil biodegradation in the shallow subsurface in and around the mud volcanoes (Nakada et al., 2011). The carbon and helium isotopes of the natural gas from the mud volcanoes suggest their typical thermogenic origin and crust-derived characteristics (Nakada et al., 2011; Dai et al., 2012). Oil and gas migration is related to the seepage system of the mud volcanoes, and some oxidation of hydrocarbons occurs with concomitant reduction of Fe^{3+} to Fe^{2+} (Zheng et al., 2010).

The DSZ and SKS sites have been active for decades (Li et al., 1996; Wang et al., 1997), and at present still vent mud and gas. Moreover, oil slicks were observed on the pools, suggesting some migration from a deep oil and gas reservoir.

The concentrations of Cl^- in the pore fluids from the DSZ and SKS sites range from 274 to 1023 mM and 111 to 170 mM, respectively. These levels are significantly greater than those of the bubbling fluid which represents the characteristics of the fluid sources for the DSZ and SKS areas, with Cl^- concentrations of 72.4–180 mM to 92.3–109 mM, respectively (Nakada et al., 2011). Considering the high rate of evaporation in the Junggar Basin and that halite is not observed in the area studied, the higher concentration of

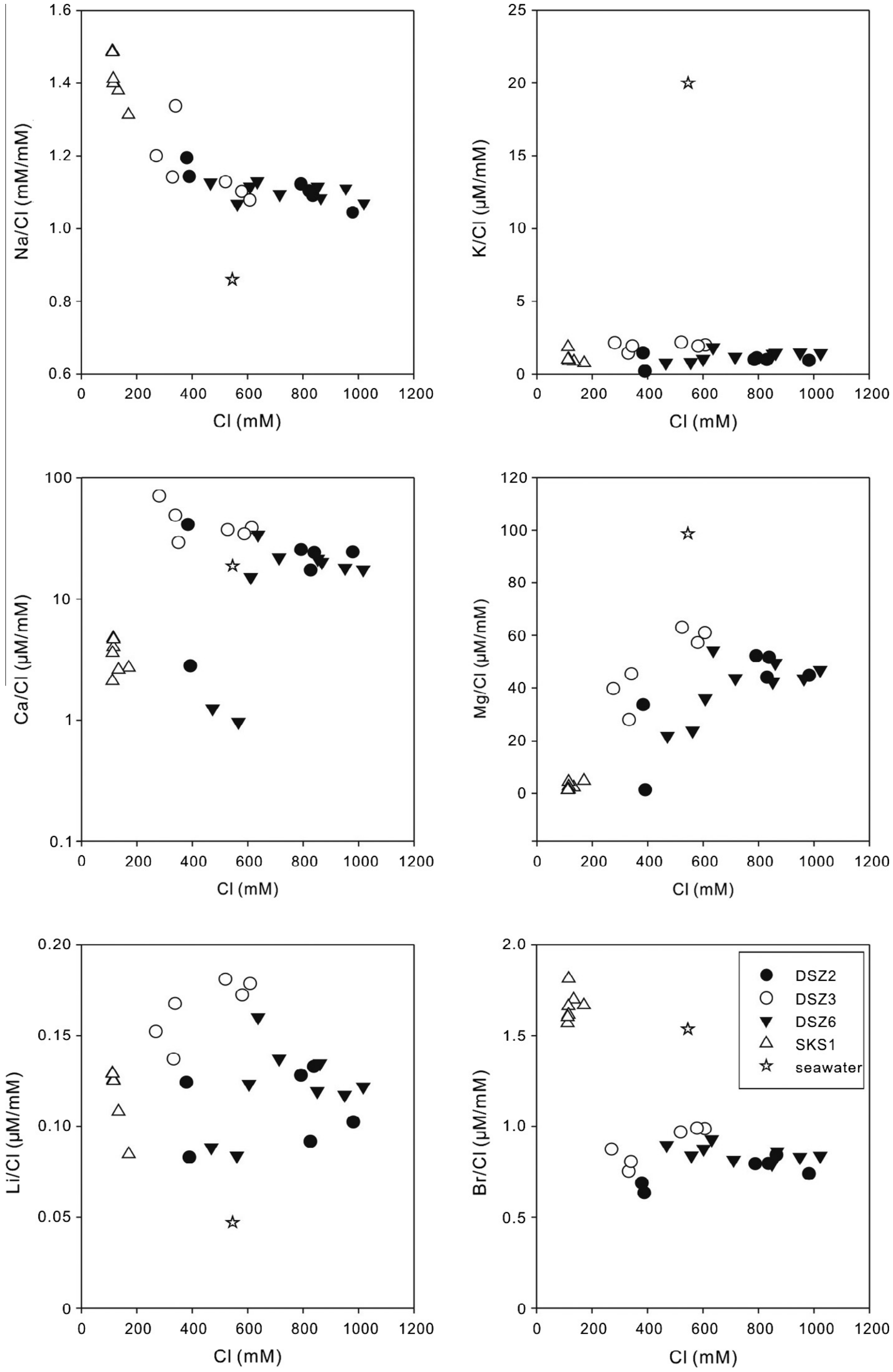

Fig. 6. Plot of element/Cl ratio vs. Cl for all mud volcano fluids in this study. Seawater composition is shown for reference.

Cl⁻ in the pore fluid relative to that in the bubbling fluid may be caused by strong surface evaporation. This is consistent with the significant positive correlation between the Na^+ and Cl⁻ concentrations in the pore fluids of DSZ and SKS. Similarly, the high Cl⁻ in the saline lakes associated with the Dashgil mud volcano is also due to surface evaporation (Mazzini et al., 2009). Furthermore, the Cl⁻ concentrations in the pore fluids of the three cores (DSZ2, DSZ3, DSZ6), increase with depth, reach their maximum at approximately 30 cm, and then gradually decrease with increasing depth, especially in DSZ6 the Cl⁻ drops to 471 mM at 75 cm. The variations of Cl⁻ in the pore fluid of the DSZ site were similar to those of the Lei-Gong-Huo mud volcano in eastern Taiwan, with Cl⁻ from 527 to 666 mM maximizing at a depth of approximately 9 cm (Chang et al., 2012). For this reason, the lower Cl⁻ concentrations below 30 cm in DSZ suggest the input of a lower-salinity fluid from a deep source. The ionic compositions of the pore fluids below 30 cm could result from mixing of deep sourced lower-salinity fluids and fluids that experienced evaporation at the surface, whereas the pore fluids above 30 cm may have been diluted by meteoric water.

In the pore fluids collected from the SKS mud volcano, the Cl⁻ concentrations decrease with depth and finally approach the value of the bubbling fluid (Fig. 3). This trend is similar to that of the Shin-Yan-Ny-Hu mud volcano in southwest Taiwan, which mainly consists of mud, contains little water, and is the product of mixing of low salinity fluids from a deep source and surface evaporation (Chang et al., 2012).

4.4. Carbonate precipitation

Because the concentrations of Cl^- and Na^+ are not affected by biological reactions, their concentrations are mainly controlled by mixing of source fluids, surface evaporation and upward fluid migration. The vertical variation in the Na/Cl ratio in each core is very small (Fig. 7). In contrast, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and TOC are susceptible to biological effects, precipitation and adsorption, and thus the vertical variations in the Ca/Cl, Mg/Cl, SO_4/Cl, and TOC/Cl ratios for the cores are complex (Fig. 7). In cores DSZ2 and DSZ3, the ratios of Ca/Cl, Mg/Cl, and SO_4/Cl in the pore fluid show a trend similar to that of TOC/Cl, and only the Ca^{2+} concentration has a high value at a depth of 10 cm. Interestingly, below a depth of 50 cm in DSZ6, the ratios of Ca/Cl, Mg/Cl, and SO_4/Cl exhibit a decreasing trend with depth, while TOC/Cl increases with depth. In core SKS1, the concentrations of Ca^{2+} and Mg^{2+} are very low, and the ratios of SO_4/Cl and TOC/Cl decrease with depth, followed by the appearance of a high value at approximately 50 cm, which is presumably controlled by other factors. In addition, the calculation using PHREEQC (Parkhurst, 1995) with the WATEQ4F database (Ball and Nordstrom, 1991) showed that water samples from bubbling fluid of the DSZ and SKS mud volcanoes are saturated with calcite and dolomite (Nakada et al., 2011).

At the same time, sediments in core DSZ6 below 50 cm contain a higher concentration of calcite than the sediments above 50 cm, and the highest value reached is 12.5%. The ratios of Mg/Ti and Fe/

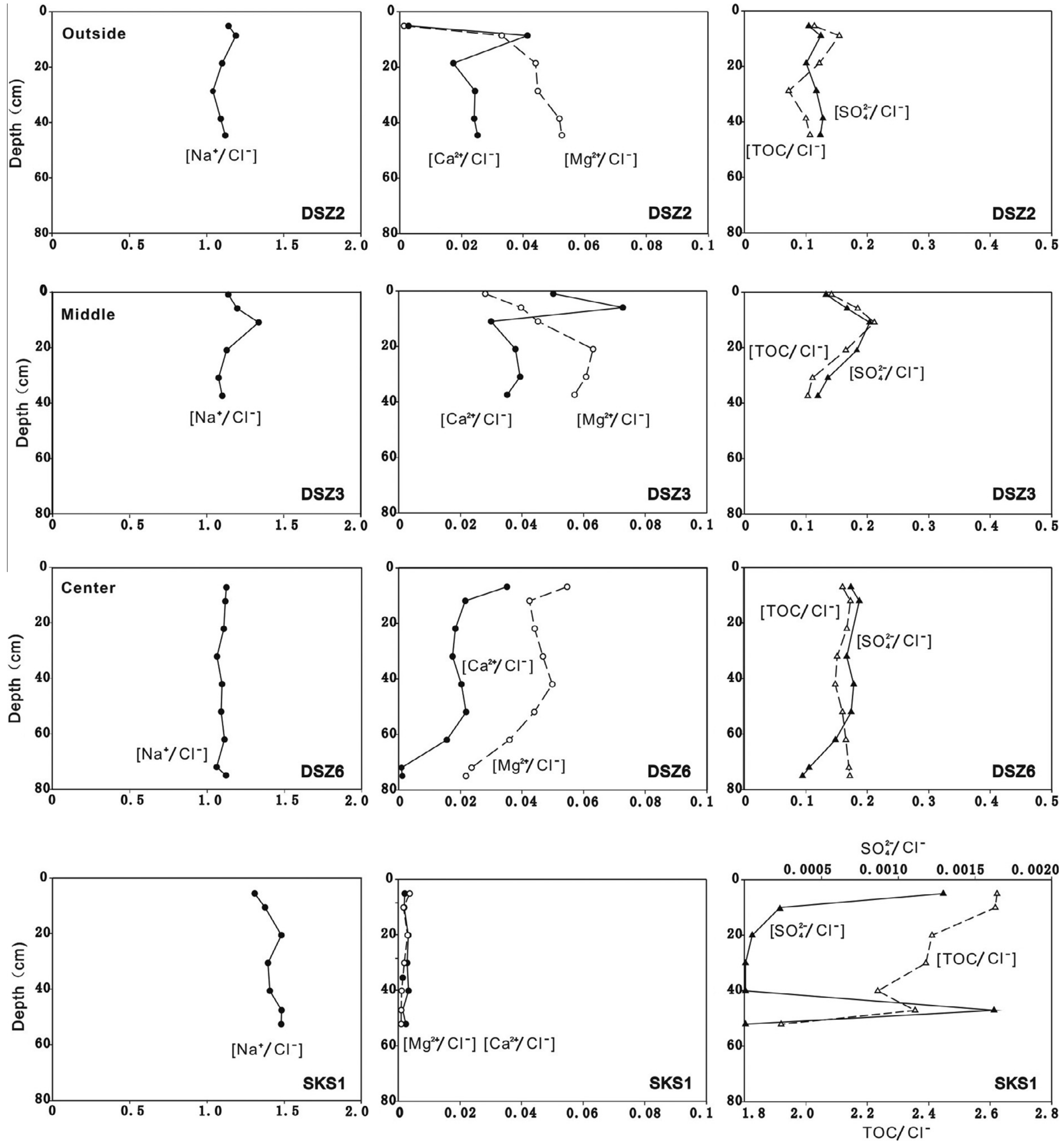

Fig. 7. Major ion composition and TOC normalized to the Cl^- in cores DSZ2, DSZ3, DSZ6 and SKS1.

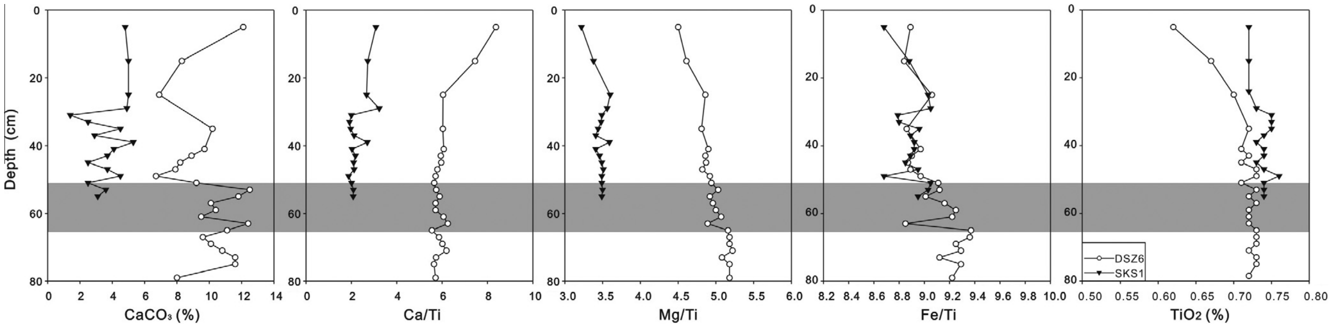

Fig. 8. Depth profiles of $CaCO_3$, Ca/Ti, Mg/Ti, Fe/Ti, and TiO_2 for cores of this study. Labels DSZ6 and SKS1 marked in the diagrams indicate the respective cores.

Ti are also higher below 50 cm than above (Fig. 8). Furthermore, the significant correlations between Mg and Ti and Fe and Ti in cores DSZ6 and SKS1 indicate that Mg and Fe are mainly present in the clay minerals, such as chlorite. There is no significant change in Ti content below 50 cm in DSZ6, indicating that the increases in Mg and Fe below that depth are mainly due to their presence in calcite. However, no significant changes are seen in the amount of Ca in DSZ6 and SKS1, and Ca possibly is hosted in feldspar and other minerals.

The results of the XRD and XRF analyses show that, compared with the wall rock (DSZ-00), the sediment cores from the DSZ and SKS sites are enriched in calcite, illite and chlorite, and the major elements are characterized by enrichments in Ca and Mn, followed by Fe, Mg and P, and depletion in Si. These results indicate that in the DSZ and SKS systems, the formation of authigenic calcite decreased the Ca and Mg concentrations of the pore fluid, but increased the contents of Fe and Mg in the mud sediments. Microbial activity may have resulted in the enrichment of P in the sediments (Fleischer, 1986; Fortin et al., 2000; Zheng et al., 2007). The continual water–rock interaction causes the sediments of the mud volcanoes to become enriched in Fe and Mn and depleted in Si, and transforms smectite to illite.

5. Conclusion

The geochemical studies of the pore fluids and sediments of the mud volcanoes on the southern margin of the Junggar Basin, Xinjiang, show that the major dissolved constituents of the fluids are Na^+ and Cl^-, mainly derived from ancient sedimentary pore fluids. However, the fluid composition is influenced by a combination of factors, including strong surface evaporation, water–rock interaction, dehydration of clay minerals (such as alteration of smectite to illite), organic matter decomposition, release of interlayer ions from smectite, carbonate precipitation, and the incursion of meteoric water. The fluid geochemistry stresses that different fluid sources and reactions occur at different mud volcanoes. The SKS mud volcanoes have a deeper fluid source, while the DSZ mud volcanoes experience strong surface evaporation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2014.04.007.

References

Aquilina, L., Dia, A.N., Boulègue, J., Bourgois, J., Fouillac, A.M., 1997. Massive barite deposits in the convergent margin off Peru: implications for fluid circulation within subduction zones. Geochim. Cosmochim. Acta 61, 1233–1245.

Ball, J.W., Nordstrom, D.K., 1991. User's manual for WATEQ4F, with revised thermodynamic data base and test cases calculating speciation of major, trace and redox elements in natural waters. US Geol. Surv. Open-File Rep., 91–183.

Brown, K.M., Saffer, D.M., Bekins, B.A., 2001. Smectite diagenesis, pore-water freshening, and fluid flow at the toe of the Nankai wedge. Earth Planet. Sci. Lett. 194, 97–109.

Carroll, A.R., 1998. Upper Permian lacustrine organic facies evolution, Southern Junggar Basin, NW China. Org. Geochem. 28, 649–667.

Chan, L.H., Gieskes, J.M., You, C.F., Edmond, J.M., 1994. Lithium isotope geochemistry of sediments and hydrothermal fluids of the Guaymas basin, Gulf of California. Geochim. Cosmochim. Acta 58, 4443–4454.

Chang, Y.-H., Cheng, T.-W., Lai, W.-J., Tsai, W.-Y., Sun, C.-H., Lin, L.-H., Wang, P.-L., 2012. Microbial methane cycling in a terrestrial mud volcano in eastern Taiwan. Environ. Microbiol. 14, 895–908.

Chao, H.-C., You, C.-F., Wang, B.-S., Chung, C.-H., Huang, K.-F., 2011. Boron isotopic composition of mud volcano fluids: implications for fluid migration in shallow subduction zones. Earth Planet. Sci. Lett. 305, 32–44.

Chao, H.-C., You, C.-F., Liu, H.-C., Chung, C.-H., 2013. The origin and migration of mud volcano fluids in Taiwan: evidence from hydrogen, oxygen, and strontium isotopes. Geochim. Cosmochim. Acta 114, 29–51.

Cheng, T.-W., Chang, Y.-H., Tang, S.-L., Tseng, C.-H., Chiang, P.-W., Chang, K.-T., Sun, C.-H., Chen, Y.-G., Kuo, H.-C., Wang, C.-H., Chu, P.-H., Song, S.-R., Wang, P.-L., Lin, L.-H., 2012. Metabolic stratification driven by surface and subsurface interactions in a terrestrial mud volcano. ISME J. 6, 2280–2290.

Clayton, J.L., Yang, J., King, J.D., Lillis, P.G., Warden, A., 1997. Geochemistry of oils from the Junggar Basin, Northwest China. Am. Assoc. Petrol. Geol. Bull. 81, 1926–1944.

Dählmann, A., de Lange, G.J., 2003. Fluid-sediment interactions at Eastern Mediterranean mud volcanoes: a stable isotope study from ODP Leg 160. Earth Planet. Sci. Lett. 212, 377–391.

Dai, J.X., Wu, X.Q., Ni, Y.Y., Wang, Z.C., Zhao, C.Y., Wang, Z.Y., Liu, G.X., 2012. Geochemical characteristics of natural gas from mud volcanoes in the southern Junggar Basin. Sci. China Ser. D 55, 355–367.

Dia, A.N., Castrec-Rouelle, M., Boulègue, J., Comeau, P., 1999. Trinidad mud volcanoes: where do the expelled fluids come from? Geochim. Cosmochim. Acta 63, 1023–1038.

Dimitrov, L.I., 2002. Mud volcanoes – the most important pathway for degassing deeply buried sediments. Earth-Sci. Rev. 59, 49–76.

Etiope, G., Feyzullayev, A., Milkov, A.V., Waseda, A., Mizobe, K., Sun, C.H., 2009. Evidence of subsurface anaerobic biodegradation of hydrocarbons and potential secondary methanogenesis in terrestrial mud volcanoes. Mar. Petrol. Geol. 26, 1692–1703.

Etiope, G., Nakada, R., Tanaka, K., Yoshida, N., 2011. Gas seepage from Tokamachi mud volcanoes, onshore Niigata Basin (Japan): origin, post-genetic alterations and CH_4–CO_2 fluxes. Appl. Geochem. 26, 348–359.

Fleischer, S., 1986. Aerobic uptake of Fe(III)-precipitated phosphorus by microorganisms. Archiv für Hydrobiologie 107, 269–277.

Fortin, D., Goulet, R., Roy, M., 2000. Seasonal cycling of Fe and S in a constructed wetland: the role of sulfate-reducing bacteria. Geomicrobiol. J. 17, 221–235.

Gieskes, J., Blanc, G., Vrolijk, P., Moore, J.C., Mascle, A., Taylor, E., Andrieff, P., Alvarez, F., Barnes, R., Beck, C., Behrmann, J., Brown, K., Clark, M., Dolan, J., Fisher, A., Hounslow, M., McLellan, P., Moran, K., Ogawa, Y., Sakai, T., Schoonmaker, J., Wilkins, R., Williams, C., 1989. Hydrogeochemistry in the Barbados accretionary complex: Leg 110 ODP. Palaeogeogr. Palaeoclimatol. Palaeoecol. 71, 83–96.

Hensen, C., Nuzzo, M., Hornibrook, E., Pinheiro, L.M., Bock, B., Magalhaes, V.H., Brueckmann, W., 2007. Sources of mud volcano fluids in the Gulf of Cadiz – indications for hydrothermal imprint. Geochim. Cosmochim. Acta 71, 1232–1248.

Hower, J., Eslinger, E.V., Hower, M.E., Perry, E.A., 1976. Mechanism of burial metamorphism of argillaceous sediment.1. Mineralogical and chemical evidence. Geol. Soc. Am. Bull. 87, 725–737.

James, R.H., Allen, D.E., Seyfried, W.E., 2003. An experimental study of alteration of oceanic crust and terrigenous sediments at moderate temperatures (51 to 350 °C): insights as to chemical processes in near-shore ridge-flank hydrothermal systems. Geochim. Cosmochim. Acta 67, 681–691.

Kastner, M., Elderfield, H., Martin, J.B., 1991. Fluids in convergent margins: what do we know about their composition, origin, role in diagenesis and importance for oceanic chemical fluxes? R. Soc. Lond. Philo. Trans. Ser. A 335, 243–259.

Kastner, M., Elderfield, H., Jenkins, W.J., Gieskes, J.M., Gamo, T., 1993. Geochemical and isotopic evidence for fluid in the western Nankai subduction zone, Japan. In: Hill, I.A., Taira, A., Firth, J.V. (Eds.), Proc. Ocean Drilling Program Scientific Reports 131. Ocean Drilling Program, College Station, TX, pp. 397–413.

Kholodov, V.N., 2002. Mud volcanoes, their distribution regularities and genesis: communication 1. Mud volcanic provinces and morphology of mud volcanoes. Lithol. Miner. Resour. 37, 197–209.

Kopf, A.J., 2002. Significance of mud volcanism. Rev. Geophys. 40, 1–52.

Lein, A., Vogt, P., Crane, K., Egorov, A., Ivanov, M., 1999. Chemical and isotopic evidence for the nature of the fluid in CH_4-containing sediments of the Hakon Mosby mud volcano. Geo-Mar. Lett. 19, 76–83.

Li, M., Wang, D., Li, M.F., Dai, X.M., 1996. A research on eruption characteristics of Dushanzi mud volcano in Xinjiang. Inland Earthquake 10, 359–362 (in Chinese with English abstract).

Li, X.H., Qi, C.S., Liu, Y., Liang, X.R., Tu, X.L., Xie, L.W., Yang, Y.H., 2005. Petrogenesis of the Neoproterozoic bimodal volcanic rocks along the western margin of the Yangtze Block: new constraints from Hf isotopes and Fe/Mn ratios. Chin. Sci. Bull. 50, 2481–2486.

Li, X.H., Li, Z.X., Wingate, M.T.D., Chung, S.L., Liu, Y., Lin, G.C., Li, W.X., 2006. Geochemistry of the 755 Ma Mundine Well dyke swarm, northwestern Australia: part of a Neoproterozoic mantle superplume beneath Rodinia? Precambrian Res. 146, 1–15.

Liu, C.-C., Jean, J.-S., Nath, B., Lee, M.-K., Hor, L.-I., Lin, K.-H., Maity, J.P., 2009. Geochemical characteristics of the fluids and muds from two southern Taiwan mud volcanoes: implications for water-sediment interaction and groundwater arsenic enrichment. Appl. Geochem. 24, 1793–1802.

Martin, J.B., Kastner, M., Henry, P., LePichon, X., Lallement, S., 1996. Chemical and isotopic evidence for sources of fluids in a mud volcano field seaward of the Barbados accretionary wedge. J. Geophys. Res. 101, 20325–20345.

Mazzini, A., 2009. Mud volcanism: processes and implications. Mar. Petrol. Geol. 26, 1677–1680.

Mazzini, A., Svensen, H., Planke, S., Guliyev, I., Akhmanov, G.G., Fallik, T., Banks, D., 2009. When mud volcanoes sleep: insight from seep geochemistry at the Dashgil mud volcano, Azerbaijan. Mar. Petrol. Geol. 26, 1704–1715.

Milkov, A.V., 2000. Worldwide distribution of submarine mud volcanoes and associated gas hydrates. Mar. Geol. 167, 29–42.

Nakada, R., Takahashi, Y., Tsunogai, U., Zheng, G.D., Shimizu, H., Hattori, K.H., 2011. A geochemical study on mud volcanoes in the Junggar Basin, China. Appl. Geochem. 26, 1065–1076.

Nath, B., Jean, J.S., Lee, M.K., Yang, H.J., Liu, C.C., 2008. Geochemistry of high arsenic groundwater in Chia-Nan plain, Southwestern Taiwan: possible sources and reactive transport of arsenic. J. Contam. Hydrol. 99, 85–96.

Neurauter, T.W., Bryant, W.R., 1990. Seismic expression of sedimentary volcanism on the continental slope, northern Gulf of Mexico. Geo-Mar. Lett. 10, 225–231.

Parkhurst, D.L., 1995. User's guide to PHREEQC—a computer program for speciation, reaction-path, adjective transport, and inverse geochemical calculation. US Geol. Surv. Water-Resour. Invest. Rep., 95–4227.

Planke, S., Svensen, H., Hovland, M., Banks, D.A., Jamtveit, B., 2003. Mud and fluid migration in active mud volcanoes in Azerbaijan. Geo-Mar. Lett. 23, 258–268.

Song, Y., Dai, J., Xia, X., Qin, S., 2004. Genesis and distribution of natural gas in the foreland basins of China. J. Petrol. Sci. Eng. 41, 21–29.

Sun, C.-H., Chang, S.-C., Kuo, C.-L., Wu, J.-C., Shao, P.-H., Oung, J.-N., 2010. Origins of Taiwan's mud volcanoes: evidence from geochemistry. J. Asian Earth Sci. 37, 105–116.

Taylor, J.C., 1991. Computer programs for standardless quantitative analysis of minerals using the full powder diffraction profile. Powder Diffr. 6, 2–9.

Vrolijk, P., Fisher, A., Gieskes, J., 1991. Geochemical and geothermal evidence for fluid migration in the Barbados accretionary prism (ODP Leg 110). Geophys. Res. Lett. 18, 947–950.

Wang, D., Li, M.W., Li, M., Dai, X.M., 1997. A preliminary study on eruption of the mud volcano in Dushanzi, Xinjiang. Seismol. Geol. 19, 14–16 (in Chinese with English abstract).

You, C.F., Castillo, P.R., Gieskes, J.M., Chan, L.H., Spivack, A.J., 1996. Trace element behavior in hydrothermal experiments: implications for fluid processes at shallow depths in subduction zones. Earth Planet. Sci. Lett. 140, 41–52.

You, C.F., Gieskes, J.M., Lee, T., Yui, T.F., Chen, H.W., 2004. Geochemistry of mud volcano fluids in the Taiwan accretionary prism. Appl. Geochem. 19, 695–707.

Zheng, G.D., Fu, B.H., Duan, Y., Wang, Q., Matsuo, M., Takano, B., 2004. Iron speciation related to colors of Jurassic sedimentary rocks in Turpan Basin, Northwestern China. J. Radioanal. Nucl. Chem. 261, 421–427.

Zheng, G., Lang, Y., Miyahara, M., Nozaki, T., Haruaki, T., 2007. Iron oxide precipitate in seepage of groundwater from a landslide slip zone. Environ. Geol. 51, 1455–1464.

Zheng, G., Fu, B., Takahashi, Y., Kuno, A., Matsuo, M., Zhang, J., 2010. Chemical speciation of redox sensitive elements during hydrocarbon leaching in the Junggar Basin, Northwest China. J. Asian Earth Sci. 39, 713–723.