Geochemical characteristics of absorbed gases in fault gouge from the Daliushu dam area, NW China

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A total of eleven fault gouge samples were collected from the Daliushu Dam area in the Zhongwei-Tongxin Fault Zone (ZTFZ) and analyzed for the absorbed gas geochemistry. The concentration of absorbed gas was between 0.04 and 1.65 cm³STP/g, and the chemicals were determined as mainly CO₂, N₂, H₂, Ar, and a few hydrocarbon gases. The ratios of N₂ and Ar suggest the presence of water in the fault zone, leading to water-rock interaction and lower N₂/Ar ratios. CO₂ and H₂ showed some signatures implying abiogenic origin, with relatively high δ¹³C CO₂ (–1.7‰ to 0.95‰) and H₂ being positively correlated to CO₂ (r = 0.83). We speculate that the CO₂ and H₂ are correlated to lithic origins in the fault zone, carbonate and silicate, respectively. On the other hand, CH₄ did show a biogenic signature, with low δ¹³C CH₄ (–44.2‰ to –45.6‰). The variation trends among the absorbed gases in the fault profile show that the gas concentration is mainly related to the fault zone structure, petrology of the fault material, and porosity. The total amounts of absorbed gases including H₂, CO₂, and Ar observed were higher at site F201 than those at site F3, and since the F201 site is known to be much more active than F3, we propose that CO₂, H₂, and Ar could be useful indicators of fault activity.

Keywords: fault gouge, absorbed gas, geochemical characteristics, fault activity

INTRODUCTION

There are several large-scale and important tectonic faults located in the northeast edge of the Qinghai-Tibet Plateau, including the Zhongwei-Tongxin and Haiyuan fault zones. These fault zones are seismically very active, with numerous major earthquakes recorded in human history, such as the Ms 7.5 Zhongwei Earthquake in Zhongwei County in 1709 and the Ms 8.5 Haiyuan Earthquake in Haiyuan County in 1920 (Han, 2004). Each caused severe damage to human society. At present, several large construction projects have been carried out and/or are planned in this region (for example, the Ding-Wu highway, the Baotou-Lanzhou railway, the petroleum pipe from western to eastern China, and the Daliushu Dam) and all are located in parallel with, or crossing, the Zhongwei-Tongxin Fault Zone (ZTFZ). Since seismic activity from these faults may cause significant damage to these projects, it is essential to study the geological properties of these fault zones. Gas geochemistry has previously been used for this because the fault fractures and porosity permit geological fluid and deep gas migration, which may reveal significant information on the properties and kinetics within the faults (Annunziatellis et al., 2008; Ioannis and Dimitris, 2009), even pointing out the locations of particular intense fault activity (Wang et al., 1991).

Gases in fault zones often show significant difference in chemical speciation and relative concentrations. Some, such as radon and helium, have even been proposed to be effective earthquake predictors, (e.g., Bräuer et al., 2003; Stephen et al., 2004; Fu et al., 2005, 2008) and indicators of concealed faults (e.g., Ciotoli et al., 1999; Walia et al., 2013) because these gases are mainly derived from the deep Earth and transferred to the surface through active fault zones. Although many reports describe soil gases in fault zones (e.g., Ciotoli et al., 1998; Karsten, 2008; Zhou et al., 2010; Walia et al., 2010), only a few are focused on the spatial distribution of absorbed gas patterns within the context of certain fault zone profiles, in order to probe the relationship between these gases and fault activity (e.g., Lewicki et al., 2003; Mahajan et al., 2010). In this study, we investigate the distribution and geochemical characteristics of absorbed gases in fault...
gouges within the Daliushu Dam area, and then discuss their significance with regard to the fault zone features and activity.

**GEOLOGICAL SETTING**

The Daliushu Dam area, located in Gansu Province, northwest China, is a key area in that part of the Yellow River using dams. It is also a significant tectonic region located along the northeast edge of the Qinghai-Tibet Plateau (Chu, 2009), where many large-scale faults have developed, mainly including F201 and F3 (Guo et al., 2004). F201 is the backbone fault of the ZTFZ, and is the seismogenic fault of the Ms 7.5 Zhongwei Earthquake in 1709. F201 has a strike angle of 290° and a dip angle of 45° to 70°. The surface rupture of this fault zone is approximately 110 km long and 10 to 35 m wide. The F201 fault has mainly developed through Cambrian and Carboniferous strata and cuts through Holocene strata (Han, 2004). The Carboniferous strata overthrusts the Holocene strata, indicating that the last activity of the F201 fault occurred after the Holocene period.

The F3 fault borders the southern part of Daliushu Dam. F3 has a strike angle of 60°, a dip angle of 45°, a trace length of 13 km, and width of 100 m. The Cambrian strata overthrusts the Carboniferous strata at the sampling location. The last activity of F3 occurred before the Pleistocene and after the Carboniferous (Han, 2004; Liang et al., 2006). It is an old thrust fault (Han, 2004).

The stratum in the study area consists mainly of Cambrian, Carboniferous, and Quaternary systems. Greenish gray quartzite arkose with a phylliteis is common within the Cambrian strata while the Carboniferous and Quaternary strata primarily contain black silty shale.

**SAMPLES AND EXPERIMENTS**

The faults F201 and F3 were selected for this study mainly because they are the border faults of the Daliushu Dam, and thus are relevant for the security of the dam. Second-order faults around the dam axis also formed part of this study (Fig. 1). Study samples were collected perpendicular to F201 (site-F201), where the Changliushui river joins the Yellow river, at the point where a newly unearthed section crosses the fault on a fresh scarp. To avoid cross contamination, nine samples of fault gouge and rocks with different weathered surfaces were stripped and collected from depths between 0.2 and 0.5 m in a vertical, bottom-up profile (GK-03 to GK+06), as shown in Fig. 2. The samples of GK-01, GK-02, and GK-03 were collected from the footwall, while GK+01 to GK+06 were...
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collected from the upper wall. Two samples were collected from F3 (site-F3) near the Daliushu Dam axis, both located on the upper wall near the fault plane. Sample characteristics and locations are shown in Table 1.

Samples were first crushed into powder (about 200 mesh) using an agate mortar and pestle in a clean laboratory. The samples were then placed in an ultrasonic vibrator and cleaned using CH₂Cl₂ solution to remove impurities on the particle surfaces. Finally, the samples were dried at 80°C. Subsequently, 1 g of processed sample was prepared for testing. We then used the heat mass spectrometry method employing a Finnigan MAT 271 mass spectrometer. The prepared samples were placed in a quartz glass tube and then sealed and evacuated for approximately 0.5 h at 1 × 10⁻⁴ Pa before sealing. Next, they were grade heated from 0°C to 280°C to ensure that all gases were released. The released gases were passed through a refrigeration system at approximately –60°C to eliminate H₂O and to prevent the chemical reaction of CO₂ and H₂O at high temperatures. Finally, the gases were input to the MAT 271 mass spectrometer for gas composition analysis then sent on to a Thermo Finnegan

Table 1. Samples for study: Petrological properties and location

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Petrological characteristics</th>
<th>Location</th>
<th>Porosity (%)</th>
<th>Host rock</th>
</tr>
</thead>
<tbody>
<tr>
<td>GK+01</td>
<td>Fault gouge, black mudstone</td>
<td>Upward to fault plane 0–2 cm</td>
<td>1.6</td>
<td>Black silty shale</td>
</tr>
<tr>
<td>GK+02</td>
<td>Fault gouge, black mudstone</td>
<td>Upward to fault plane 3–6 cm</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>GK+03</td>
<td>Fault gouge, grayish olive mudstone</td>
<td>Upward to fault plane 7–10 cm</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>GK+04</td>
<td>Fault gouge, black mudstone</td>
<td>Upward to fault plane 16–18 cm</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>GK+05</td>
<td>Fault cataclastic, yellow mudstone</td>
<td>Upward to fault plane 25–30 cm</td>
<td>2.1</td>
<td>Glutenite</td>
</tr>
<tr>
<td>GK+06</td>
<td>Fault cataclastic, black mudstone</td>
<td>Upward to fault plane 50–60 cm</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>GK-01</td>
<td>Fault gouge, yellow mudstone</td>
<td>Downward to fault plane 0–3 cm</td>
<td>1.3</td>
<td>Black silty shale</td>
</tr>
<tr>
<td>GK-02</td>
<td>Fault cataclastic, yellow mudstone</td>
<td>Downward to fault plane 4–9 cm</td>
<td>4.3</td>
<td>Glutenite</td>
</tr>
<tr>
<td>GK-03</td>
<td>Fault cataclastic, yellow siltstone</td>
<td>Downward to fault plane 25–30 cm</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>BK+01</td>
<td>Fault gouge, black mudstone</td>
<td>Fault zone</td>
<td>1.8</td>
<td>Black silty shale</td>
</tr>
<tr>
<td>BK+02</td>
<td>Fault gouge, black mudstone</td>
<td>Fault zone</td>
<td>1.9</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Photograph showing the outcrop of fault F201 with gouge and sampling points. The dotted line represents the fault plane.
RESULTS AND DISCUSSION
Composition and origins of absorbed gases

The chemical and isotopic composition of the absorbed gas samples are listed in Table 2. The concentration of absorbed gases is variable in a range from 0.04 to 1.65 cm$^3$STP/g relative to solid materials or rocks. The fault gouges from F201 and F3 were found to contain mainly carbon dioxide (0.033 to 1.49 cm$^3$STP/g), with nitrogen (0.00062 to 0.082 cm$^3$STP/g), hydrogen (0.0019 to 0.039 cm$^3$STP/g), and a few hydrocarbon gases and noble gases in lesser amounts. Methane (0 to 0.032 cm$^3$STP/g), ethane (17 to 1590 ppm), and propane (0 to 8710 ppm) were the dominant hydrocarbon gases while argon (5.13 to 315 ppm) was the only noble gas detected (Table 2). Therefore, it seems the fault gouge in the Daliushu area is enriched in absorbed CO$_2$.

With the exception of sample GK-01, the ratios of absorbed N$_2$/Ar were between 7 and 58. The samples GK-03 and BK+02 lay between atmospheric (84) and air-saturated groundwater (ASW = 38.4) the others were in the range between 7 and 38.4. It has been suggested there was a clear negative correlation between the N$_2$/Ar ratio and water temperature (Xu et al., 2012). Such a variation can be explained by the different rates of gas release from individual samples. At very low rates of degassing (low temperature), as may have occurred for GK-03, the composition of gases released from waters originally saturated with air approaches that of air itself, with N$_2$/Ar ratios approaching the 84 level typical of the atmosphere. At high rates of gas release (high temperature), as may have occurred for GK-06, all the water-dissolved gases get released and N$_2$/Ar ratios approach those of typical ASW. Since the N$_2$/Ar ratios of the other samples were lower than that of ASW, we speculate that rock/water in-
teractions were limited in these locations.

Carbon dioxide comprised over 80% of total absorbed gases, ranging from 0.03 to 1.49 cm$^3$STP/g, with the $\delta^{13}$CCO$_2$ ranging from $-1.7\%$ to $0.95\%$, indicating both biotic and abiotic origins. Xu et al. (2012) considered that the $\delta^{13}$CCO$_2$ ratio of CO$_2$ derived from carbonate thermal decomposition in metamorphic rock was close to that of carbonate rocks, i.e., around $0 \pm 3\%$, while the $\delta^{13}$CCO$_2$ of magmatic and mantle-derived CO$_2$ mainly cluster around $-6 \pm 2\%$. The carbon isotope ratios found among the fault samples in this study were also mostly similar to that of carbonate rocks and close to the typical secondary calcite standard value of $0.5\%$ (Sugisaki et al., 1983). This may be an indication of newly formed calcite brought on by faulting and water infiltration in the fault zone.

Hydrogen concentration was in a range between 1.85 and 4.86%. There is a positive correlation between H$_2$ and CO$_2$ ($r = 0.83$, not shown), suggesting a common origin of the two end members. Moreover, biogenetic hydrogen is always associated with methane production, but the absorbed gases contained little hydrogen gases. Instead, hydrogen atom groups could be liberated from quartz surfaces when they are grinding and crushing during fault movement; such atoms may react with water to produce gaseous H$_2$ (see Eq. (1)), as shown in laboratory experiments (Sugisaki et al., 1983).

$$3Si^+ + H_2O = 3Si-OH + H^+ \quad 2H^+ = H_2. \ (1)$$

Methane was in the range between 110 and 581 ppm with $\delta^{13}$CCH$_4$ $\approx -44\%$, indicating a biogenic origin, probably due to microbial action and/or oxidization effects on organic matter.

**Absorbed gas variation trend in the vertical profile**

In the vertical profile of site F201, absorbed gases from samples GK+01, GK+02, GK+04, and GK+05 exceeded those of GK+03, GK-02, GK+03, GK-03, and GK+05. The distribution of the absorbed gases follows a pattern. Based on samples taken from the upper wall of the fault, the total amount of absorbed gas increased with the distance from the fault plane. There is an exception in the case of GK+03. It had a grayish olive color indicative of a clay content (5%) half that of the black samples (10%). Its adsorptive capability was likely weaker than the other samples owing to this compositional difference. The total amount of absorbed gases starts to decrease upon nearing the vicinity of the fault gouge-cataclasite boundary. At the footwall and in thin fault gouges, the total amount of absorbed gases decreased with distance from the fault plane, reaching a minimum at the damaged host rock. A similar pattern was evident for the hydrocarbon gases and CO$_2$ (Fig. 3).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>H$_2$</th>
<th>N$_2$</th>
<th>O$_2$</th>
<th>Ar</th>
<th>CO$_2$</th>
<th>CH$_4$</th>
<th>C$_2$H$_6$</th>
<th>C$_3$H$_8$</th>
<th>Total N$_2$/Ar</th>
<th>$\delta^{13}$C$_{CO2}$</th>
<th>$\delta^{13}$C$_{CH4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site-F201</td>
<td>2.20E-2</td>
<td>3.66E-2</td>
<td>3.68E-3</td>
<td>2.75E-4</td>
<td>1.13E+0</td>
<td>1.20E-5</td>
<td>4.66E-4</td>
<td>8.37E-4</td>
<td>3.71E-4</td>
<td>1.42E-0</td>
<td>133</td>
</tr>
<tr>
<td>GK-01</td>
<td>2.07E-2</td>
<td>2.08E-2</td>
<td>n.d.</td>
<td>2.05E-5</td>
<td>6.43E-1</td>
<td>n.d.</td>
<td>1.91E-4</td>
<td>1.37E-3</td>
<td>7.90E-5</td>
<td>6.46E-5</td>
<td>309</td>
</tr>
<tr>
<td>GK-02</td>
<td>6.93E-3</td>
<td>4.83E-3</td>
<td>n.d.</td>
<td>1.20E-5</td>
<td>2.81E-1</td>
<td>n.d.</td>
<td>2.24E-4</td>
<td>1.70E-5</td>
<td>n.d.</td>
<td>2.93E-1</td>
<td>58.2</td>
</tr>
<tr>
<td>GK+01</td>
<td>2.56E-2</td>
<td>3.45E-2</td>
<td>8.85E-4</td>
<td>1.16E-4</td>
<td>1.10E+0</td>
<td>n.d.</td>
<td>4.19E-4</td>
<td>8.61E-4</td>
<td>3.49E-4</td>
<td>1.16E+0</td>
<td>31.9</td>
</tr>
<tr>
<td>GK+02</td>
<td>3.82E-2</td>
<td>7.19E-2</td>
<td>n.d.</td>
<td>2.70E-4</td>
<td>1.06E+0</td>
<td>1.41E-4</td>
<td>1.75E-3</td>
<td>1.31E-3</td>
<td>4.47E-4</td>
<td>1.17E+0</td>
<td>14.7</td>
</tr>
<tr>
<td>GK+03</td>
<td>2.77E-2</td>
<td>6.37E-2</td>
<td>n.d.</td>
<td>2.37E-4</td>
<td>4.82E-1</td>
<td>n.d.</td>
<td>1.81E-3</td>
<td>1.03E-3</td>
<td>1.64E-3</td>
<td>5.78E-1</td>
<td>7.57</td>
</tr>
<tr>
<td>GK+04</td>
<td>3.93E-2</td>
<td>8.18E-2</td>
<td>n.d.</td>
<td>3.15E-4</td>
<td>1.49E+0</td>
<td>4.97E-5</td>
<td>3.23E-2</td>
<td>1.59E-3</td>
<td>8.71E-4</td>
<td>6.61E-4</td>
<td>8.47E-1</td>
</tr>
<tr>
<td>GK+05</td>
<td>2.69E-2</td>
<td>2.28E-2</td>
<td>n.d.</td>
<td>3.04E-5</td>
<td>7.08E-1</td>
<td>n.d.</td>
<td>1.10E-3</td>
<td>5.24E-4</td>
<td>1.66E-3</td>
<td>8.47E-1</td>
<td>31.1</td>
</tr>
<tr>
<td>Site-F301</td>
<td>2.34E-3</td>
<td>6.21E-4</td>
<td>n.d.</td>
<td>5.13E-5</td>
<td>4.82E-2</td>
<td>3.31E-5</td>
<td>5.81E-4</td>
<td>2.18E-3</td>
<td>n.d.</td>
<td>5.40E-2</td>
<td>12.1</td>
</tr>
<tr>
<td>BK-01</td>
<td>1.90E-3</td>
<td>3.40E-3</td>
<td>5.85E-5</td>
<td>7.80E-5</td>
<td>3.25E-2</td>
<td>n.d.</td>
<td>1.25E-3</td>
<td>n.d.</td>
<td>n.d.</td>
<td>3.09E-2</td>
<td>4.6</td>
</tr>
<tr>
<td>BK-02</td>
<td>2.34E-3</td>
<td>8.18E-3</td>
<td>n.d.</td>
<td>3.15E-4</td>
<td>1.49E+0</td>
<td>4.97E-5</td>
<td>3.23E-2</td>
<td>1.59E-3</td>
<td>8.71E-4</td>
<td>6.61E-4</td>
<td>8.47E-1</td>
</tr>
</tbody>
</table>

Note: n.d. - not detected, ASW - air-saturated groundwater.
The fault zone consists of the fault plane, fault gouge, fault cataclasite, and damaged host rock. The absorbed gas variation trend in the vertical profile was found to be mainly related to the fault material structure and porosity of the fault zone (Fig. 4). In the vicinity of the fault plane, voids were produced during faulting, and gases were released en masse owing to increased porosity. Accordingly, lower amounts of gas could be absorbed in the nearby gouge. As the distance from the fault plane increases, so does the clay content in the fault gouge, which may indicate a self-sealing by fine particles within the fault zone (Zheng et al., 2008) and a stronger adsorptive capacity to trap much more gas. The absorbed gas concentrations in this study are likely lowered dramatically at the cataclasite zone because of these changes in porosity and fracture structures.

Relationship between fault activity and absorbed gas concentrations

Table 2 shows that the absorbed gases from the two faults are very different, possibly a reflection of differences in seismic activity. In comparison, the samples GK+01 and GK+02 (from site-F201) and BK+01 and BK+02 (from site-F3) are similar: they are belong to the same lithological formation (black silty shale) as the host rock and they have similar porosity (about 2.0%). All these samples were collected from areas that are nearest to the fault plane so that their location might be best-suited to represent the latest fault activity. However, the absorbing gases in these samples are sharply different from each other.

The average of absorbed gas amount from site-F201 was 0.94 cm³STP/g, with CO₂, H₂, and Ar levels at 0.89 cm³STP/g, 0.021 cm³STP/g, and 148 ppm, respectively. The average of the amount of absorbed gas from site-F3 was 0.047 cm³STP/g, with CO₂, H₂, and Ar levels at 0.040 cm³STP/g, 0.0021 cm³STP/g, and 6.5 ppm, respectively. Since the absorbed gases in the fault gouge of F201 exceeded those from F3 by an order of magnitude (Fig. 5) we speculate that the higher absorbed gas levels correspond to increased fault activity. This is based on the reasoning that as the fault becomes more active, water and rock interaction becomes more frequent, leading to increases in the amount of the absorbed gases H₂, CO₂, and Ar.

CONCLUSIONS

The absorbed gases within the fault gouge from F201 and F3 in the Daliushu area are dominated by CO₂, N₂, and H₂ that is most likely derived from rock-water interactions in the fault zone. Comparing F201 with F3, it is shown that CO₂, H₂, and Ar could be an indicator for the degree of rock-water interactions and fault activity; the more active the fault, the greater the degree of water-rock interaction and the higher the concentration of absorbed gases in the gouge. Primarily because of the material structure and porosity, the vertical profile of the F201 fault zone shows a trend with concentrations of absorbed gases increasing with distance from the fault plane until reaching the fault gouge-cataclasite boundary whereupon concentrations decrease and reach minimum values at the damaged host rock.

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