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3 **Ge/Si ratios indicating hydrothermal and sulfide weathering input to rivers of the**
4 **Eastern Tibetan Plateau and Mt. Baekdu**

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Abstract: Concentrations of dissolved silicon in river waters reflect a complex interplay among chemical weathering of primary silicate minerals, formation and weathering of secondary clay minerals, hydrothermal input and biological cycling (formation and dissolution of opal phytoliths and growth of diatoms). We applied the Ge/Si ratio to assess the different sources of dissolved Si in rivers hailing from the eastern Tibetan Plateau – the Salween, Mekong, Chang Jiang (Yangtze), Hong (Red) and Huang He (Yellow) – and from Mt. Baekdu – the Duman. Elevated riverine Ge/Si ratios were observed in arid regions with high geothermal activity in the Salween, Chang Jiang and Mt. Baekdu streams. In the Huang He and Hong River basins geothermal influence was not as pronounced, but weathering of sulfide- and coal-bearing minerals seemed to be responsible for the high Ge/Si ratios. In rivers where inputs from hydrothermal and sulfide weathering are minimal, our data mostly fall in the weathering-limited regime of high riverine Si concentrations and low Ge/Si ratios.

Keywords: germanium; silicon; Chang Jiang; Mekong; Salween; Huang He; Duman; Hong River

1. Introduction

Dissolved silicon (DSi) levels in river waters carry two important implications for the global carbon cycle. The primary source of riverine DSi is chemical weathering of silicate minerals, which is a net sink for atmospheric CO₂ on geologic timescales. If secondary sources can be independently accounted for, the riverine DSi should be a measure of the consumption rate of atmospheric CO₂ in the drainage basin. DSi is also an essential nutrient for diatom growth, and its riverine transport to the ocean can be a significant control on diatom productivity in the surface ocean and hence on the amount of CO₂ transported into the deep sea by the biological pump (Struyf et al., 2009). The factors controlling the riverine DSi are not well understood, because they involve a complex interplay among chemical weathering of primary silicate minerals, formation and dissolution of secondary clay minerals, hydrothermal input and biological cycling by diatoms and phytoliths (Conley, 2002).

Germanium (Ge) is a trace element typically present at a few $\mu\text{g g}^{-1}$ level in Earth's crust. It behaves similarly to Si, but elemental fractionation between Ge and Si during biogeochemical processes result in a range of Ge/Si ratios. For example, during incongruent weathering of silicate rocks ($\text{Ge/Si} = 1\text{--}3 \mu\text{mol/mol}$; Bernstein, 1985) (Ge/Si in 10^{-6} atom ratios hereafter), Ge preferentially partitions into secondary minerals (Anders et al., 2003; Kurtz et al., 2002; Mortlock and Froelich, 1987; Murnane and Stallard, 1990). Schematically illustrated, this results in secondary minerals with higher Ge/Si ratios (~ 3 to 6) and dissolved substances with lower values (~ 0.3 to 0.7) than the parent silicate rock (~ 1.5 to 2.5) (Kurtz et al., 2002).

The global mean Ge/Si for rivers (0.6) is lower than the crustal average (Mortlock and Froelich, 1987). This is consistent with preferential retention of Ge in secondary minerals

during incongruent weathering. However, what governs the riverine Ge/Si ratios is much more complex. First, geothermal waters display a wide range of Ge/Si (2 – 1000) (Evans and Derry, 2002), and fluxes from hot springs can significantly increase the riverine Ge/Si (Evans et al., 2004). Second, while silicate crustal material has relatively homogeneous and low Ge/Si ratios, two non-silicate crustal materials are high in Ge – the zinc- and copper-rich sulfide ore deposits and coal (Bernstein, 1985). Fly ash is enriched in Ge relative to the coal from which it is generated and is responsible for high Ge/Si in polluted rivers (Froelich et al., 1985). Third, further weathering of high-Ge/Si secondary minerals will result in elevation of riverine Ge/Si (Kurtz et al., 2002). As such, Ge/Si has been proposed as a proxy for weathering intensity, defined as the fraction of Si in the bedrock that is dissolved during weathering (Murnane and Stallard, 1990). Fourth, plants preferentially take up Si from soil solution to produce opal phytoliths (Ge/Si = 0.25; Derry et al., 2005) which elevates the riverine Ge/Si ratio. Conversely, dissolution of opal phytoliths will lower the riverine Ge/Si ratio. Diatoms do not fractionate between Ge and Si during uptake (Azam, 1974; Compton et al., 2000; Filippelli et al., 2000) and therefore do not affect the Ge/Si ratios of rivers. Overall, the Ge/Si ratio in river water is determined by the relative contributions from all these sources and sinks, and if they can be teased apart the Ge/Si ratio can be useful for identifying the sources of DSi in river water.

In this study, we measured the Ge concentrations in river waters and used the Ge/Si ratios to trace the sources of DSi for rivers draining the Eastern Tibetan Plateau (ETP) and Mt. Baekdu (Fig. 1). Several major rivers hail from the ETP. The Chang Jiang, Mekong and Salween are sometimes called the Three Rivers, because they lie very close in parallel as they flow off the ETP. The Hong (Red) River straddles China and Vietnam. The Huang He

(Yellow) flows northeastward from the ETP through the Loess Plateau. These rivers draining the ETP are some of the highest exporters of DSi to the coastal zone (Beusen et al., 2009). In northeast China at the border with North Korea, the Duman River flows from the Baekdu Mountain into the East Sea/Sea of Japan. Both the ETP and Mt. Baekdu area have widespread geothermal activity associated with tectonics and volcanism. One of our aims is to assess the effect of hot spring input on the DSi of these regions. The aqueous geochemistry of these rivers, including major elements and $^{87}\text{Sr}/^{86}\text{Sr}$, has been published and interpreted in terms of chemical weathering (Han and Huh, 2009; Moon et al., 2007; Noh et al., 2009; Wu et al., 2005). The original authors also used forward/inverse models to calculate rates of silicate weathering and the amount of CO_2 consumed in the process and examined the correlation with climatic, lithologic and morphologic parameters. However, in those calculations DSi data were not used to full potential due to the uncertainty in non-silicate weathering sources and sinks of DSi.

2. Description of the study area

The potential contribution of geothermal waters to the surface water may be approximated using the temperature of the geothermal waters. The location and temperature of geothermal waters for China are available in the Hydrogeological Atlas of the People's Republic of China (Institute of Hydrogeology and Environmental Geology, 1979) (Fig. 2). The Xizang-Yunnan Geothermal Zone extends along the Yarlung-Tsangpo River in Tibet and then makes a southeasterly turn to follow the Three Rivers (Kearey and Hongbing, 1993). Geothermal waters occur extensively over the ETP even including permafrost and lake regions (Cheng and Jin, 2013; Grimaud et al., 1985; Yokoyama et al., 1999) (Fig. 2), but

individual geochemical properties are not well documented. In Vietnam, a large number of geothermal springs (50 - 75°C) appear along the fault system in NW-SE direction in the area of the Thao main channel and the Da tributary and to a lesser extent in the basin of the Lo tributary (Cuong et al., 2005; Quy, 1998). The Duman basin is a part of the East Coast Geothermal Zone (Kearey and Hongbing, 1993).

Geothermal water temperatures are representative of a geographically confined point and are spatially heterogeneous, whereas river samples integrate over the whole drainage basin. Therefore, the geothermal temperatures cannot be interpolated to give a meaningful average for a basin to be compared with the Ge/Si data of river water samples. As an alternative, we turned to the heat flow distribution (Fig. 2). The ETP region had relatively high (70 – >100 mW/m²) and Mt. Baekdu region moderate (70 – 80 mW/m²) heat flow.

Both the ETP and Mt. Baekdu have been geologically active regions in the Cenozoic. The ETP uplifted from collision between India and Eurasia, and Mt. Baekdu and the surrounding volcanic plateau have formed by successive volcanic eruptions (Chen et al., 2007).

The Three Rivers basin is underlain primarily by consolidated sedimentary rocks consisting of carbonate, silici-clastic and evaporite material (Dürr et al., 2005). However, Triassic low-grade metamorphic rocks and Precambrian medium- to high-grade metamorphic rocks are widely exposed in the Chang Jiang and the Mekong basins, respectively (Noh et al., 2009; Wu et al., 2008). The consolidated rocks occurring in the Salween basin are characterized by relatively high carbonate content of up to ~80% (Noh et al., 2009). In the downstream area straddling the Salween and Mekong basins is the coal-hosted Lincang Ge deposit which lies on top of the Lincang Batholith (Hu et al., 2009) (Fig.

3).

The main tributaries of the Hong River drain different lithologies (Fig. 4). The main channel, the Thao, flows through coal-bearing clastic rocks in the headwater region and metamorphic and igneous rocks along the Red River Fault Zone that host sulfide-bearing ultramafic intrusions (Moon et al., 2007). Sedimentary rocks with some low-grade metamorphic rocks and igneous intrusions dominate the river basins of the Da and Lo tributaries.

The Huang He basin is dominated by semi- to un-consolidated sedimentary rocks mainly consisting of sandstone, mudstone, slate, (dolomitic) limestone and evaporite and partly covered by loess (Wu et al., 2005) (Fig. 5). Granite occurs as a minor lithology. Volcanogenic sulfide deposits are found in the Huang Shui tributary basin, and their oxidation seems to contribute to the high dissolved sulfate concentrations (Wu et al., 2005).

Successive eruptions of Mt. Baekdu through the Cenozoic produced a large amount of basaltic to trachytic/rhyolitic rocks covering an area >15,000 km² (Han and Huh, 2009). The Duman River basin is composed predominantly of volcanic rock in the upper reaches, and exposure of granitic basement rock increases downstream (Han and Huh, 2009). The Musan iron ore mine is on the North Korean side of the Duman River (Fig. 6).

3. Analytical methods

Ninety-eight surface water samples were used in this study (Fig. 1; Table 1). In the ETP region, samples were taken from the Three Rivers (n = 30; Salween, Mekong and Chang Jiang) (Noh et al., 2009), Huang He (n = 10) (Wu et al., 2005) and the Hong (n = 43) (Moon et al., 2007). The Hong River was sampled twice, during high-flow (summer; n = 20) and

low-flow (winter; $n = 23$) (Table 1). The samples from Mt. Baekdu region include springs ($n = 3$) and nearby streams ($n = 3$) and the Duman River ($n = 9$) (Han and Huh, 2009). The samples were collected in pre-cleaned HDPE bottles, filtered within 24 hours through $0.4\ \mu\text{m}$ polycarbonate filters, acidified to $\text{pH} < 2$ with ultrapure HNO_3 or HCl , and stored in pre-cleaned HDPE bottles.

Dissolved Ge concentrations were determined using isotope-dilution hydride generation (Mortlock and Froelich, 1996) on an inductively coupled plasma sector field mass spectrometer (Element2, Thermo Finnigan MAT, Germany) at Cornell University (Kurtz et al., 2002). Samples were spiked with an enriched ^{70}Ge tracer solution (Oak Ridge National Laboratories). Although there is a small but measurable isotopic variation in natural Ge, we take the $^{70}\text{Ge}/^{74}\text{Ge}$ of normal Ge to be 0.5635 ± 0.0029 (Kipphardt et al., 1999). Inversion of data from multiple analyses of different spike-sample mixtures corrected for mass fractionation yields a $^{70}\text{Ge}/^{74}\text{Ge}$ of our tracer solution to be 161.4 ± 2.4 . Samples are reacted online to generate Ge hydride with a 2% NaBH_4 solution buffered to $\text{pH} 6$ using a Tris-HCl buffer in a custom reaction vessel with a membrane gas-liquid separator. The resulting GeH_4 is continuously sparged and swept into the plasma using an Ar stream. There is currently no generally recognized natural Ge standard for water samples. Ge standards were prepared from a stock $1000 \pm 5\ \mu\text{g ml}^{-1}$ solution obtained from High-Purity StandardsTM by dilution with 2% trace metal grade HNO_3 . During a sample run, both spiked and unspiked standards were run at 5, 20, 50 and 200 ppt to correct for instrumental mass bias and determine reproducibility. Total reagent blank for Ge was less than 1.0 ppt and reproducibility was approximately $\pm 3\%$. The DSi concentrations in the original literature were measured by silica molybdate colorimetry except for the CB200 series, which were analyzed by ICP-OES

(Noh et al., 2009; Wu et al., 2005; Moon et al., 2007; Han and Huh, 2009).

ArcGIS v10.2 was used to display the drainage basins, streams, elevation, heat flow and location of geothermal springs. The drainage basins were modified from the USGS Hydro1k database for Asia, which comes with the GTOPO30 digital elevation model. The location and temperature of geothermal waters for China were digitized from the Hydrogeological Atlas of the People's Republic of China (1979) (Fig. 2). The most up-to-date compilation and interpolation ($1^{\circ} \times 1^{\circ}$ grid) of the heat flow data for the study area was obtained from Tao and Shen (2008).

4. Results

The dissolved Ge concentrations in ETP rivers span two orders of magnitude (12 – 3100 pM; $n = 83$), which is much larger than the range in DSi (26 – 270 μM) (Table 1). The resulting Ge/Si ratios also span a large range (0.1 – 20 $\mu\text{mol/mol}$). The Ge/Si ratios for the furthest downstream main channel samples in our sampled sub-basins were 3.8 for the Chang Jiang (TR113), 2.4 for the Mekong (RD126), 3.5 for the Salween (TR103), and 1.8 for Huang He (CJ111) (Fig. 7). These are the estimates for the rivers as they exit the Tibetan Plateau. The Ge/Si for the Da, Thao and Lo above their confluence to form the Hong River were 1.1, 1.4, and 1.1, respectively. These riverine values are all greater than the global river mean of 0.6 (Mortlock and Froelich, 1987).

When examined more closely, the Ge/Si ratios display significant spatial variation within each river basin. In the Chang Jiang and Salween headwaters on the arid Tibetan Plateau, the Ge/Si values were high (up to 18) but decreased downstream to values of 1 – 3 (Figs. 3 and 7; Table 1). A second high (up to 20) is observed where the Three Rivers bend to

form a “wasp’s waist” and a third high (up to 11) near the Lincang Ge deposit (Fig. 3). In the Hong River basin, the Thao main channel exhibited the highest Ge/Si values in the headwaters (up to 4.2 during low flow) and decreased downstream, while the other two tributaries (Da and Lo) displayed ratios closer to the global mean (Figs. 4 and 7). The Huang He samples had relatively low Ge/Si (0.3 – 0.8) but rose at the terminal main channel site (1.8 at CJ111) after confluence with the Huang Shui tributary which had high Ge/Si of up to 4.5 (Figs. 5 and 7).

The set of low and high discharge samples of the Hong River did not display noticeable seasonal variation in Ge/Si. Only the headwaters of the Thao had a significant difference, with higher Ge/Si in the low-flow season (RD228 and RD229) than in the high-flow season (RD130 and RD131) (Fig. 4; Table 1).

The springs of Mt. Baekdu were greatly enriched in Ge (961 – 337 nM) and had the highest Ge/Si (78 – 125) among our samples (Fig. 7). Nearby streams also had higher Ge (2 – 34 nM) and Ge/Si (5 – 58) than other freshwater samples (Fig. 7). In contrast, the Duman River exhibited some of the lowest Ge/Si ratios (0.2 – 0.4) (Figs. 6 and 7). Three samples of the Duman River (CB209, CB210 and CB211) had relatively high Ge/Si ratios (1.7 – 4.8). Anthropogenic input is suspected for these samples, because they are from a relatively populated area and are high in dissolved chloride and sulfate (Han and Huh, 2009).

5. Discussion

5.1. Geothermal source of Ge

The widespread presence of geothermal waters is most likely the major reason for the above average Ge/Si in our study area. Such was the case in the streams of the Himalayan

front, where Evans et al. (2004) evaluated the contribution of geothermal water in the Narayani river system using the Ge/Si ratios in rivers and hot springs. However, we lack direct samples of geothermal water, and the large variability in their chemical composition from one to the other prohibits us from making assumptions about the average composition of hot springs in our area. As an alternative, one may examine the spatial coincidence between the occurrence and temperature of geothermal waters and the Ge/Si ratios for the sampled drainage basins. The drawback is that the geothermal temperatures are for specific locations and are heterogeneous, whereas river samples integrate over the whole drainage basin. Heat flow distribution was used as a complement, and when the digitized geothermal water temperatures are compared with the heat flow for that location, there is a broad positive relationship (Fig. 8). That is, geothermal waters with higher temperature tend to be found where heat flow is higher. Thus, we examined the spatial correspondence between high heat flow and high Ge/Si ratios (Figs. 3 – 6).

The elevated Ge/Si in the Three Rivers broadly coincided with the spatial distribution of the geothermal waters with high temperatures (Fig. 3) (Cheng and Jin, 2013). The Ge/Si was especially high in the source areas of the Chang Jiang and Salween. This can be attributed to the severe aridity in the headwater region (annual runoff <200 mm yr⁻¹; Noh et al., 2009) (Table 1), where geothermal water can make the greatest influence on the stream composition. In the source areas of the Chang Jiang, conditions are favorable for groundwater-to-surface water conversion, and groundwater along with snow- and ice-melt water continually feed the rivers (Cheng and Jin, 2013). The Ge/Si decreased in the lower reaches as the surface runoff increased downstream (Fig. 3; Table 1). There is a positive correlation ($r^2 = 0.72$, $p < 10^{-6}$, $n = 24$) between Ge/Si of Three Rivers and 1/runoff (Fig. 9a).

As runoff increases, the Ge/Si ratio of river water decreases, suggesting dilution of the geothermal water input. In weathering systems not affected by geothermal inputs, low Ge/Si is usually observed at base flow. The time series for Alaskan rivers reported in Mortlock and Froelich (1987) is an example. That is because clay mineral dissolution (high Ge/Si) becomes more evident at high discharge, but at low discharge feldspar dissolution is dominant (Lugolobi et al., 2010; Kurtz et al., 2011). In areas affected by geothermal inputs, the opposite trend is seen with high Ge/Si at low runoff. That was the case for Nepali rivers where the hydrothermal component is diluted at high runoff (Evans et al., 2004; their Fig. 6). Therefore, the seemingly non-standard concentration-discharge relation of the Three Rivers is actually evidence for the impact of geothermal contributions there. The five outlier samples must have anomalously high Ge input from one of three sources: high hot spring water flux, high Ge/Si ratio of the hot spring and/or high bedrock Ge concentration (e.g. sample RD127 from the Lincang Ge deposit; Fig. 3). There is a generally negative relationship between Ge/Si and heat flow averaged for individual drainage basins (Fig. 9b). This reflects that dilution by runoff is a more important governing factor than heat flow or geothermal waters alone.

In the Hong River, hot springs are also widely distributed but did not spatially correlate with high Ge/Si in our river samples (Fig. 4). The Ge/Si did not show any dependence on runoff or heat flow, which can be attributed to the relatively high and uniform runoff over the drainage basin (Figs. 9c and 9d; Table 1). Only two headwater samples of the Thao (RD228 and RD229) under high heat flow displayed high Ge/Si during the low-flow season (Fig. 9d). In the Lo, a good correlation between Ge and Si concentrations was observed ($r^2 = 0.50$, $p = 0.01$), reflecting that they were derived from a single source without

noticeable elemental fractionation. Moon et al. (2007) noticed correlations between Si and $\text{Na}^* + \text{K}$ (where $\text{Na}^* = \text{Na} - \text{Cl}$) and between $^{87}\text{Sr}/^{86}\text{Sr}$ and $\text{Na}^* + \text{K}$ and suggested that silicate weathering was the major source of Si and $\text{Na}^* + \text{K}$ in the Lo. Additional correlation with Ge suggests that the geothermal contribution was not the major factor in the Lo samples. No such inter-elemental correlations were found in the Da samples, but the similarly low values and narrow range of Ge/Si (Fig. 7) suggest that the geothermal contribution was minor in the Da.

In the Huang He, the absence of the geothermal waters in the upper reach was responsible for the lower Ge/Si ratios (Fig. 5). The increase in Ge/Si downstream (CJ111) and the Huang Shui tributary system (CJ112, CJ113, CJ245) can be related to the occurrence of hot springs, the increase of heat flow and the lower runoff (Figs. 5, 9e and 9f).

The Mt. Baekdu samples were adequately described by binary mixing between geothermal water and surface fresh water (Fig. 10). All results plotted near the mixing curve, which had CB101 as an end-member for the geothermal water. According to the Na-K-Ca geothermometric calculation, the other two spring samples, CB104 and CB106, were more immature and equilibrated less with the host rocks than CB101 (Han and Huh, 2009). However, the good fit to the binary mixing trend of Fig. 10 suggests that mixing with surface water was responsible and not some inherent geothermal process. The Duman River samples plotted close to the end-member for the fresh water with the lowest Ge/Si (0.2 – 0.4) (Fig. 10), reflecting negligible contribution of geothermal waters in spite of the relatively high heat flow (70 – 80 mW m⁻²) in the drainage basin (Figs. 6 and 9f). The low Ge/Si ratios are due to the high Si concentrations up to 616 μM, stemming from weathering of trachytic rock in the upper reaches of the Duman River (Han and Huh, 2009).

5.2. Variations in hydrothermal Ge/Si

In general the Ge/Si ratios are high in geothermal waters (Evans and Derry, 2002; Evans et al., 2004). In the ETP, geothermal waters are widespread yet we did not observe high Ge/Si ratios in rivers other than the Three Rivers. The lack of high Ge/Si ratios does not necessarily indicate the lack of hot spring influence. Dilution of geothermal water with local groundwater is quite common in hot spring systems and as seen in Fig 10, mixing with surface fresh water can also lower the Ge/Si ratio in geothermal waters. The hydrothermal component clearly will be strongly diluted in a large river system as the hydrothermal water flux will be a very small fraction of the total water flux and will strongly decrease downstream (Evans et al., 2004).

Temperature is also an important condition governing the Ge/Si ratio of geothermal waters, and it is possible that the Ge/Si ratio in river water does not reflect sensitively the geothermal influence. This can be illustrated using the Rayleigh-type model that Evans and Derry (2002) proposed: geothermal water originally enriched in both Ge and Si precipitates Ge-poor quartz as it cools and the water becomes enriched in Ge.

$$\left(\frac{\text{Ge}}{\text{Si}}\right)_w = \left(\frac{\text{Ge}}{\text{Si}}\right)_0 \times F_{\text{Si}}^{(\alpha-1)},$$
$$\alpha = \left(\frac{\text{Ge}}{\text{Si}}\right)_{ppt} / \left(\frac{\text{Ge}}{\text{Si}}\right)_w$$

where $(\text{Ge}/\text{Si})_0$ and $(\text{Ge}/\text{Si})_w$ are the initial and final Ge/Si ratios in geothermal water before and after its cooling, respectively, F_{Si} is the remaining fraction of the initial Si in the cooling geothermal water and α is a temperature-dependent fractionation factor of Ge/Si between the precipitates and the geothermal water. If one assumes cooling of the geothermal water from an initial to a final temperature under equilibrium conditions, the enrichment factor, $\text{EF} =$

$(\text{Ge/Si})_{\text{w}}/(\text{Ge/Si})_0 = F_{\text{Si}}^{(\alpha-1)}$, becomes a function only of temperature. The F_{Si} can be calculated from the solubility of Si at the initial and final temperatures, and α can be derived from the equilibrium constants, which vary only with temperature. Figure 11 shows the calculated EFs upon various initial and final temperature conditions. For example, when the geothermal water equilibrated with the host rock at 250°C cools down to 45°C, the Ge/Si ratio becomes ~30 times higher than the initial ratio. The most influential factor for geothermal water to have a high EF is the high initial temperature. If geothermal water has a low initial temperature, possibly due to the tepid geothermal field, its influence on riverine Ge/Si ratio will be small. In addition, if geothermal water is undersaturated with respect to quartz at the initial temperature due to limited water-rock interaction by its short residence in the geothermal field or if it is oversaturated at the final temperature (Evans and Derry, 2002), Ge/Si would be lower than estimated.

5.3. Weathering of coal and sulfide as a source of Ge

In the Salween drainage of the Three Rivers, sample RD127 close to the Lincang Ge deposit displayed a high Ge/Si ratio of 11.2 (Fig. 3). This is higher than in any other nearby samples with similar heat flow and we attribute this to the coal-hosted Ge (Hu et al., 2009). The dissolved sulfate concentrations were low, and we do not think that Ge here is associated with disseminated sulfides.

The Thao main channel of the Hong River runs close and parallel to the Da and Lo but exhibited relatively higher Ge/Si (Figs. 4 and 7) even in the high-flow season when the geothermal contribution should be diluted (Fig. 9d). We attribute the higher Ge/Si to the coal- and sulfide-bearing rocks occurring along the Red River Fault Zone that the Thao drains

(Moon et al., 2007). This is consistent with the previous suggestion that sulfide oxidation led to the higher dissolved SO_4^{2-} in the Thao (130.3 μM) than in the Da (49.6 μM) and Lo (56.4 μM) (Moon et al., 2007).

In the Huang He, the spatial distribution of the geothermal waters or the slight difference in heat flux cannot explain the large difference in Ge/Si between the Huang Shui (1.1 – 4.5) and other samples (0.3 – 0.8) (Fig. 5). The volcanogenic sulfide deposits distributed in the Huang Shui basin may be responsible for the higher Ge/Si in this tributary. Sulfide oxidation was pointed out as a major source of dissolved SO_4^{2-} in the Huang Shui tributary in the previous study (Wu et al., 2005). Weathering of sulfide deposits has also been suggested as a possible reason for elevated Ge/Si in the Copper River basin of SE Alaska (Anders et al., 2003).

One can suspect input of Ge from fly ash, since the rate of coal combustion is high in China and fly ash is enriched in Ge. The original literature that reported the major element data for these rivers assumed low anthropogenic impact based on the low population density. This could be true regarding fly ash input of Ge too, since judging from the distribution of atmospheric antimony emission inventories from coal combustion, the impact of fly ash will be greatest in eastern China and smallest in the provinces near the Tibetan Plateau (Tian et al., 2011). The thermal power plants, more than 90% of which are coal-based, are also found disproportionately on the eastern part of China (Fig. 1) (Karlsen et al., 2001). As of 2005, the provinces where our samples come from account for at most 10% of the national coal consumption (National Resources Defense Council, 2015). Even this is an upper limit, since eastern Sichuan and Yunnan provinces are also included. On the other hand, recycled coal ash in China is used in the manufacture of cement and other building materials, raising concern

over more widespread contamination. Dissolved trace elements like Cu or Zn are not very effective proxies for fly ash input because they are removed by adsorption to suspended sediments and precipitation of oxides, hydroxides and salts (Zhang, 1995), whereas Ge is easily hydrolyzed and exist as $\text{Ge}(\text{OH})_4$. Other metalloids such as antimony (Sb) or arsenic (As) may be better tracers but the relationship is not simple (Chimenos et al., 2013), and a more extensive chemical survey is beyond the scope of this study.

We calculated the potential fly ash contribution to background riverine Ge concentrations following Froelich et al. (1985). Assuming coal consumption in China in year 2000 of $1.2 \times 10^{15} \text{ g yr}^{-1}$, average fly ash emission factor of 0.014, average Ge concentration in fly ash of 25 ppm, and river discharge in China of approximately $2.2 \times 10^{15} \text{ L yr}^{-1}$, we obtained fly ash-originated contaminant Ge concentration in rivers of about 2.5 nM. This is significant compared to our measured values (Table 1) and is a first order constraint on the available pool of Ge and how much riverine Ge concentrations could be increased by fly ash. The above calculation assumes that the fly ash Ge is equally distributed over all river basins, which is certainly a gross exaggeration, since as mentioned before the western provinces of China account for at most 10% of the national coal consumption. Also, there are large uncertainties in the average Ge concentration in fly ash (1 – 356 ppm) (Mayfield and Lewis, 2013) and the river discharge within China. The effect of fly ash on riverine Ge remains an issue, which will require further work. As coal consumption has grown rapidly since our sampling campaign mostly around 2000, a reoccupation of the sampling sites may show the effect of fly ash.

5.4. Effect of weathering intensity on Ge/Si

Weathering intensity was suggested as an important control on the dissolved Ge/Si in river water (Kurtz et al., 2002; Murnane and Stallard, 1990). We examined the relationship between the weathering intensity and the riverine Ge/Si ratio using a plot of Ge/Si vs. $1/\text{Si}$, on which Froelich et al. (1992) observed a correlation ($r^2 = 0.47$) for global “clean” rivers not affected by fly ash (Fig. 12). From the data set of Table 1, we selected only those samples that had minimal input from hydrothermal, sulfide or coal, which left only one tributary of the Salween with high runoff, Lo and Da tributaries of the Hong River, Huang He above confluence with the Huangshui tributary system, and the Duman excluding the lowermost three samples. Then, the data fall into the same region as the “clean” rivers of Froelich et al. (1992) but predominantly in the high DSi, low Ge/Si region (Fig. 12). This is the low chemical weathering intensity or weathering-limited regime.

We can also use a ternary diagram of Si-Ge-Cation_{sil} to examine the weathering intensity and Ge/Si (Fig. 13). Ratios of elements are preferable for examining weathering reactions, because they are more conservative against the influence of dilution and evaporation. Some limiting ratios can be calculated from simplified weathering reactions (Froelich et al., 1992). Weathering of primary silicate minerals would yield Si:Cation_{sil} in the ratio of 3:1, 2:1 or lower and preferentially incorporate Ge in the clays thereby lowering the Ge/Si ratio in rivers. Indeed, most of our samples plotted in Fig. 13 fall in this area. When clay minerals weather, the Si/Cation_{sil} and Ge/Si ratios in solution are expected to be high (Fig. 13). Our samples do not occupy this region. Therefore, we conclude that most of the ETP rivers not affected by geothermal springs or weathering of coal- and sulfide-bearing rocks reflect chemical weathering of primary minerals in a weathering-limited regime.

Among the Da and Lo tributary systems of the Hong River, the low-flow and high-

flow season samples occupied different areas of the ternary diagram. Weathering of primary minerals characterized the low-flow season samples and placed them in the weathering-limited regime, whereas weathering of secondary minerals made a greater contribution to the stream composition during the high-flow season and placed them closer to the transport-limited regime. The Thao samples were parallel to the low-flow samples of the Da but shifted toward the Ge apex, reflecting the predominance of the primary mineral weathering and the additional input of Ge from weathering of sulfide- and coal-bearing rocks. The higher cation fraction was a common feature during the low-season in all three tributaries of the Hong River, suggesting that the weathering intensity was greater during the high-flow season. This is quite similar to what Ge/Si ratios indicated for the Icacos River in Puerto Rico (Kurtz et al., 2011; Lugolobi et al., 2010), which was interpreted as short-term interaction between water and soil and release of Si and Ge sorbed to the surface of soil minerals. Such labile Si and Ge do not seem to be exhausted rapidly, such that intense storms do not produce a dilution effect.

The Mt. Baekdu and most of Three Rivers samples fell close to the Ge apex due to the geothermal contribution and could be discriminated from those rivers mainly showing weathering influence (Fig. 13).

The opal phytolith is depleted in both Ge and cations, and its dissolution will make river composition plot close to the Si apex on the Si-Ge-Cation_{sil} ternary diagram. This effect may obscure or enhance the weathering trend of secondary minerals (Fig. 13). Our data fall away from the Si apex, except for a small tributary of the Da (RD102) in the Hong River system at high flow. Although it is difficult to be quantitative about this, we think that the impact of phytoliths was minor in most of our ETP and Mt. Baekdu samples compared to the prevailing contribution from the geothermal and weathering controls. Some context can be

provided by silicon isotopes of river dissolved and suspended load, although the data set in the literature is still in its early stages. Formation of secondary minerals and biological uptake (both phytoliths and diatoms) take up light Si and leave the river water heavier. Investigating the Si cycle of the Chang Jiang downstream of Yibin (Fig. 1), Ding et al. (2004) measured $\delta^{30}\text{Si}$ value of 0.7‰ in the dissolved load at Yibin and an increasing trend downstream to 3.0‰ in Shanghai. They interpreted this as weathering of primary silicate minerals upstream, the $\delta^{30}\text{Si}$ value at Yibin being very close to what is expected from weathering of feldspar (0.75‰), and silicon absorption by grass and rice downstream (Ding et al., 2004). Our samples are all in the extreme headwaters of the Chang Jiang drainage and above the major agricultural area of the Sichuan basin; therefore, we may surmise that they have not been affected significantly by rice cultivation. In the case of the Huang He, the $\delta^{30}\text{Si}$ values of some samples analyzed by Ding et al. (2011) approximately coincided with our sample locations (CJ116, CJ114, CJ111 and CJ112), and their $\delta^{30}\text{Si}$ values ranged from 1.0 to 1.8. Ding et al. (2011) did not offer interpretations for specific samples but expected the Huang He to be less impacted by plant productivity than the Chang Jiang due to the drier and cooler climate and vegetation type less favorable to phytolith growth (conifers and wheat versus bamboo and rice). Our data are not adequate to rigorously address the effect of terrestrial biological cycling of Si and Ge on the riverine Ge/Si, but studies in the literature using $\delta^{30}\text{Si}$ have shown that not all rivers are under direct biological impact on DSi: for example, the Amazon River (Hughes et al., 2013) and Swiss and Iceland rivers (Georg et al., 2006; Georg et al., 2007).

6. Conclusion

The dissolved Ge/Si ratio provided valuable information on the source of DSi in the rivers of the eastern Tibetan Plateau (ETP) and Mt. Baekdu regions. Geothermal waters were widespread in the ETP region, but its contribution to the riverine DSi was noticeable only in the Three Rivers. The high Ge/Si ratios in the Three Rivers is a signal of how tectonically induced heat flow anomalies can be represented in river chemistry, and these geochemical signals offer the potential to quantify hydrothermal heat loss in tectonically or volcanically active areas (Derry et al., 2009). In the Hong River and the Huang He, weathering of sulfide- and coal-bearing rocks was responsible for the spatial variation in the riverine Ge/Si. Geothermal contribution was relatively minor in those rivers, which can be attributed to the lower temperature of the geothermal field, limited water-rock interaction and/or the small influx of geothermal waters. The dependence of the river composition on the weathering intensity can be visualized on the Si-Ge-Cation_{sil} ternary diagram, on which geothermal contribution or the effect of phytoliths can also be displayed. Mt. Baekdu samples show binary mixing between the geothermal water and fresh surface water end members, but the geothermal water did not influence the Duman river samples. The impact of fly ash on riverine Ge remains an issue, and future work will require a more extensive chemical survey and re-occupation of the sampling sites. Our work provides a basis for comparison to such future work that would reflect the increase of coal utilization during the last decade.

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Figure captions

Figure 1. Location map of the study area. The drainage basins of the sampled rivers are shown in color, and the sample locations are marked with black dots. The Tibetan Plateau is the area shown in white on the grey scale digital elevation map. The Three Rivers are composed of the Chang Jiang, Mekong and Salween. Red dots indicate locations of thermal power plants (Karlsen et al., 2001).

Figure 2. The location and temperature of geothermal waters in the eastern Tibetan Plateau are shown as colored circles. The information was digitized from the Hydrogeological Atlas of the People's Republic of China (1979). Geothermal activity was not reported in the Atlas for the Duman River basin. The Hong River basin lying outside China were not included in the Atlas. The heat flow distribution of the study area (Tao and Shen, 2008) is shown as colored background. Figure 3. The Ge/Si ratios ($\mu\text{mol/mol}$) in the Three Rivers with the size of the large circles corresponding to the Ge/Si ratios. The locations of the furthest downstream samples are marked with open squares. The location and temperature of geothermal waters are indicated with colored small circles, and heat flow distribution is shown as background color. The scales for geothermal water temperatures are as for Fig. 2.

Figure 4. The Ge/Si ratios ($\mu\text{mol/mol}$) in the Hong River and the heat flow distribution. The size of the large circle indicates the Ge/Si ratio, and the locations of the furthest downstream samples are marked with open circles. The location and temperature of geothermal waters are indicated with colored small circles, and heat flow distribution is shown as background color. The scales for geothermal water temperatures and heat flow are as for Fig. 2. The dot-dash line indicates national boundaries.

Figure 5. The Ge/Si ratios ($\mu\text{mol/mol}$) in the Huang He and the heat flow distribution. The size of the large circle indicates the Ge/Si ratio, and the location of the furthest downstream sample is marked with an open triangle. The location and temperature of geothermal waters are indicated with colored small circles, and heat flow distribution is shown as background color. The scales for geothermal water temperature and heat flow are as for Fig. 2.

Figure 6. The Ge/Si ratios ($\mu\text{mol/mol}$) in Mt. Baekdu and the Duman River. There were no geothermal waters reported for the Duman River basin in the Hydrogeological Atlas of PRC (1979). The size of the large circle indicates the Ge/Si ratio of the Duman River samples, and the location of the furthest downstream sample is marked with an open cross. The locations for Mt. Baekdu samples are marked with diamonds and the range of Ge/Si ratios are given in Fig. 7. The scale for heat flow is as for Fig. 2.

Figure 7. The Ge/Si ratios in different river basins. Notice that the Mt. Baekdu hot spring and nearby stream samples are plotted on a different scale. The furthest downstream samples for each basin are marked with open symbols.

Figure 8. Box and whisker plot for heat flow corresponding to the geothermal waters at various temperature intervals. The heat flow data are from Tao and Shen (2008) and the geothermal water temperature data are from the Hydrogeological Atlas of PRC (1979).

Figure 9. The relationship between the Ge/Si ratio and (a, c, e) runoff and (b, d, f) heat flow for the Three Rivers, Hong River, Huang He and Duman River samples. Sample CJ239 has been omitted from (a) and (b) because of the low runoff (2 mm/yr). The dashed line in (a) indicates a linear fit to all Three Rivers data except for the five

outliers marked with their sample numbers and CJ239 (n=24).

Figure 10. The binary mixing curve for the Mt. Baekdu samples. The Duman River samples are also plotted for reference.

Figure 11. The calculated Ge/Si ratio in geothermal water cooling down from the initial to final temperatures according to the Rayleigh-type model of Evans and Derry (2002).

Figure 12. Ge/Si versus 1/Si in rivers not affected by hydrothermal springs or coal and/or sulfide weathering (symbols) compared to the least squares fit to global rivers not influenced by coal combustion (line; Froelich et al., 1992).

Figure 13. The ternary diagram of Si-Ge-Cation_{sil}. The Ge concentrations were multiplied by 10⁶. Cation_{sil} indicates the sum of cations (Na⁺+K⁺+Ca²⁺+Mg²⁺, μmol L⁻¹) derived from weathering of silicate minerals; these were from either forward or inverse modeling in the original literature. The Ge/Si ratios marked on the inset are from Froelich et al. (1992). The samples that show silicate weathering signatures are plotted in color; the rest are in grey.

Fig. 1 (2 columns)

Fig. 2 (1.5 column)

Fig. 3 (1.5 column)

Fig. 4 (1.5 column)

Fig. 5 (1 column)

Fig. 6 (1 column)

Fig. 7 (1 column)

Fig. 8 (1 column)

Fig. 9 (2 columns)

Fig. 10 (1 column)

Fig. 11 (1 column)

Fig. 12 (1.5 column)

Fig. 13 (2 columns)

Table 1. Dissolved Ge in the rivers draining the eastern Tibetan Plateau and Mt. Baekdu. The Si concentrations are from literature (see text).

River name ^a	Sample ID	Date mm/dd/yyyy	Latitude deg	Longitude deg	Basin area km ²	Runoff mm yr ⁻¹	Si μmol kg ⁻¹	Ge pmol kg ⁻¹	Ge/Si μmol/mol	Heat flow mW m ⁻²
Hong River (Moon et al., 2007), n = 43										
<i>Da</i>										
Amo Jiang	RD120	09/07/2001	101.51	23.35	3664	1256	176	160	0.9	74
Amo Jiang	RD217	01/07/2003	101.51	23.35	3664	266	123	103	0.8	74
Babian Jiang	RD121	09/07/2001	101.33	23.24	5600	1390	150	176	1.2	75
Babian Jiang	RD218	01/07/2003	101.33	23.24	5600	322	108	60	0.5	75
Da @ Lai Chau	RD105	08/19/2001	103.16	22.08	26360	1422	214	156	0.7	72
Da @ Lai Chau	RD203	12/29/2002	103.16	22.08	26360	303	202	139	0.7	72
Namna @ Lai Chau	RD104	08/19/2001	103.16	22.08	6537	1314	264	80	0.3	72
Namna @ Lai Chau	RD204	12/29/2002	103.16	22.08	6537	247	247	185	0.7	72
Da @ Muong La, ab reservoir	RD103	08/18/2001	104.04	21.46	43470	1551	228	152	0.7	72
Da @ Muong La, ab reservoir	RD202	12/28/2002	104.04	21.46	43470	317	207	132	0.6	72
Trib of Da @ Yen Chau	RD102	08/17/2001	104.36	21.03	834	1489	150	27	0.2	67
Da @ Hoa Binh, bl reservoir	RD101	08/17/2001	105.36	20.83	51060	1560	210	224	1.1	71
Da @ Hoa Binh, bl reservoir	RD201	12/27/2002	105.36	20.83	51060	313	176	126	0.7	71
<i>Thao</i>										
Upper Lishe Jiang LB	RD131	09/11/2001	100.55	25.09	890	1298	176	213	1.2	77
Upper Lishe Jiang LB	RD229	01/12/2003	100.55	25.09	890	336	107	230	2.2	77
Upper Lishe Jiang RB	RD130	09/11/2001	100.53	25.06	1634	1145	160	206	1.3	78
Upper Lishe Jiang RB	RD228	01/12/2003	100.53	25.06	1634	308	145	604	4.2	78
Hong @ Yuan Jiang	RD119	09/05/2001	101.98	23.63	20760	983	166	209	1.3	76
Hong @ Yuan Jiang	RD216	01/06/2003	101.98	23.63	20760	212	167	218	1.3	76
Huanien He	RD118	09/05/2001	102.17	23.88	2400	512	185	267	1.4	75
Huanien He	RD215	01/06/2003	102.17	23.88	2400	77	118	126	1.1	75
Hong @ Cua Khao	RD106	08/22/2001	103.85	22.59	34090	918	213	264	1.2	75
Hong @ Cua Khao	RD205	12/30/2002	103.85	22.59	34090	188	237	324	1.4	75
Nan Xi	RD117	09/04/2001	103.88	22.68	3156	1098	200	342	1.7	73
Xiao Nan Xi	RD116	09/04/2001	103.94	22.65	275	1530	126	24	0.2	72
Namthe @ Lao Cai	RD107	08/22/2001	104.01	22.52	4011	1208	198	165	0.8	73
Namthe @ Lao Cai	RD206	12/31/2002	104.01	22.52	4011	239	180	250	1.4	73
Hong @ Yen Bai	RD109	08/23/2001	104.84	21.74	44690	1087	219	322	1.5	74
Hong @ Yen Bai	RD208	12/31/2002	104.84	21.74	44690	225	231	215	0.9	74
Hong @ Phu Tho	RD115	08/26/2001	105.23	21.40	48420	1131	210	288	1.4	74
Hong @ Phu Tho	RD214	01/02/2003	105.23	21.40	48420	233	219	202	0.9	74
<i>Lo</i>										
Lo @ Ha Jiang	RD111	08/24/2001	104.98	22.84	7133	1233	141	40	0.3	73
Lo @ Ha Jiang	RD211	01/01/2003	104.98	22.84	7133	235	97	12	0.1	73
Con @ Vinh Tuy	RD112	08/25/2001	104.89	22.27	1234	1985	150	188	1.3	71
Con @ Vinh Tuy	RD212	01/02/2003	104.89	22.27	1234	405	218	165	0.8	71
Gam @ Chiem Hoa	RD113	08/25/2001	105.28	22.14	15060	1845	169	40	0.2	70