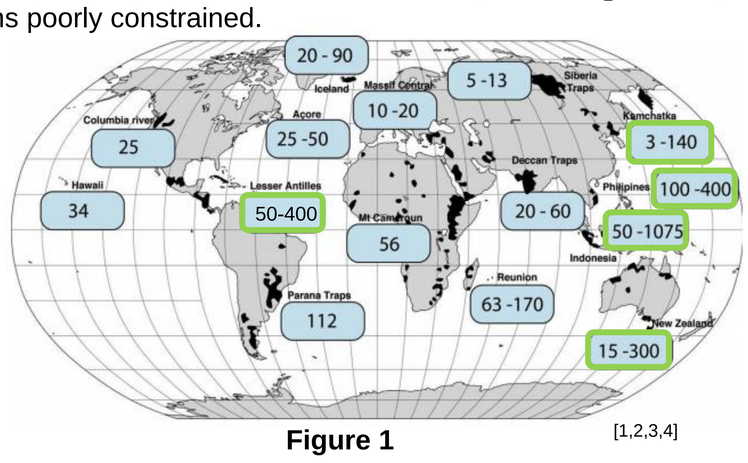
Seasonal variations of dissolved Ge/Si ratios in streams from the Aso caldera, Kyùshù, Japan

François GASPARD[1], Sophie OPFERGELT[1], Jens HARTMANN[2], Takahiro HOSONO[3], Pierre DELMELLE[1]

[1]Earth and Life Institute, Environmental sciences, Université catholique de Louvain, Louvain-la-Neuve, Belgium (francois.gaspard@uclouvain.be).
[2]Institut for Geology, Universität Hamburg, Germany.
[3]Priority Organization for Innovation and Excellence, Kumamoto University, Japan.

1. Introduction

- Volcanic island arcs display the highest chemical weathering rates on Earth (Fig. 1).
- Chemical weathering rates are typically calculated from dissolved SiO_2 and cationic concentrations in rivers measured during the dry season.
- In volcanic regions, hydrothermal alteration contributes to the weathering fluxes, potentially leading to overestimation of atmospheric CO_2 consumption. This effect remains poorly constrained.



[1,2,3,4]

Figure 1

- Since hydrothermal waters usually exhibit higher Ge/Si ratio [µmol/mol] values than river waters (Fig. 2), the Ge/Si ratio may be a useful tool to trace hydrothermal contribution.

Terrestrial hydrothermal springs : 2 – 1000 µmol/mol **River waters :** 0.16 – 2.72 µmol/mol

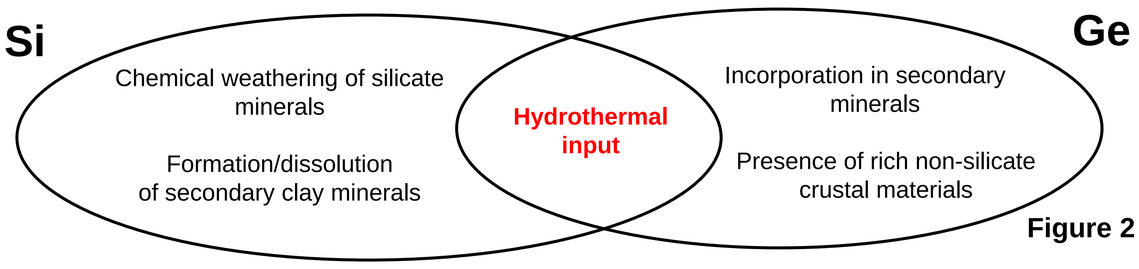


Figure 2

- Runoff variability affects weathering fluxes in volcanic island arcs, where seasonal changes in runoff during extreme rainfall events (flash flood) produce about 25% of the annual dissolved inorganic carbon flux [5].
- Question: What is the impact of runoff variability on the hydrothermal contribution to weathering fluxes ?

2. Study site and methods

- Aso volcano (Kyùshù Island, Japan) is one of the largest calderas in the world (353 km^2).
- 18 hydrothermal springs, 29 river waters, 12 groundwaters and 1 rainwater were sampled at six different periods between 2014 and 2016 including dry and wet seasons. (Fig. 3).

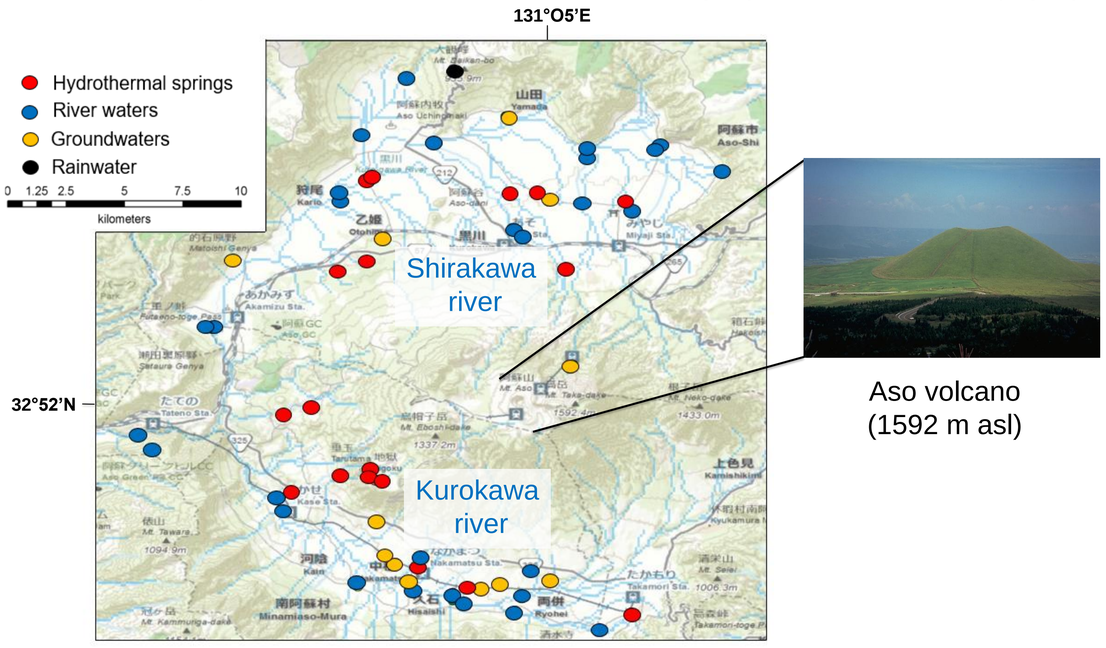


Figure 3

- Dissolved Ge and Si concentrations were measured by ICP-MS and ICP-AES, respectively. Uncertainty on Ge concentration for an internal springs standard is 4 % (n=14).

3. Ge/Si in hydrothermal springs, groundwaters and rainwater

- The highest Ge/Si values were obtained for the hydrothermal springs waters (Fig. 4), relative to groundwaters and rainwater (Fig. 5).

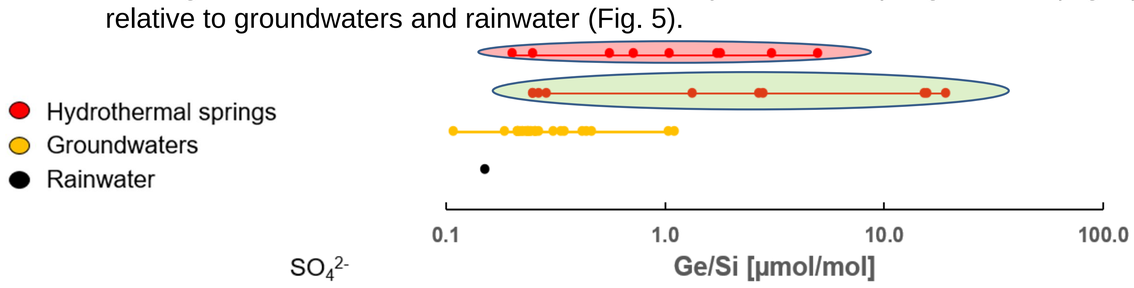


Figure 5

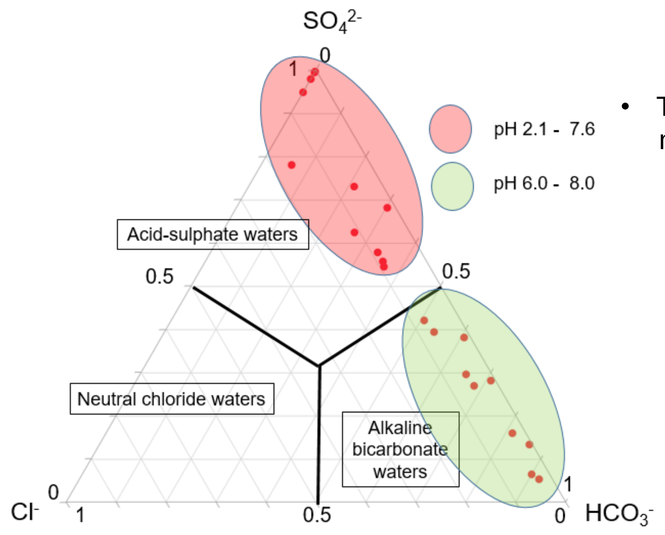


Figure 4

- The high Ge/Si values of hydrothermal springs may be due to silica precipitation [6] (Fig. 6)

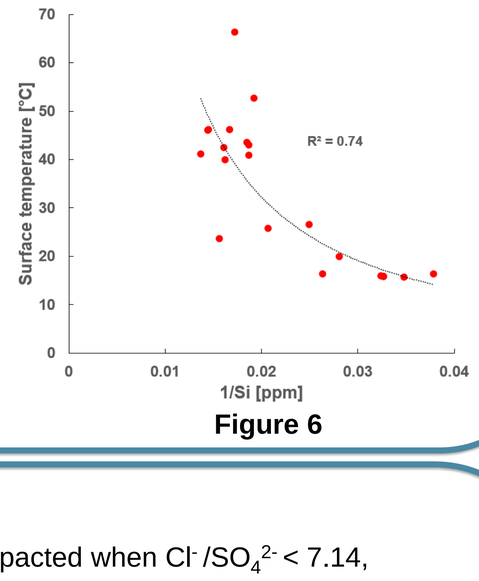


Figure 6

4. Ge/Si in river waters

- River waters are considered as hydrothermally-impacted when $Cl^-/SO_4^{2-} < 7.14$, $[SO_4^{2-}] > 5$ ppm and high SO_4^{2-}/Na^+ [3] (Fig. 7).

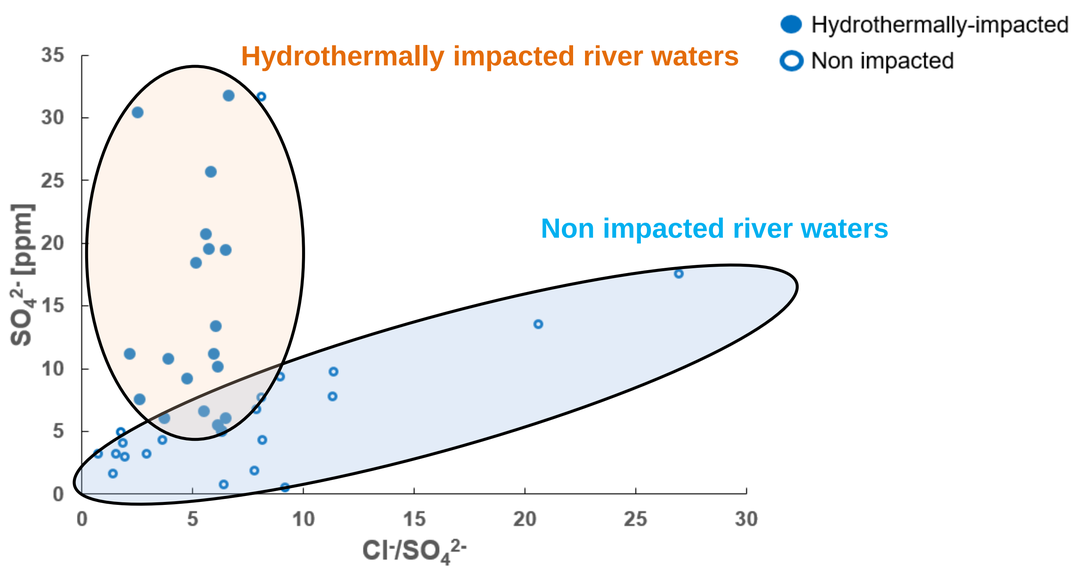


Figure 7

- Ge/Si values in hydrothermally-impacted river waters increase with hydrothermal contribution, and are higher than the Ge/Si values of non impacted river waters (Fig. 8).

Figure 8

5. Seasonal variations of Ge/Si ratios in streams

- Ge/Si ratios in hydrothermal springs, groundwaters and rainwater vary little between sampling seasons (Fig. 9).
- Hydrothermally-impacted rivers have lower Ge/Si ratios during the wet season, suggesting dilution of the hydrothermal input (Fig. 9).

Figure 9

6. Concluding remarks

- The Ge/Si ratio is a useful parameter for assessing the relative contributions of hydrothermal springs, groundwaters and rainwater to river waters.
- The Ge/Si ratios of hydrothermally-impacted rivers are sensitive to dilution during the wet season. This suggests that previous studies have overestimated the contribution of hydrothermal input to yearly weathering fluxes. This may have consequences for estimating CO_2 consumption in volcanic islands accurately.

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