

# Report for the Joint Use/Research of the Institute for Planetary Materials, Okayama University for FY2023

05/12/2024

**Category:** International Joint Research General Joint Research Joint Use of Facility  
Workshop

**Name of the research project:** Biogenicity and preservation of trace metals in hot spring deposits:  
preparing for a Mars sample return mission

**Principal applicant:** Michael Rowe

**Affiliated institution and department:** University of Auckland, School of Environment

## **Collaborator**

**Name:** Tak Kunihiro; Eizo Nakamura

**Affiliated institution and department:** Institute for Planetary Materials, Okayama University

## **Research report:**

### Purpose

This research is to conduct isotopic analyses on hot spring silica samples to understand the potential bio-utilisation of trace metals. This specific application seeks to examine hot spring sinter deposits. The overarching outcome of this collaboration between Kunihiro, Nakamura and Rowe is to identify geochemical tracers of microbial activity that may be implemented on samples returned from Mars for the identification of potential evidence of ancient of life. Specifically, this project aims to examine the extent to which gallium isotopes are biologically fractionated in hot spring/geothermal environments.

### Conducted Research

Principal applicant Rowe visited the IPM between June 8 and July 5, and September 7 to 17, 2023. Research assistant Ema Nersezova visited IPM from September 7 to 30<sup>th</sup>, 2023.

- 1) 23 epoxy mounts were prepared and polished for ion probe analysis and with backscatter mapping of the sample surfaces (SEM).
- 2) Ion Microprobe: 4 digitate samples which were analyzed in detail (8-10 images) on the ion microprobe (Cameca 1280) to determine the Ga and B concentrations and distributions and

relative Ga isotopic composition ( $\delta^{71}\text{Ga}$ ). The remaining 19 samples were analyzed only to get representative Ga and B distribution and  $\delta^{71}\text{Ga}$  (between 1-5 analyses). Ion probe images were  $50\mu\text{m} \times 50\mu\text{m}$ .

- 3) Bulk trace element analyses were completed on 20 samples in duplicate, including major elements and Ga on the Element HR-ICPMS and TE + REE on the T-Q ICPMS.
- 4) Four bulk samples were analyzed for Ga isotopes by MC-ICPMS.
- 5) Electron microprobe major element maps and spot analyses were conducted on 20 epoxy mounts.

### Research Outcomes

Bulk chemical results suggest that Ga enrichment is not directly correlated to B enrichment (although both seem to be variably enriched in hot spring deposits and related to microbial activity). Gallium abundance in the bulk material varies from 1.2ppm to 416ppm. Bulk Ga concentrations will be utilized to help identify samples with enough Ga for bulk isotopic analysis.

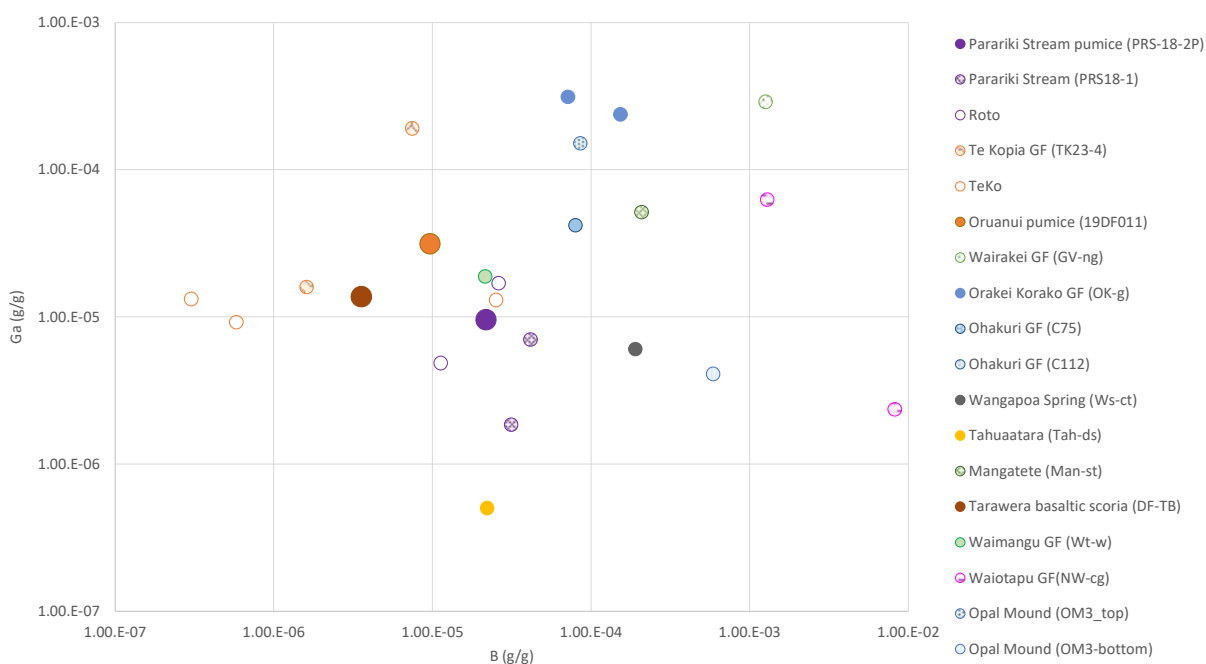


Figure 1: Bulk ICPMS analysis of sinter hot spring silica and volcanic substrate. For bulk materials no obvious correlation between Ga and B exists.

From ion probe imaging, it is clear that Ga is heterogeneously distributed in the hot spring silica, primarily enriched around cyanobacteria (Figure 2). Diatoms, a common microbe in acidic hot springs shows no evidence of trace metal enrichment- so the enrichment process seems unique to specific microbial activity (to be further tested with additional species). Localized Ga enrichments are up to  $\sim 700$  ppm, significantly higher than observed in bulk material, again demonstrating the heterogeneity of Ga in these materials.

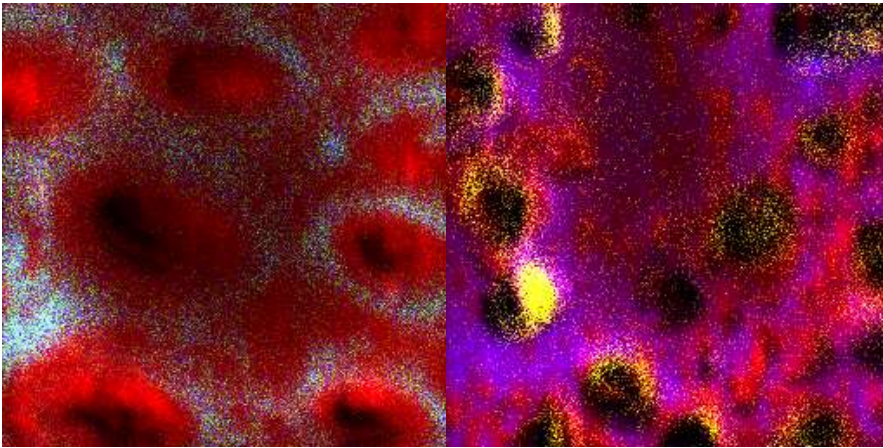
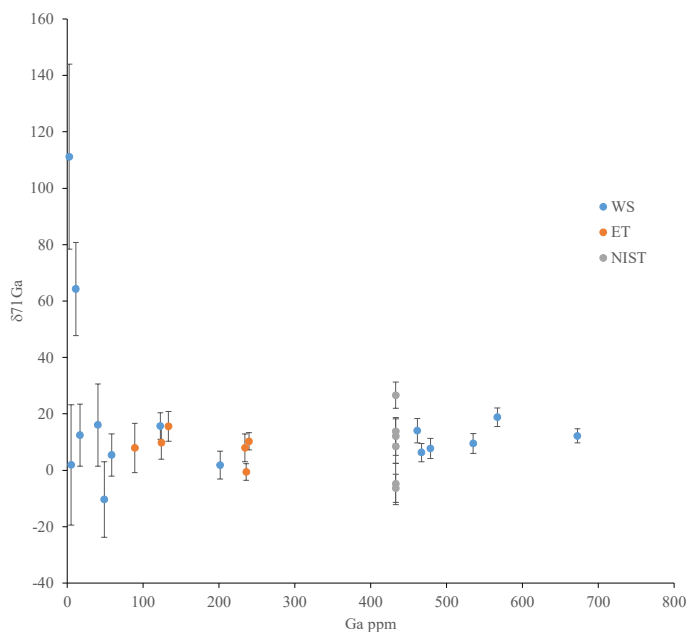


Figure 2: 50x50 micrometer ion probe images of microbial filaments in cross section (Ga in blue, Si in red, B in yellow). Note Ga enrichment (blue) around the silica sheath and trichome (indicated by the dark regions - lower Si) of the microbe- left. In the image on the right, note that B enrichment is zoned relative to the Ga and appears to be concentrated in the interior of the microbes (dark regions), compared to Ga which is enriched to the exterior of the microbes.

Using the ion imaging procedure (50 x 50 micrometer raster),  $\delta^{71}\text{Ga}$  results were all overlapping in isotopic composition. Note that using these conditions, concentrations below  $\sim 400$  ppm had very high standard deviation and would make it difficult to resolve natural differences in composition. NIST 610 was utilised as a standard material- a high isotopic variability was observed in this material (18 ‰). A new standard will need to be developed if we are to make precise measurements of at this spatial scale. It was also determined that at low abundances, there is an unknown interference on the  $^{71}\text{Ga}$  that becomes influential in the calculation of isotopic compositions.



We determined the Ga isotope ratios for rock reference materials (BHVO2, basalts), standard solutions passed through the columns to evaluate isotope fractionation during separation (NIST 994), and synthetic solutions (In-house STD, PML-Ga1). Ga isotope results were reported as  $\delta^{71}\text{Ga}$ , in units per mil (‰):

$$\delta^{71}\text{Ga} = [({}^{71}\text{Ga}/{}^{69}\text{Ga})_{\text{sample}}/({}^{71}\text{Ga}/{}^{69}\text{Ga})_{\text{standard}} - 1] \times 1000$$

The  $\delta^{71}\text{Ga}$  values for the rock references fall within the published range (0.77–0.82 ‰). The Standard solutions, passed through the columns, have  $\delta^{71}\text{Ga}$  values (NIST 994 normalized to itself) that are close to 0 (0.06–0.9 ‰) confirming the separation procedure. Long-term analysis for the In-house STD yielded a consistent value at  $\delta^{71}\text{Ga} = 1.59$  ( $\pm 0.06$  ‰, 2SD, n=40). Four digitate samples yielded  $\delta^{71}\text{Ga}$  of 0.94–1.4 ‰ (Table 1; Figures 2 and 3).

Strong correlation between Ga isotopic ratio and concentration is observed (Figure 2). This is evidence of isotope fractionation in a hot-spring environment. The isotope enrichment factor (variation) is around 0.5 (‰) (Figure 4). Ga isotope fractionation in digitates appears to follow the Rayleigh fractionation line. If the prediction of Rayleigh fractionation model is accurate, then the  $\delta^{71}\text{Ga}$  value can reach  $\sim 0.43$  (‰) and  $[\text{Ga}] \sim 2000$  ppm (Figure 4). This may observe in spot analysis when  $[\text{Ga}]$  is probably significantly high. Water-rock interaction leads to lower  $\delta^{71}\text{Ga}$  values and  $[\text{Ga}]$  in water. If the water-rock ratio is extremely high,  $[\text{Ga}]$  in water is significantly low, and vice versa. At the very beginning of the water-rock interaction process, if cyanobacteria can uptake Ga from water (or tiny clay particles) and deposit as digitate species then Ga isotope fractionation of digitate can be explained by Rayleigh fractionation law.

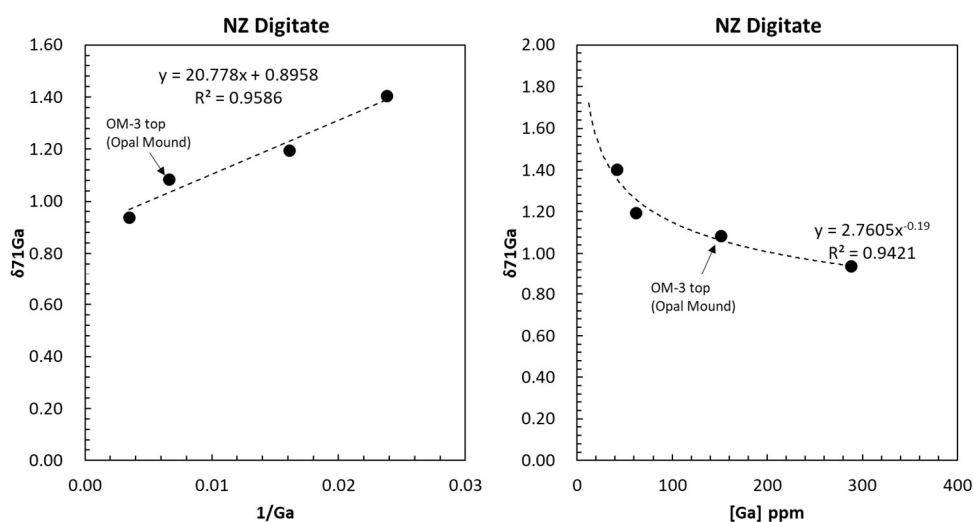


Figure 4: Gallium isotopic variation of 4 analyzed samples with up to 0.5‰ isotopic variation.