

Revisiting the ^{142}Nd deficits in the 1.48 Ga Khariar alkaline rocks, India

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The short-lived ^{146}Sm - ^{142}Nd chronometer is a sensitive tracer of early silicate Earth differentiation. Expected variations in the abundance of ^{142}Nd are small (max 10-30 ppm) and their detection requires very clean separation of Nd to lower isobaric interferences to negligible levels and multidynamic acquisition scheme during TIMS measurements to account for drifts in detector and amplifier efficiency. The detection of ^{142}Nd deficits may also be hampered by inappropriate mass bias correction if Nd evaporates from multiple domains that are fractionated to different degrees [1].

Whereas early mantle depletion is well documented by <15 ppm ^{142}Nd excesses in Archean rocks [2], evidence for complementary early-enriched reservoirs remains sparse, e.g., [3]. Deficits in ^{142}Nd of up to about 20 ppm were reported for the 1.48 Ga alkaline rocks from the Khariar nepheline syenite complex in southeastern India [4]. These rocks crystallized long after ^{146}Sm was effectively extinct. It was therefore concluded that the Khariar rocks had inherited the Nd signature of an early-formed, low-Sm/Nd reservoir that was preserved (i.e., escaped mixing back into the convecting mantle) for at least 2.7 billion years.

Here we report the results of replicate analyses (double-blind experiment) performed at ETH Zurich for the four Khariar rocks DU-36, DU-1/2, DU-1/4, and DU-9/2. Each sample was digested once. Nd was isolated by classical ion exchange chromatography and Ce was removed using liquid-liquid extraction. Each Nd cut was then split onto two filaments and measured as Nd⁺ with a Thermo Triton (TIMS) in multidynamic mode. Repeated measurements of the JNdi-1 standard yielded an external precision of ± 5 ppm 2 SD (n=7). Our replicate analyses for the four Khariar rocks show no resolvable ^{142}Nd anomalies and no evidence of mixing among differently fractionated domains on the filament, e.g., [1]. This is in contradiction with previously reported anomalies for the samples DU-1/4 (-13.6 ppm) and DU-36 (-14.4 ppm) [4].

We are currently investigating the reason for the discrepancy between the two data sets, such as mass fractionation, detector linearity, and duration of measurements.

[1] Upadhyay et al. (2008) *JAAS*, **23**, 561-568.

[2] Caro et al. (2006) *GCA*, **70**, 164-191.

[3] O'Neil et al. (2008) *Science* **321**, 1828-1831.

[4] Upadhyay et al. (2009) *Nature* **459**, 1118-1121.

Helium isotopes and gas compositions in Aira caldera: Comparative study of hydrothermal activity at Sakurajima volcano and Wakamiko submarine crater, Japan

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Aira caldera, located in Kagoshima bay, southern Kyushu, Japan, is a typical example of submerged caldera; it is composed of an active subaerial volcano, Sakurajima, and an active submarine crater, Wakamiko. Sakurajima is a stratovolcano which had its eruptive activity reinforced in the Showa crater since October 2009. Hydrothermal activity such as hot springs is widely observed in the foot of Sakurajima volcano. Wakamiko crater is a submarine depression where lies a hydrothermal activity such as fumarolic gas emissions on the seafloor. Wakamiko hydrothermal activity is considered to be related to the magmatic activity of Sakurajima volcano, but there have been no comparative studies yet to prove it.

In this study, we report He isotopes and gas compositions of hydrothermal waters for both Sakurajima volcano (hot springs) and Wakamiko crater (seawater) to constrain this relationship. First results of helium isotopes for Sakurajima and Wakamiko indicate very consistent values between the two edifices. The $^3\text{He}/^4\text{He}$ ratios for Sakurajima and Wakamiko range from 0.99 to 5.74Ra and 1.09 to 2.81Ra, respectively. Sakurajima $^3\text{He}/^4\text{He}$ ratios are explained by mixing of mantle-derived (MORB) and atmospheric helium dissolved in water (air-saturated water, ASW). Helium ratios in Wakamiko seawater samples increase with depth below the sea surface. Higher $\delta^3\text{He}$ in samples from 150 to 200m depth indicate a mixing between a mantle-derived component and ASW, as deduced for Sakurajima volcano. The $^3\text{He}/^4\text{He}$ ratio of injected mantle-derived helium component is $6.0 \pm 0.3\text{Ra}$ for Sakurajima volcano and $5.9 \pm 0.2\text{Ra}$ for Wakamiko crater. This similarity of He signatures for the magmatic source of Wakamiko seawater and Sakurajima hot springs suggests that (1) Wakamiko and Sakurajima share the same magmatic system and (2) the injected mantle-derived helium into the Wakamiko system comes from Sakurajima volcano itself. First results of $\text{CO}_2/^3\text{He}$ ratios (207 to 611×10^9) in Sakurajima hot springs are higher than the average $\text{CO}_2/^3\text{He}$ ratios observed in gas samples in Japan (10×10^9) [1]. High $\text{CO}_2/^3\text{He}$ ratios in hot springs are commonly explained by physical fractionation processes, related to the difference of solubility between He and CO_2 in ground water [2]. However, the $^3\text{He}/^4\text{He}$ and $\text{CO}_2/^3\text{He}$ ratios for Sakurajima decrease with increasing distance from the vent (Showa crater), suggesting that the source of CO_2 (as it is for He) is related to the volcanic activity. These correlations suggest that high $\text{CO}_2/^3\text{He}$ ratios are also the result of addition of CO_2 by decomposition of carbonates from sediment rocks [3].

[1] Hilton et al. (2002). *Rev. Mineral. Geochem.* **47**, 319-370. [2] Sano et al. (1998) *J. Geophys. Res.* **103**, 22,863-22,873. [3] Urabe et al. (1985) *Geoch. J.* **19**, 11-25.