

## Silicon isotopes in granitoid rocks

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Granites (and other felsic lithologies) constitute ~50% of the mass of the upper continental crust [1] and play a major role in global weathering [2], yet little information exists on their Si isotopic composition and systematics. In principle, S-type granites (that is, those with a pelitic sedimentary affinity [3]) should be isotopically light, as weathering enriches sediment in the lighter Si isotopes, whereas 'igneous' granites (I- and A-type) should be isotopically heavier. Previous work [4] reveals relatively large Si isotopic variation in granitoid rocks, but no systematic differences between granite types - however, the large uncertainties associated with these data makes interpretation difficult.

Here we revisit this problem and provide a Si isotopic perspective on granite petrogenesis with the benefit of high-precision techniques. We have analysed a representative suite of over 30 I-, S- and A-type granitoid samples and mineral separates, using a HF-free alkali fusion method and high-resolution MC-ICP-MS [5].

The data fall between  $\delta^{30}\text{Si} = -0.41$  and  $-0.11 \pm 0.06\text{‰}$  (2 s. d. external precision), although the variation within each batholith is small, providing evidence of a strong source control. However, Si isotopes do not distinguish between I- and S-type granites; both groups display a similar range of isotopic compositions. In contrast, the data for A-type granites are more restricted and comparable to extrusive felsic material [6]. A strong negative correlation with initial  $^{87}\text{Sr}/^{86}\text{Sr}$  provides evidence that Si isotopic variation in both I- and S-type granites can be explained by contamination of an 'igneous' source region magma by an enriched (high Rb/Sr) end-member, possessing a light  $\delta^{30}\text{Si}$  signature, such as sediment derived from continental crust.

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## Volcanic ashes as the source of dissolved calcium in seawater

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The geochemical balance of carbon in the modern ocean indicates that 487 million ton of  $C_{\text{org}}$  annually oxidizes and form Ca–Mg carbonates. The reaction of carbonate formation requires 1 628 million ton of Ca (Mg) from silicates. Volcanic terrigenous ashes coming into the ocean possess of great specific surface and can pretend to the role of significant source of labile Ca (Mg). It was tested experimentally.

Variable amounts of ashes were placed into artificial 35‰ seawater containing no borates and salts of weak acids with the exceptions of carbonate. Hermetically closed contents were mixed during a month, and filtered through 0.22  $\mu\text{m}$  filters. Values of pH, Alk, and concentrations of Ca, Mg, and Si were determined both in filtrates and the initial seawater.

Concentrations of calcium and silicon in all experiments increase in direct relation to the solid/water mass ratio (table). Maximal calcium mobilization was observed for the Koryaksky volcano ashes containing 2.1%  $S_{\text{tot}}$ . High sulfur content in this sample accounted for dramatic pH and Alk reduction. But pH and Alk reduction was observed also in the experiments with low-sulfur ashes from Kamchatka. This indicates that other reactions may affect acid-base equilibrium. Magnesium concentration except the Karymsky volcano ashes also increases with the solid/water mass ratio increase, but lesser than calcium concentration. Dissolved calcium and magnesium coming into the ocean can possibly bind dissolved inorganic carbon formed by oxidation of  $C_{\text{org}}$  of continental runoff in the ocean.

Volcano	Mass of ash, g/l	pH	$\Delta\text{Alk}$	$\Delta[\text{Ca}]$	$\Delta[\text{Mg}]$	$\Delta[\text{Si}]$
			meq/l			$\mu\text{M}$
Koryaksky, 2.1% S	10	7.17	-0.80	4.39	0.17	94.4
	20	6.79	-1.48	8.89	0.51	143.0
	50	5.92	-2.30	21.55	1.82	263.5
Ksudach, 0.022% S	10	7.56	-0.22	0.34	0.09	86.9
	20	7.45	-0.42	0.57	0.14	128.6
	50	7.24	-0.84	1.03	0.26	211.2
Karymsky, 0.085% S	10	7.49	<0.02	0.11	<0.02	26.4
	20	7.43	-0.16	0.23	<0.02	43.4
	50	7.32	-0.38	0.34	<0.02	86.4
Eyjafjallajökull, 0.076% S	10	7.61	0.10	1.14	0.57	89.3
	20	7.60	0.14	1.82	0.88	125.4
	35	7.61	0.19	3.19	1.08	155.6

**Table 1:** Variation of seawater composition at the interaction with volcanic ashes.