

What controls silicon isotope fractionation during dissolution of biogenic silica?

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How nutrients are distributed and cycled in the oceanic water column determines what the net effect of biological activity on ocean-atmosphere ΔpCO_2 is. Paleoceanographers and paleoclimatologists are therefore interested in the past nutrient state of the sunlit surface ocean. Biological matter production and recycling involves isotope fractionation which enables the characterization and quantification of nutrient dynamics. Isotope studies of nutrients (carbon and nitrogen) have been used to characterize the nutrient state of the surface Southern Ocean over glacial-interglacial time scales, and recent advances in analytical techniques enabled the inclusion of silicon isotopes. The marine silicon dynamics, distribution and isotopic composition has been established. In the Southern Ocean diatoms are the dominating phytoplankton species essentially controlling silicon cycling by utilizing silicon to build their opaline frustules and remineralizing after death. While the isotope fractionation associated with silicon uptake by diatoms has been found to be essentially constant, the reverse effect, remineralization, could cause diatoms to not preserve their silicon isotope fingerprint from the surface ocean.

In our study we try to assess if isotope fractionation is involved in diatom dissolution and if so, what causes the effect and what are potential implications for silicon isotopes as a tracer for the biological pump. In all experiments we used 5 mM NaOH to start diatom dissolution. To terminate dissolution diatoms were either separated from NaOH by filtering or the unfiltered solution was directly loaded onto the cation exchange resin. Temperature, amount of opal, opal grain size fraction and community structure were varied.

We find that no analytically resolvable isotope effect during dissolution is observed for all filtered samples for the grain size fraction <20 μm , independent of temperature, amount of opal and community structure. Unreproducible isotope fractionation relative to the bulk sample was associated with dissolution of the 20-63 μm grain size fractions that have a heterogeneous community structure (e.g. radiolaria included). All non-filtered samples were found to react with the cation exchange resin and produced significant isotope fractionation. In our presentation we discuss the potential causes for the variability of isotope fractionation and are able to conclude that carefully cleaned and purified diatom material with a grain size of <20 μm reliably preserves the silicon isotope composition attained in the surface ocean.

Contrasting plateau- and intra-oceanic arc (IOA)-related plagiogranites, Nicoya and Santa Elena complexes, Costa Rica

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Oceanic tonalite-trondhjemite-granodiorite (TTG) suites (i.e., oceanic plagiogranites) [1] are common in oceanic basins, subvolcanic regions of island arc systems and ophiolites. However, to our knowledge, plagiogranites are exceedingly rare in oceanic plateaus. Here, we present geochemical evidence from Costa Rica oceanic complexes for the existence of both plateau- and arc-related plagiogranites. The plateau-derived Nicoya Complex [e.g., 2] preserves low-Al (mean 12.22 wt.% Al_2O_3) plagiogranites whereby the arc-related Santa Elena Complex [3] encompasses high-Al (mean 17.96 wt.% Al_2O_3) plagiogranites.

In contrast to granites and continental trondhjemites, oceanic plagiogranites are characterized by very low K_2O (<0.5 wt.%). On a plot of SiO_2 vs. K_2O [4], all six Nicoya samples of granodioritic or granitic composition (i.e. with >63 wt.% SiO_2) and the single Santa Elena sample of granodioritic composition plot completely within the field of oceanic plagiogranite; four of five samples with 57-63 wt.% SiO_2 also fall within the field of oceanic plagiogranite. On various granite discrimination plots [5], Nicoya plagiogranites generally fall within the field of ocean ridge granite whereby Santa Elena plagiogranites consistently plot within the field of volcanic arc granites. This is consistent with the interpretation of Nicoya and Santa Elena mafic rocks as plateau/MOR and volcanic arc-related products, respectively. On the basis of chondrite-normalized REE plots, both the Nicoya and Santa Elena plagiogranites are consistent as localized, late-stage felsic differentiates of tholeiitic magma.

U-Pb SHRIMP (zircon) dating at the SHRIMP facility, Korea Basic Science Institute (KBSI) is currently underway on these Nicoya and Santa Elena plagiogranites. The geochemical data suggests that plagiogranites from each complex represent magmas which fractionated from a hydrous gabbroic source and are not the result of other mechanisms sometimes invoked for plagiogranite petrogenesis, e.g., anatexis of mafic crust. If this is accurate, Nicoya plagiogranites should be ~95-85 Ma, an interval of which corresponds to the most voluminous pulse of magmatism related to Galapagos plume activity. On the other hand, Santa Elena plagiogranites should be of the order of ~120 Ma, an age of which was obtained on associated gabbros via $^{40}\text{Ar}/^{39}\text{Ar}$ dating [3]. We integrate the new U-Pb ages with the aforementioned chemical evidence to constrain the petrogeneses of Nicoya and Santa Elena plagiogranites.

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 [2] Sinton et al. (1997) *J. Geophys. Res.* **102**, 15507-15520. [3] Hauff et al. (2000) *G³* **1**, doi 10.1029/1999-GC000020. [4] Coleman and Donato (1979), In: Barker (Ed.) *Trondhjemites, dacites and related rocks*, 149-167. [5] Pearce et al. (1984) *J. Pet.* **25**, 956-983.