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Minor impact of fresh submarine groundwater discharge on Si budget along Indian coastline: inferences from silicon isotopes and Ge/Si ratio

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The stable silicon isotope ratio (δ^{30}Si) and Ge/Si ratio of over 80 groundwater samples were measured along the Indian coast during the dry period, spanning a wide range of climates (semi-arid to tropical wet) and aquifer lithologies (crystalline granite, basalt and alluvium). Coastal groundwater exhibits an average δ^{30}Si of 0.85±1.1‰ (-1.1 to 4.5‰) and Ge/Si ratio of 1.3±1.0 µmol/mol, indicating significant spatial variability. We observed no relationship with regional rainfall or lithology. The δ^{30}Si generally followed a mix between Rayleigh and steady-state behaviour with a fractionation factor between -0.5 and -2‰, predominantly controlled by the formation of secondary clay minerals in the soil and saprolite. The exceptionally high δ^{30}Si, greater than 2‰ in groundwaters was indicative of unidirectional kinetic uptake, typically following a Rayleigh system. Some groundwaters also exhibited δ^{30}Si lighter than the upper continental crust (UCC) composition, indicative of the dissolution of secondary lighter Si bearing sources such as clays and oxyhydroxides. The average δ^{30}Si signatures of groundwaters were significantly lower than the riverine δ^{30}Si compilation from India (1.5±0.6‰, n=154). The lower δ^{30}Si compared to the surface waters and a steady state behaviour suggests a dynamic equilibrium between Si supply and formation of secondary phases, aided by the long residence time of water aquifer systems. We estimate fresh submarine groundwater discharge (SGD) Si flux along the Indian coast to be 2.9 GmolSi/yr, which is <1% of the riverine Si flux to the North Indian ocean and <2% of the global fresh groundwater Si flux to the ocean [1]. The isotopic effect of Si flux to the Indian coast is <0.3‰ and imparts no significant effect on the Si isotope budget to the North Indian ocean. Extrapolated Ge flux through fresh SGD to the global ocean can be significant in oceanic Ge cycling and can contribute up to 5 to 10% of the global riverine Ge input to the ocean.

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