Precise determination of Sc in natural waters by INAA coupled with preconcentration of Sc

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Sc is located above Y and lanthnides in periodic table. Since the classical reports by Spencer et al. (1970) and Brewer et al. (1972), to our best knowledge, almost no published literature has been available on the seawater concentration of Sc. This is very contrasting with the situation of Y and lanthanides, which have been reported numbers of concentration data on seawaters from various regions. We tackled to develope an accurate as well as precise method for determining trace Sc (45 Sc) in natural water using instrumental neutron activation analysis (INAA) employing a radionuclide 47 Sc (half-life = 3.35day) as a yield tracer for the preconcentration of Sc. We measured several seawaters and rainwaters using this newly developed method.

Carrier-free ⁴⁷Sc was prepared from a calcium carbonate reagent. After a purification of the calcium carbonate, it was irradiated at a neutron reactor. During cooling time of 5 to 6 days, the produced ⁴⁷Ca was decayed to ⁴⁷Sc. Then, the irradiated calcium carbonate was dissolved in 2M HCl. The ⁴⁷Sc produced was purified by iron coprecipitation method and was further added to natural water samples. Again, iron coprecipitation method was applied for Sc preconcentration. Recovery of the preconcentration was determined by measuring the radioactivity of ⁴⁷Sc by γ -ray spectrometry. After complete decay of the radioactivity of ⁴⁷Sc, the samples were irradiated at the neutron reactor to produce ⁴⁶Sc by a reaction of ⁴⁵Sc(n, γ) ⁴⁶Sc. The abundance of ⁴⁵Sc was determined by measuring the radioactivity of ⁴⁶Sc by γ -ray spectrometry.

Unfiltered surface seawater collected from the Kuroshio region $(35^{\circ}27'N, 142^{\circ}20'E)$ was 0.28 ± 0.04 ng/kg. This value is slightly higher than the datum on a surface sample from the Northeast Pacific reported by Spencer et al. (1970). The difference may be due to the difference in amount of mineral aerosol supplied to both areas. The concentration of rainwater sample collected on rooftop of the building of Tokyo Metropolitan University was 2.67 ± 0.05 ng/kg, which was about ten times higher than that of the seawater sample.

The sulfur isotopic composition of seawater from marine barite during the Paleocene Eocene Thermal Maximum (~55 Ma)

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The sulfur (S) isotopic composition of seawater sulfate rises from a minimum value of 17‰ at ~55 Ma, about the time of the Paleocene Eocene Thermal Maximum (PETM), to a value of ~22‰ eight million years after (~47Ma) (Paytan et al., 1998). Such a rapid shift in the marine sulfur isotope ratio suggests a major change in operation of this and related global biogeochemical cycles. The exact causes for this perturbation are not fully understood. It is not known whether or not this shift was related in any way to the short-term carbon (C) cycle perturbation associated with the PETM. To better understand the exact timing, sequence of events, causes for, and consequences of this shift, we are generating a high stratigraphic resolution (~1 sample per ~10,000 years) seawater S isotope curve using marine barite before, during, and immediately after the PETM using samples from the Pacific (Ocean Drilling Program [ODP] Leg 199 Sites 1220 and 1221) and Atlantic (ODP Leg 208 Sites 1262 and 1263) Oceans. We are comparing this S isotope curve to previously reported C isotope ratios and to barite mass accumulation rates, a marine productivity indicator. Seawater sulfur isotopic values in marine barite samples from the PETM section for ODP Leg 199 Site 1221 yield values of ~17 ‰, reflecting the global marine sulfur isotopic value, and confirming that the marine barite formed in equilibrium with sulfate in contemporanous seawater. These preliminary values indicate that minimum sulfur isotopic values occurred before the C isotopic excursion associated with the PETM. This timing is important for interpreting the relationship between the S isotope shift and the PETM.

Reference

Paytan, A., M. Kastner, D. Campbell and M.H. Thiemens (1998) Sulfur isotope composition of Cenozoic seawater sulfate, *Science*, 282, 1459-1462.