1.2.38

Helium-3 plume at 25°S on the East Pacific Rise

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Helium isotope data have been used to study the circulation of various water masses [1] and to detect active vents of mantle derived helium on the ocean floor [2]. For the deep south Pacific Ocean, an extensive plume of water enriched in helium-3, up to 50% relative to the atmospheric helium (${}^{3}\text{He}/{}^{4}\text{He}=1.39 \times 10^{-6}$:R_{atm}) was discovered at latitude 15°S on the East Pacific Rise [3]. The plume was absent east of rise, but it can be traced over 2000 kilometers to the west.

In order to clarify the westward helium-3 plume on the East Pacific Rise, we have collected 63 seawater samples at seven stations (longitude 85.8° W, 101° W, 108° W, 112° W, 114° W, 116° W, 118° W, 120° W, 127.8° W, and 140° W) along latitude about 25° S with various depths ($500m \sim 4000m$) on the KH03-1 cruise of the Research Vessel, Hakuho Maru of the University of Tokyo.

The ³He/⁴He ratios were measured on a conventional noble gas mass spectrometer (VG5400) after extraction, purification and separation using Ti getters and cryogenic charcoal traps. The observed ³He/⁴He ratios were calibrated against atmospheric helium. Experimental details were given elsewhere [4].

The ³He/⁴He ratios vary significantly from 1.020 R_{atm} to 1.475 R_{atm}. The maximum excess ³He of 47.5% is observed just on the East Pacific Rise, which is comparable with that of 50.5% at 15°S reported by Lupton and Craig [3]. Contour of excess ³He shows symmetrical pattern, that is, plume of 30% excess which can be traced up to 1500 kilometers on both east and west of the East Pacific Rise. This suggests that the deep seawater is stagnant across the rise at 25°S, which is significantly different from the westward migrating plume discovered at 15°S.

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1.2.41

Boron isotopic fractionations in high P-T aqueous fluids from *in situ* vibrational spectroscopic data

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During the last decade, boron isotopic composition ($\delta^{11}B$) of carbonate minerals has been used to reconstruct the paleopH of seawater [1,2]. This approach is based on the isotope exchange reaction between boric acid molecules B(OH)₃ and borate ions B(OH)₄⁻: ¹⁰B(OH)₃ + ¹¹B(OH)₄⁻ \leftrightarrow ¹¹B(OH)₃ + ¹⁰B(OH)₄⁻ [Eq.(1)]. Therefore, accurate determination of the isotopic fractionation coefficient ($\alpha_{3/4}$) for the above reaction is required to establish the relationship between B isotopes and pH. Moreover, B isotopic fractionations in high P-T fluids are essential data to determine fluid-mineral exchange during magmatic processus.

In order to refine and extrapolate to subduction zone conditions previous calculations of this fractionation factor by Kakihana et Kotaka [3], we have performed Raman and infrared spectroscopic measurements on aqueous solutions at various pH (3 and 12), pressures up to 3 GPa and temperatures up to 100°C. Most of the required vibrational frequencies for vibrational modelling could be observed and followed at high P and T. Unobserved values were determined using empirical force field model. Calculations of $\alpha_{3/4}(P,T)$ up to 10 GPa and 2000 K were performed using reduced partition function ratios Urey [4].

The isotopic fractionation factor obtained at 300 K, $\alpha_{3/4} = 1.0176(2)$, is slightly lower that the earlier value of 1.0194 proposed by generally accepted value of Kakihana et Kotaka [3]. The effect of P is shown to be negligible with respect to that of T and pH or speciation.

Implications for the interpretation of boron isotopic compositions in minerals are discussed

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