

Investigating clay mineral surface reactivity across scales using solid-state nuclear magnetic resonance

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Understanding environmental weathering reactions requires the determination of aluminosilicate dissolution and precipitation rates. Layered aluminosilicates such as clay minerals preferentially react on their edge sites compared to their basal planes. Therefore, a method to quantify reactive surface sites rather than specific surface area with the Brunauer-Emmett-Teller adsorption isotherm (B.E.T.) is needed to predict clay mineral dissolution rates. Solid-state nuclear magnetic resonance (NMR) spectroscopy has been utilized to investigate reactive hydroxyl species and their relation to clay surface reactivity and structure. Two kaolinite (KGa-1b and KGa-2) and two montmorillonite (STx-1b and SWy-2) samples were treated with the probe molecule (3,3,3-trifluoropropyl)dimethylchlorosilane (TFS), which binds selectively to reactive lone Q³ Si hydroxyl sites. Quantification of ¹⁹F spins in the TFS-treated samples from ¹⁹F magic angle spinning (MAS) NMR peak intensities provides a sensitive measure of the number of reactive hydroxyl sites per gram of clay, which we posit is proportional to the reactive surface area of each clay mineral.

Batch dissolution experiments of KGa-1b at 21°C and pH 2.9 have been conducted. Analysis of the remaining solids after various dissolution times indicated no change (within error) for B.E.T. specific surface area measurements. However, TFS-treatment of the same solids revealed a continual decrease in the number of reactive surface sites per gram of KGa-1b as a function of dissolution time. This observation can be tied to a concomitant decrease in the rates of release of ions into solution.

Our solid-state NMR proxy for reactive surface area is being applied to the study of mineral transformations at the Shale Hills catchment, a Critical Zone Observatory located in central Pennsylvania, USA. Quantification of number of reactive sites per gram of soil at various Shale Hills locations will help to model short-term weathering rates in the catchment.

Distribution of ³He plume and deep-sea circulation in the northwestern Pacific Ocean

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Introduction

Helium isotope data have been used to study the circulation of various water masses using the mantle derived helium [1]. In order to clarify the origin of helium and deep-sea circulation in the northwestern Pacific Ocean and the Philippine Sea where helium-3 in seawater has been less densely observed, we have collected more than 100 seawater samples at 15 stations near the Japan Islands at various depths (200m ~ 5500m) on three cruises of the Research Vessel, Hakuho Maru. Observed ³He/⁴He data were compared with the data reported previously [2, 3] and WOCE data near Japan.

Analysis

The ³He/⁴He ratios were measured on a conventional noble gas mass spectrometer after extraction, purification and separation using Ti getters and cryogenic charcoal traps. The observed ³He/⁴He ratios were calibrated against atmospheric helium. The ⁴He/²⁰Ne ratios were measured by an on-line quadrupole mass spectrometer before cryogenic separation of He from Ne.

Results and Discussion

While homogeneous excess ³He of ~15% are observed at 1000-m and 4000-m depth in the whole region, the maximum excess ³He of ~20% are observed at 2000-3000 m depth in the southern region. Based on the lateral distribution of excess ³He at 2500-m depth, helium-3 plume originated from the East Pacific Rise may flow westward in the Pacific Ocean and arrive at the Philippine Sea through the south of the Mariana Arc. It does not seem to flow northward along the Mariana Arc.

In meridional helium transect along 128°E line in the Philippine Sea, the helium-3 plume flows to the Japan Islands, although it does not reach the Japanese Islands along 137°E line, which may suggest a clockwise flow pattern of deep-seawater at 2500-m depth in the Philippine Sea.

[1] Lupton (1998) *JGR* **103**, 15853-15868. [2] Sano *et al.* (2004) *J. Oceanog.* **60**, 625-630. [3] Takahata *et al.* (2004) *Geochem. J.* **38**, 593-600.