

Geochemical clues for seafloor and subsurface gas hydrate linkage in Cascadia, Canada

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Background and objectives

A number of vertical blanking zones of a few hundreds meters in diameter have been revealed by high-resolution seismic surveys in Cascadia margin, off Vancouver. Massive gas hydrate have been also observed on the seafloor in the center of the blanking zones. PGC (Pacific Geoscience Centre) 02-08 cruise was carried out in September to October 2002 for the DTAGS (Deep-Towed Acoustic/Geophysics System) survey and piston coring to investigate the nature and the relation of the vertical blanking zones and fluid migrations. We focus on geochemical analysis of interstitial waters to characterize the relations between the fluid flow regime and processes influencing the distribution, structure, formation and dissociation of gas hydrate. A total of 12 piston cores and 3 grab samples were collected for interstitial water extraction.

Results and discussions

The SMI (Sulfate Methane Interface) depths in the area where gas hydrates occur on the seafloor are 1-3 mbsf (meters below seafloor). These depths are shallower than those of blanking area without hydrate (3-4 mbsf) and outside the blanking area (4-6 mbsf). This says that the methane flux is highest in gas hydrate bearing seafloor in the center of blanking zone. δD values in blanking area without gas hydrate are a little lighter (-0.5 ‰) than those of the referential sites outside the blanking area (0 ‰), suggesting that the upward migrating fluids were progressively depleted in deuterium as a result of gas hydrate formation within a blanking zone. To the contrary, δD values in gas hydrate bearing sediments are a little heavier (0.2-0.5 ‰). This is explained as the results of dissociation of gas hydrate during core recovery and handling. $\delta^{18}O$ values didn't show any significant variation in these area, probably because ^{18}O fractionation during gas hydrate formation was too small to be detected. In conclusion, (1) columnar blanking zones reflect upward migration of fluid, (2) subsurface gas hydrates were precipitated from the upward-migration fluids, causing significant depletion in deuterium of the interstitial waters, and (3) seafloor gas hydrates were formed by the residual waters.

Lithium isotopes in the solid Earth

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Lithium isotope data have become sufficiently abundant to begin to constrain certain global scale processes, as well as to elucidate areas where further work is needed. It is clear that: (1) the upper asthenospheric mantle is homogeneous globally, with $\delta^7Li = +4.7 \pm 1.7\%$ for normal to depleted MORB; (2) during subduction, material entering the mantle loses a component that is enriched in heavy Li; (3) despite this mass transfer, most subduction zone lavas show either no or minimal imprint of subduction-derived heavy Li; (4) components remaining after subduction zone metamorphism appear to be substantially isotopically lighter than their protoliths, such that crust recycled back into the mantle will be isotopically fractionated; (5) to the extent that they have been investigated, lavas derived at least in part from deeper asthenospheric sources show no extreme signature of isotopically fractionated Li.

So then, where might clues to isotopic variations in the mantle be identified? More detailed studies of OIB lavas are needed in order to resolve whether recycled crustal materials survive subduction and mantle convection. Xenoliths from the suprasubduction mantle may clarify the nature of Li mass transport in convergent margins. This process through time can be examined with xenoliths originating in the continental lithosphere. Outside of xenolith studies, temporal Li isotope variability in the mantle is obstructed by the potential for post-crystallization alteration of systematics in old lavas, although rare examples with pristine minerals exist, and are obvious targets.

The bulk Earth system is not yet clearly defined in terms of Li isotopes. To make an accurate terrestrial accounting of Li requires both a clearer approximation of the δ^7Li of the mantle, and, more importantly, a more accurate estimate for the continental crust. Although the upper crust is becoming better understood, vast reaches of the middle/lower crust are virtually untouched. The δ^7Li of continental rocks with complex metamorphic histories are unknown. The observation of light ($\delta^7Li < MORB$) isotopic signatures in lower crustal xenoliths spurs speculation of at least local predominance of light Li in the bowels of the continents.

On a practical note, the separation of Li from geochemical matrices appears to be the outstanding limiting component in the capacity to derive truly exceptional long term reproducibility (i.e., sub-1‰, 2σ), regardless of the mode of ratio determination. It is crucial that all groups engaged in this research recognize the potential for laboratory-induced isotope fractionation and vigilantly address these problems. This is likely best achieved through frequent recalibration of ion exchange media and consistent processing of replicates and other isotopic "knowns."