

## Leakage behavior of gases to bottom water through sediment layers with gas-hydrate stable conditions

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The water under the main thermocline in the Japan Sea is a single water mass referred to as the Japan Sea Proper Water (JSPW). It can be defined as having temperature below 2.0°C, salinity above 34.0. It is known that wintertime air-sea interaction in the Japan Sea, enhanced by outbreaks of dry and cold air masses from the Eurasian continent, generates the JSPS characteristic water mass through deep convection.

Below 10 °C, carbon dioxide hydrate is stable over the pressure of 4.4 MPa. In the Japanese archipelago side of the Japan Sea basin, the area with a water depth from 200 m to 1000 m is several tens thousand square kilometers, which is attractive for the CO<sub>2</sub> storage in the sub-seabed geological formations with at least 10<sup>11</sup> tons of CO<sub>2</sub> storage capacity; in the process of upward migration, the leaked CO<sub>2</sub> would have much chance of hydrate formation reaction *in situ*.

While the most famous natural analog is the CO<sub>2</sub> seepage in mid-Okinawa Trough backarc basin found by Sakai *et al.* [1], the recently-found seafloor methane hydrate outcrops occurring on the top of the CH<sub>4</sub> plume in the sediment layers [2] also provides an insight into the leakage mechanism for liquid CO<sub>2</sub>.

Gaseous CH<sub>4</sub> plume will be self-sustaining by its dry-out effect in the sediment and be hence developing its size as large as of several hundred meters in diameter [2], which would enhance the mixing of gas with the ambient water to make hydrate crystal growing effectively. The key is the low density of CH<sub>4</sub> hydrate (less than 1.0) that brings about buoyant behavior of the hydrate solid out of the bottom sediment into the overlying water column in the long run. On the contrary, liquid CO<sub>2</sub> might not make a gaseous plume due to its higher solubility in water and small upward migration driving force. The upward migration path could be like a dispersed mesh network in shape, partly due to the increased density of the interstitial water in contact with liquid CO<sub>2</sub> (*i.e.*, partial molar volume of CO<sub>2</sub> gas in aqueous solution is *ca.* 32cm<sup>3</sup>/mol). Self sealing of the leaked CO<sub>2</sub> *in situ* is probably effective, if there exist no fractures or conduits in the sediment layers.

[1] Sakai *et al.* (1990) *Science* **248**, 1093-1096. [2] Matsumoto (2013) personal communication.

## The spatial distribution of chalcophile elements in terrestrial and marine areas of Japan

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The Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology, has conducted research on the spatial distribution of 51 elements (Geochemical Maps) both in terrestrial and marine environments [1]. Japan is surrounded by vast sea, so it is important to know the spatial distribution patterns of elemental concentrations comprehensively in land and sea. This project is intended: 1) to elucidate background of elemental abundance in terrestrial and marine areas; 2) to find mass transport from land to sea or in marine environment; and 3) to estimate diffusion processes of pollutants.

Chalcophile elements such as Cu, Zn, As, Cd, Sb, Hg, and Pb are highly enriched in stream sediments associated with metalliferous deposits and anthropogenic activity. However, coastal seas sediments that were supplied by rivers flowing through metalliferous province are not significantly enriched in these elements. We assumed that the sulfide ores are oxidized, consequently releasing heavy elements in river water during transportation. However, Zn and Pb are exception. The high concentration areas of these elements are found both in terrestrial area associated with metalliferous deposits and the adjacent coastal sea area. It is possible that aqueous Zn and Pb released through oxidation process of sulfide are derived to coastal seas and sorbed on the sediment surface.

The influence of anthropogenic activity on geochemical maps is different from the case of metalliferous deposit. The concentrations of chalcophile elements are elevated in both the metropolitan area and adjacent inner bay. Chalcophile elements are enriched in the inner bay but poor in the outer bay. The spatial distributions suggest that the contaminated materials remain in the bay without extending to the outer sea. It is probable that the estuarine circulation prevents fine particles associated with chalcophile elements from reaching the outer sea because it flows from the outer sea to the bays.

[1] Imai, N. *et al.* (2010) Elemental distribution in Japan – Geochemical map of Japan. GSJ, AIST.

[2] Ohta, A. and Imai, N. (2011) *Advanced Topics in Mass Transfer*. (Mohamed El-Amin, ed.), pp. 373-398, InTech.