

Geochemical studies of the submarine ground water discharge by using methane concentration and its carbon isotope ratio as a tracer; Toyama Bay, Japan

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Submarine groundwater discharge (SGD) in the coastal area plays an important role in hydrologic cycles between the land and the ocean. Besides, SGD supply chemical materials such as nutrient and organic carbons to the ocean, so that it could be also important for discussing geochemical cycles. We have to estimate the amount of SGD, and to elucidate its origin and chemical changes during the flowing process at strata. However, the number of studies concerning to the behavior of the hydrocarbon in SGD are limited. We present here a geochemical study on the SGD in the Toyama Bay, northwestern coast of Japan, using the distribution of CH₄ and its carbon isotope ratio as a tracer. We took SGD samples from depths of 8 m to 33 m. Besides, we also took ambient seawaters, land groundwaters and river waters in the coastal area of alluvial fans of the Kurobe River and Katagai River.

We found that the whole SGD fluids and many of land groundwaters collected in this study contain less methane than natural water in equilibrium with the atmospheric CH₄ (0.5-2.5 nmol kg⁻¹). The δ¹³C values CH₄ range from -50 to -20 ‰, almost comparable or slightly higher than that of the atmospheric CH₄. High CH₄ content (>50 nmol kg⁻¹) together with low δ¹³C values (-95 to -80 ‰) were observed for groundwater samples take from a deep aquifer or distant aquifer from the Katagai river, where CH₄ may have been formed by microbial activities under the anaerobic environment of the aquifer. The results suggest that most of methane in SGD fluids derived from atmosphere and a part of the CH₄ is oxidized in the course of groundwater flow through the aquifer. Generally, deep sea seeping groundwater is highly anoxic so that contents of methane are extremely higher than that in equilibrium with the atmospheric CH₄. The SGD fluids, however, are still oxic in the discharging area. The relatively short residence time until discharge might be responsible for the difference. By using CH₄ and their δ¹³C values as a tracer, we can confirm that the CH₄-enriched, anoxic groundwater of deep aquifers and/or distant aquifers from the Katagai river don't contribute in the SGD fluids in this area, so that the SGD fluid must have been flowing from the underground along the river of Katagai River alluvial fan.

Multicollector dynamic measurement of cerium isotopic composition by a thermal ionization mass spectrometer

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Precise measurement of Cerium isotopic composition is essential for the La-Ce dating of geological materials and for the use as a geochemical tracer (e.g. Tanaka & Masuda, 1982). Most of the published cerium isotopic data are by single collector or multicollector static measurement. The former needs very stable ion beam lasting for a long time, and the latter needs the appropriate correction of various factors of each detector and their stability. As for multi-dynamic measurement, the factors of individual collectors are cancelled out by peak jumping giving more reliable data compared to static method. Also measuring time is much shorter than that of single collector measurement.

In this work, nine-collector dynamic method is developed using a thermal ionization mass spectrometer VG SECTOR54. High purity cerium oxide reagent JMC304 from Johnson Matthey Chemicals Co. is used to test the reliability of this method. Table 1 shows the collector configuration and the sequence for the measurement.

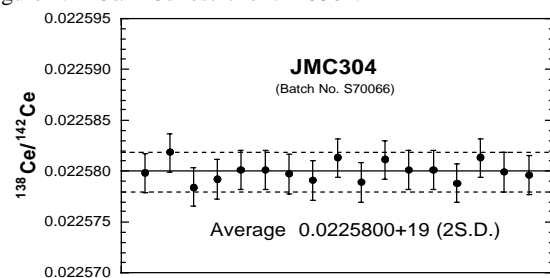
Table 1: Collector configuration.

	L4	L3	L2	L1	Ax	H1	H2	H3	H4
Base	149.5	150.5	155.5	153.5	154.5	155.5	156.5	157.5	158.5
1	149	150	152	153	154	155	156	157	158
2	151	152	154	155	156	157	158	159	160

Cerium mono oxide ion beams are measured at the intensity of 1x 10⁻¹¹ A for ¹⁴²CeO⁺. Oxygen gas is leaked into the ion source chamber to get stable oxide ion beam. Measuring time for 250 ratios is about 2.5 hours.

Isotopic data are normalized to ¹³⁶Ce/¹⁴²Ce = 0.01688 using the exponential law. Isobaric interferences by Ce¹⁷O, Ce¹⁸O, ¹³⁸LaO, ¹⁴¹PrO and ¹⁴²NdO are also corrected. The result for JMC304 is shown in Figure 1. The figure reveals that this method gives stable and reliable cerium isotopic data.

Figure 1: ¹³⁸Ce/¹⁴²Ce result for JMC304.



References

Tanaka and Masuda, (1982), Nature 300, 515-518.