

Effect of Dissolved Ions on $\delta^{18}\text{O}$ Measurement of Saline Aqueous Solutions: Experimental Results

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The oxygen isotope ratios of aqueous solutions have been typically determined by either “the classic $\text{CO}_2\text{-H}_2\text{O}$ equilibration method” or a quantitative conversion of H_2O to a gas (e.g., CO , CO_2 , or O_2), followed by an isotopic analysis of the gas on an isotope ratio mass spectrometer (IRMS). However, many stable isotope laboratories use the classic $\text{CO}_2\text{-H}_2\text{O}$ equilibration technique for their routine $\delta^{18}\text{O}$ analysis of aqueous solution samples due to its analytical simplicity. In recent years, the classic $\text{CO}_2\text{-H}_2\text{O}$ equilibration method has gained more popularity because of the introduction of an automated on-line $\text{CO}_2\text{-H}_2\text{O}$ equilibration system coupled to a continuous-flow isotope-ratio mass spectrometer (CF-IRMS). This relatively new but innovative CF-IRMS technique requires a considerably smaller amount of aqueous solutions, compared to the conventional off-line or on-line $\text{CO}_2\text{-H}_2\text{O}$ equilibration technique for a dual-inlet isotope ratio mass spectrometer (DI-IRMS).

Whatever the type of preparation technique or the stable isotope ratio mass spectrometry, the kinetics of oxygen isotope exchange for a given $\text{CO}_2\text{-H}_2\text{O}$ system have to be carefully evaluated in order to accurately determine the oxygen isotope ratio of the corresponding aqueous solution when the classic $\text{CO}_2\text{-H}_2\text{O}$ equilibration method is employed. This is because oxygen isotope exchange kinetics in the $\text{CO}_2\text{-H}_2\text{O}$ system for a high ionic strength solution (e.g., hydrothermal brines) are not the same as that for a low ionic strength solution (e.g., freshwater) [1, 2]. Guidelines for the $\delta^{18}\text{O}$ analysis of high ionic strength solutions of geological importance will be presented at the meeting based on the experimentally determined results of oxygen isotope exchange kinetics and equilibrium isotope effects in various $\text{CO}_2\text{-high}$ ionic strength solution systems, such as $\text{CO}_2\text{-a}$ 1.0 molal solution of Na_2SO_4 .

[1] Fortier (1994) *Chem. Geol.* **116**, 115-162.

[2] Lécuyer *et al.* (2009) *Chem. Geol.* **264**, 122-126.

Lithium isotopic signature Oman ophiolite during hydrothermal alteration of the ancient oceanic crust

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Oman ophiolites are regarded as a fossil oceanic crust which was hydrothermally altered by seawater-derived fluid [1]. Li isotopes can be utilized for tracing hydrothermal alteration because of their large isotopic fractionation at low-to-medium temperature between rock and fluid phase [2]. Here, we determined the Li abundances and isotopic compositions of the ophiolites from the Wadi Fizh section in Oman with multi-collector ICP-MS, IsoProbe in the University of Tokyo and Neptune in JAMSTEC. The precisions of $\delta^7\text{Li}$ measured by IsoProbe and Neptune are ± 0.7 and 0.3 ‰ (2σ), respectively.

The Li abundances vary from 0.1 to 8.0 ppm, and decrease with depth. The $\delta^7\text{Li}$ values of the Wadi Fizh section represent a variation ranging from +2.9 to +23.5‰, which is heavier than those of normal MORB. The samples deeper than 2 km also show heavy Li-isotopic signatures, different from drill hole samples of the ODP sites 504B and 896A in the present oceanic crust [3]. There is no distinct correlation between the $\delta^7\text{Li}$ values and depth. The sheeted dike and dolerite dike samples near the boundary between the sheeted dike and gabbro layer have heavy $\delta^7\text{Li}$ values up to ca. +23‰. These large variations in the $\delta^7\text{Li}$ values are likely to result not only from temperature variation, but from changes in the Li composition of hydrothermal fluid and water/rock ratios.

The Li compositions of initial hydrothermal fluid which altered the samples of ophiolites were calculated with changing water/rock ratios, and show deviation from the reaction array between seawater and fresh MORB. This suggests that the initial fluid of the Wadi Fizh section has evolved via other pathway than the simple interaction array between seawater and fresh MORB. The range of inferred initial fluid is similar in the Li compositions with pore fluids in high-temperature diagenetic environment and marine brines [4, 5]. It is suggestive that the Li composition of initial hydrothermal fluid in the Wadi Fizh section is modified by another process by the interaction between original seawater-derived fluid and sediment or secondary mineral at the surface level of the oceanic crust.

[1] Kawahata *et al.* (2001) *Jour. Geophys. Res.* **106**, 11083-11099.

[2] Seyfried *et al.* (1998) *GCA* **62**, 949-960. [3] Chan *et al.* (2002) *EPSL* **202**, 187-201. [4] Chan and Kastner (2000) *EPSL* **183**, 275-290. [5] Chan *et al.* (2002) *GCA* **66**, 615-623.