

## 特別講演 2

## Isotope Fractionation of Water Under Pressure, Positive and Negative

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In our water planet Earth, the exogenic and endogenic water cycles in the atmosphere, on the surface, and within the interiors, including the crust and perhaps the mantle, have been shaping and transforming our planet since its birth. In the application of stable isotope tracers (<sup>1</sup>H, <sup>2</sup>H, <sup>16</sup>O, <sup>17</sup>O, and <sup>18</sup>O) of water to these Earth processes over the last several decades, isotope fractionation associated with the phase transition among the three bulk phases (vapor, liquid, and ice) has exclusively been considered, particularly in the exogenic hydrologic cycle of evaporation, condensation, and precipitation. In the endogenic water cycle within the Earth interior, water has been treated either simple liquid or supercritical fluid similar to vapor. However, an increasing number of experimental and theoretical studies in the past two decades or so have demonstrated that under deep Earth conditions, the effect of high pressure is not insignificant on the reduced partition function ratio ( $\beta$ -factor) of vapor, liquid, and supercritical waters. With increasing pressure (and water density) to the range of GPa, the  $\beta$ -factors for D/H decrease by 20-30 ‰ or more and those for <sup>18</sup>O/<sup>16</sup>O may increase by 2-3 ‰. Recently, it was found that the effect of negative pressure on water down to ~ - 0.2 GPa, namely water adsorbed on the surface and confined within pores of earth materials, is significant, decreasing its  $\beta$ -factors from those of the bulk liquid water to more like water vapor with increasing negative pressure (matrix potential). Therefore, beyond the phase transitions, water under pressures, positive or negative, exhibits very unique isotopic behaviors, including its triple-oxygen isotope fractionation (<sup>18</sup>O/<sup>16</sup>O vs. <sup>17</sup>O/<sup>16</sup>O). These unique behaviors of water under pressure are relevant, not only to fundamental science, but also to the study of the water cycles on the surface and within the interior of the Earth, including soil waters in the vadose zone, and water and hydrous minerals carried by subduction slabs down deep into the mantle.