Analytical and experimental means for studying triple oxygen isotope variations in Earth surface materials

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A prerequisite to studies of triple oxygen isotope variations in Earth surface materials is means for measuring isotope ratios with extreme high precision and accuracy. The first target for such study was atmospheric O₂ and it led to the discovery of deficiency of ¹⁷O in air O₂. This opened the way to projects on rates of photosynthesis in glacial and interglacial times in ice cores and all over the present ocean. Globally, photosynthetic O₂ is produced from water and the isotopic composition of air O₂ depends on that of the various water sources and hydrological processes affecting them. It is not surprising then, that the first indication of significant triple isotope effects in meteoric waters became evident in photosynthesis experiments aimed to explain the triple isotopic composition of atmospheric O2. In addition to expected variations along the global meteoric water line (GMWL), it became evident that evaporation results in significant deviations from the GMWL. This discovery motivated the development of improved fluorination method that permitted direct analysis of water. The improved method was utilized for measuring triple isotope fractionation between liquid water and its equilibrium vapor and showed that the triple isotope slope (0.529) was independent of temperature. This was followed by measurements of the isotope effects of vapor diffusion in air for which the triple isotope slope was 0.518. The difference between the equilibrium and diffusion slopes explains the ¹⁷O excess of meteoric water and marine vapor with respect to seawater. The potential demonstrated in the pioneering studies has led to initiation of further studies on triple isotope hydrology and encouraged the development of commercial user-friendly means for isotope ratio measurements.