

Variations in triple isotope fractionation exponents

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Introduction: High-precision analyses of triple isotope ratios of coexisting phases (minerals, fluids, gases) allow the identification of the isotope fractionation effect [1]. Not considering true mass-independent effects, only a few studies, made use of triple isotope relations [e.g., 2, 3, 4]. Understanding complex triple isotope fractionation networks [5-7] requires knowledge of θ for each fractionation process. We present the first experimental triple oxygen isotope equilibrium fractionation exponents θ including water, solids and gaseous CO₂. First data on Si isotopes will also be presented.

Technique: Isotope analyses of oxides, silicates and phosphates are conducted by means of IR-laser fluorination in combination with GC-CF-irmMS (Thermo MAT 253). The precision in $\Delta^{17}\text{O}$ varies between ± 0.02 and ± 0.04 ‰ for a single analysis [8]. We use NBS-28 quartz ($\Delta^{17}\text{O}_{\text{TFL}} \equiv 0$) and a rocks- and minerals-defined reference line (TFL) with a slope of $\lambda_{\text{TFL}} = 0.5251$ and zero intercept when reporting $\Delta^{17}\text{O}$. For CO₂ we apply a novel technique that includes equilibration with solid CeO₂ and subsequent analysis of CeO₂ by fluorination [8, 9] with an accuracy and precision of ± 0.03 ‰. For water, we have chosen literature data [e.g., 3, 4, 10] or had the water analyzed in the laboratory of A. Landais (Paris). Silicon isotopes have been measured on gaseous SiF₄ that was extracted by laser fluorination.

Results: We have experimentally determined the triple isotope fractionation factor $\theta = \ln(\alpha^{2/1}) / \ln(\alpha^{3/1})$ for oxygen for: (i) low-T oxygen isotope equilibrium fractionation between apatite and water with $\theta_{\text{apatite-water}} = 0.526 \pm 0.004$ (2σ) [6], (ii) low-T oxygen isotope equilibrium fractionation between CO₂ and water with $\theta_{\text{CO}_2\text{-water}} = 0.522 \pm 0.002$ (2σ , independent of T, $4 \leq T \leq 37$ °C [8]), (iii) low-T oxygen isotope equilibration between silica and water with $\theta_{\text{silica-water}} = 0.518 - 0.521$. For silicon, we present first data on biogenic silica.

Discussion: We show that θ varies for different equilibria and those variations in θ are not solely due to kinetic isotope effects. For three low-T processes (apatite-water, CO₂-water, silica-water), θ is considerably lower than the high-T approximation of 0.5294 [1]. For the rocks- and minerals-defined TFL, slopes of $0.524 \leq \lambda_{\text{TFL}} \leq 0.526$ were reported [11-14]. Our data show that variations in λ_{TFL} can solely explained by variations in θ . The understanding of triple isotope fractionation processes requires knowledge of θ 's not only for kinetic, but also for each equilibrium fractionation process involved. Implications for the usability of triple isotope ratios for the identification of e.g. diagenesis will be discussed.

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