



Improved Online Hydrogen Isotope Analysis of Halite Aqueous Inclusions: Insights into the Proterozoic water cycle

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The large range of stable oxygen isotope range values of for phosphate-bearing minerals and dissolved phosphate of both inorganic or organic origins requires the use of calibrated material of in-house made internal standards of silver phosphate of which isotopic ratios must closely bracket those of studied samples. Such calibrated materials do not exist yet in the various catalogs of stable isotope calibrated standards. Therefore, we propose a simple and cheap protocol to synthesize in house silver phosphate in with a predictable wide range ($\approx 40\%$ of oxygen isotope isotopic compositions). It is based on the equilibrium isotopic fractionation factor and the kinetics and temperature of isotopic exchange in the phosphate-water system. Silver phosphate crystals are obtained from a highly soluble salt such as KH_2PO_4 that is dissolved in water of known oxygen isotope composition. Isotopic exchange between dissolved phosphate and water takes place at a desired and constant temperature into Ace GlassTM pyrex tubes that are placed in a high precision temperature regulation oven for run-times defined by the user. Samples of dissolved phosphate are withdrawn at desired times, quenched in cold water, and quantitatively precipitated as silver phosphate. We propose an “Excel calculation sheet” that computes the oxygen isotope composition of the precipitated silver phosphate depending as a function of on time t (≤ 1 month), temperature T (recommended range from 110°C to 130°C with a precision of $\pm 0.5^\circ\text{C}$) and the oxygen isotope compositions of both reactants KH_2PO_4 and H_2O at $t = 0$. Predicted oxygen isotope compositions of synthesized silver phosphate range from -7 to $+31\%$ VSMOW for a temperature range comprised between 110°C and 130°C and a range of water $\delta^{18}\text{O}$ from -20 to $+15\%$ VSMOW. We present practical applications of this protocol comparing theoretical values with real measurements obtained from phosphate samples generated using this method.