High-precision triple oxygen isotope analysis of Archean and Proterozoic carbonates

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Oxygen isotopes are a widely used tracer in the field of paleoceanography and provide unique information on mineral formation and environmental conditions. Carbonate sediments record a shift in δ18O of 10 to 15‰ from the Archean towards higher values in the Phanerozoic. Three different scenarios are suggested to explain this observation: (I) hot Archean oceans, (II) depletion of 18O in Archean oceans compared to present day and (III) diagenetic alteration of the primary isotopic signature [1]. Recent advances in high-resolution gas source isotope ratio mass spectrometry provide a new tool that may allow to decipher the origin of this isotopic shift observed in the early rock record. We performed high-precision 18O/16O and 17O/16O measurements on oxygen ion fragments (16O+16O, 17O16O+) generated in the ion source from CO2 gas [2]. Isobaric interferences on m/z=17 (16OH+) and m/z=18 (H216O) are separated by means of high mass resolution. The CO2 gas is first liberated from carbonate samples by orthophosphoric acid digestion and then analyzed on a Thermo Scientific Ultra dual-inlet gas source isotope ratio mass spectrometer [3]. By adding the dimension of 17O/16O to the classical 18O/16O system, equilibrium trajectories of carbonates that are defined by the equilibrium fractionation factor (18Aeq) and the triple isotope fractionation exponent (θ) can be predicted as a function of temperature. Minerals that were altered by or formed in meteoric water can be distinguished from those that precipitated in equilibrium with ambient sea water. Therefore, triple oxygen isotope analysis of carbonates does not only hold the potential for a new single-phase paleothermometer, but may also be used to trace the origin of carbonates. Here, we present high-precision triple oxygen isotope data for carbonates from the Pilbara and the Kaapvaal cratons that cover nearly one billion years from the Paleoarchean to the Paleoproterozoic. Phanerozoic carbonates record equilibrium conditions with modern sea water at moderate temperatures. The majority of Precambrian carbonates plot below the predicted equilibrium curve in the δ18O-Δ17O space and do not reflect equilibrium conditions with modern
sea water at elevated temperatures that were proposed for the Archean oceans. Modeling the triple oxygen isotope composition of carbonates in equilibrium with sea water, that is depleted in $^{18}O$ also cannot explain the observed isotopic shift. Further modeling of post-depositional alteration suggests that most carbonates interacted and re-equilibrated with meteoric waters at variable water-rock ratios and temperatures.
