Geophysical Research Abstracts,
Vol. 11, EGU2009-10706, 2009
EGU General Assembly 2009

Tracing the oxygen triple isotopic composition of tropospheric molecular oxygen in biogenic apatite – a new tool for palaeoclimatology

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It has been demonstrated that tropospheric molecular oxygen posses a significant isotope anomaly [1, 2 and refs. therein]. Relative to the rocks- and minerals-defined terrestrial fractionation line (TFL), tropospheric O2 has an anomaly of –0.35‰ [2]. Because almost all oxygen on Earth is contained in rocks, we suggest that the rocks- and minerals-defined TFL [3] should be used as reference when reporting isotope anomalies with Δ17O = '17OSMOW – TFL '18OSMOW. We have developed a new technique for the determination of 17O and 18O of silicates by means of laser fluorination GC-CF-irmMS. We have determined TFL to 0.5247 (N > 100), which is identical to the value reported by other laboratories and techniques [2, 3]. The uncertainty in Δ17O is ±0.03 (1) for a single analysis. It was suggested that Δ17O of tropospheric O2 can be used as proxy for the global bioactivity rate [GBR, 1] as well as for past atmospheric CO2 concentrations [4]. Past Δ17O of tropospheric O2 can be determined by analyzing O2 trapped in ice [1, 5] or by analyzing sulfates from terrestrial sulphide oxidation [4]. Disadvantage of ice core data is the limitation in time back <1 Myrs. The sulfate approach is used to trace Δ17O of air O2 back to Proterozoic times. Disadvantage of this technique is the uncertainty in the proportion of oxygen from O2 and oxygen from ambient water during oxidation of the sulphides.
We suggest that oxygen from tooth and bone phosphate can be used as proxy for the Δ17O of air O2. Mass balance calculations [e.g. 6] suggest that a considerable portion of oxygen in biogenic apatite sources from respired air O2. We have analyzed tooth (enamel, dentine) and bone material by means of direct fluorination for their 17O and 18O. We have chosen material of mammals of different body mass (Mb) from Northern Germany (except Indian Elephant). The Δ17O of apatite varies between –0.16‰ for a wood mouse (Apodemus sylvaticus) and +0.04‰ for a wild boar (Sus scrofa). Samples were analyzed between 5 and 7 times in order to reduce the analytical uncertainty to ±0.012–0.025‰.
Our data confirm the prediction from mass balance that animals inherit a Δ17O signature from anomalous air O2. We have developed a detailed mass balance for mammals with respect to Δ17O. The mass balance considers the oxygen fluxes (drinking and food water, respired O2, metabolic water, excrements, evaporated water and exhaled CO2). The fractionation in 18O and Δ17O (from associated -value) was considered for each of the fluxes. The result is an allometric scaling model for Δ17O as function of log Mb. Predicted and measured data agree within the uncertainty of the model and the measurements, respectively. Small mammals with their high specific metabolic rate show the greatest portion of oxygen from air O2 in their body water and in their bones and teeth. With this approach, Δ17O of air O2 can be determined with an uncertainty in the range of 0.05–0.1‰. This is more precise than what can be obtained from analyses of terrigene sulfate. With well-preserved fossil material, it may be possible to determine Δ17O of air O2 beyond the time limit of ice core data. The high precision of our approach may allow identifying variations in Δ17O of air O2 between glacial and interglacial periods.
With mammal material, we will construct a Δ17O-profile of tropospheric O2 back to the Palaeogene. Using the same approach with reptile apatite, we expect to be able to extend the database beyond the Cretaceous/Palaeogene boundary.
Correct interpretation of Δ17O of biogenic apatite, however, requires knowledge of the metabolic parameters for the analyzed groups as well as the -values for all isotope fractionation processes involved.
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