Oxygen-17 anomalies generated by thermal decomposition of carbonates

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Since the initial discovery, nearly twenty years ago, that ozone formation from molecular oxygen is associated with anomalous enrichment of ^{17}O in the reaction product, ‘mass-independent’ oxygen isotopic compositions have been found in many constituents of the Earth’s atmosphere. In such cases, however, the isotopic anomaly is generally inherited by chemical reaction sequences, with the source being attributed to stratospheric ozone. UV-initiated photodissociation of CO_2 is another process by which anomalous ^{17}O distributions may be created. At *Goldschmidt X*, data were presented which indicate that, surprisingly, in vacuo pyrolysis of Ca±Mg carbonates also generates anomalous ^{17}O compositions in the residual solid oxides. The interpretation of that initial observation has since been substantiated by further experiments, including (crucially) confirmation that the released CO_2 is also characterised by anomalous ^{17}O composition, with the magnitude of the anomaly, Δ^{17}O, being half (and opposite in sign to) that found in the solid oxides. Use of high vacuum conditions is necessary to minimise back reaction (and thus isotopic exchange) between the reaction products.

Accurate quantification of Δ^{17}O values of this order is critically dependent on the slope of the attendant three-isotope fractionation line. High precision measurements have shown that, for a fractionation line of slope identical to that characteristic of terrestrial silicates and waters, derived using a non-approximated form of the mass-dependent relationship between δ^{17}O and δ^{18}O, the corresponding line for the residual solid oxides is offset by -0.241 ± 0.042‰ (95% confidence level), with the related CO_2 value being $+0.147 \pm 0.047$‰.

A further finding is that the slope of the fractionation line is controlled by empirical factors relating to the thermolysis procedure. Slow, protracted decarbonation produces a notably shallower slope.

Extending the investigation to other carbonates (Pb, Ba, Sr, Zn, Fe and Mn), using natural terrestrial sources, shows that the magnitude of Δ^{17}O generated in the residual solid oxide ranges up to -0.4‰ and appears to be linked to the thermal stability of the carbonate. Of this group, only $BaCO_3$ (greatest thermal stability) generates essentially no anomaly.

We believe that this phenomenon is the first example of a mass-independent isotopic fractionation arising from thermal decomposition of a solid. Furthermore, no photochemical excitation or electrical discharge is required to initiate the effect. A satisfactory explanation of these findings poses new challenges to established theories of isotopic fractionation.

Hydrothermal clays as tracers of seafloor sulphide mound evolution

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Samples of Fe-oxide-rich hydrothermal sediments were collected from active and inactive portions of the TAG hydrothermal field on the Mid-Atlantic Ridge. Clay-rich Fe-oxyhydroxide deposits are common alteration products in both modern and ancient hydrothermal systems. Clays separated from metalliferous sediments in this study consist predominantly of Al-poor nontronite. Oxygen isotope thermometry of the clays yields formation temperatures of 54-67°C for samples from the currently inactive Alvin zone compared to 81-96°C for samples from the active TAG mound. Sr –isotopic analysis of the clays from the active mound (^{87}Sr/^{86}Sr = 0.70859) suggests that they were formed from seawater dominated fluids, containing less than 15% hydrothermal end-member fluid. Nontronite form the Alvin mound in contrast has an average ^{87}Sr/^{86}Sr value of 0.72210, which closely resembles that of typical North Atlantic clays (^{87}Sr/^{86}Sr = 0.72285), suggesting a detrital source for the Sr in the clays from the inactive site. Rare earth element analysis indicates that the clay minerals at both sites formed in close proximity to high temperature hydrothermal venting and during subsequent lower temperature alteration of the sediments. Crystallographic fractionation of the trivalent REEs is apparent in the heavy REE enrichments of the nontronite. REE patterns of the clay separates from the active mound reveal patterns that are most consistent with formation from solutions that were dominated by hydrothermal signature, whereas some overprinting by a pelagic source is apparent in the clays from the inactive site. The proposed model of formation for the nontronite-rich Fe-oxyhydroxide deposits at the surface of the active mound is precipitation directly from diffuse fluids. At the inactive Alvin site, in contrast the clays formed during alteration of carbonate-rich sediments of pelagic origin by acidic low temperature fluids. This has lead to complete re-mineralisation of pelagic clays, removal of the carbonate and replacement with authigenic nontronite and Fe-oxyhydroxide. The formation of clay minerals may have a significant influence on the permeability of the hydrothermal deposit in this and other settings. They may thus play a role in defining the circulation of fluids in hydrothermal mounds, with implications for element distribution and preservation of such deposits.