

A New Source of Mass Independent Fractionation of Oxygen Isotopes: Evidence and Geochemical Implications

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Although of major application to the study of extraterrestrial materials, following the discovery (Clayton et al., 1973) that primordial oxygen isotopic heterogeneities from the early solar system are preserved in primitive meteorites, little use has hitherto been made of $\delta^{17}\text{O}$ measurements in terrestrial geochemistry. This is largely because the long-established theoretical basis of the quantitative effects of isotopic substitution (Urey, 1947) predicts that the $^{17}\text{O}/^{16}\text{O}$ fractionation factor (α^{17}) relative to the attendant $^{18}\text{O}/^{16}\text{O}$ value (α^{18}) depends only on the respective masses of the isotopomers, and is described by $\alpha^{17} = (\alpha^{18})\lambda$, where λ takes a value of close to 0.52 (Li and Meijer, 1998). Recent, as yet unpublished, data by our laboratory give a value of 0.52466 ± 0.00036 (std. error) for λ . On this basis, it is to be expected that no additional, independent information may be procured by measurement of $\delta^{17}\text{O}$ rather than $\delta^{18}\text{O}$ isotopic compositions. The greater natural abundance of ^{18}O , by a factor of ~ 5.3 relative to ^{17}O , together with the simpler and well-established experimental procedures for $\delta^{18}\text{O}$ measurements, have also served to favour the use of ^{18}O , rather than ^{17}O , to investigate oxygen isotopic fractionations associated with terrestrial processes.

The discovery during the past two decades, however (reviewed by Thiemens, 1999), of isotope effects which do not conform to mass dependent fractionation, has presented a considerable challenge to the theoretical framework that describes the principles of stable isotope distributions and which successfully underpins a diversity of applications to terrestrial geochemistry. The earliest discovery of a chemical process associated with mass independent isotopic fractionation was that approximately equal enrichments of ^{17}O and ^{18}O are associated with ozone formation from molecular oxygen (Thiemens and Heidenreich, 1983). Seventeen years later, there is still no accepted explanation for the mechanism responsible. Molecular symmetry considerations were originally considered to play an important role, although recent experimental data on ozone formation by the photolysis of molecular oxygen (Mauersberger, 1999) cast doubt on this.

Mass independent oxygen isotopic compositions have been found in several components of the Earth's atmosphere, specifically O_3 , O_2 , CO_2 , CO , N_2O , H_2O_2 and sulphate aerosols. In most cases, the isotopic anomalies are linked to photochemical reactions; an example is the transfer, in the stratosphere, of ^{17}O and ^{18}O from molecular oxygen to CO_2 , via ozone. Apart from certain photochemical processes, however, there are few documented sources of mass independent isotopic fractionation (as distinct from chemical reactions which transfer an existing isotopic anomaly from one molecular entity to another). The production of ozone from molecular oxygen by electrical discharge or photolysis are examples of processes giving rise to mass independent fractionation; other reported examples are the electrolysis of water and salt hydration (Li and Meijer, 1998).

Evidence will be presented for the surprising discovery that mass independent isotopic fractionation appears also to be associated with some simple chemical processes of geochemical significance. The potential consequences of these findings will be discussed, both in terms of the reporting of oxygen isotope data and for the potential contribution of the new results towards progress in understanding the mechanisms which give rise to mass independent fractionation.

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