Geophysical Research Abstracts, Vol. 7, 03561, 2005
SRef-ID: 1607-7962/gra/EGU05-A-03561

The Use of ^{17}O and ^{18}O in Paleo Sulfate and Nitrates to Deduce Past Climate and Chemistry

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Single isotope ratios in paleo samples e.g. water has been used for decades to study temperature changes. With the discovery of the chemically produced mass independent isotope effect in 1983 by Thiemens, and subsequent atmospheric studies, it is now known that all oxygen bearing molecules in the earth's atmosphere possess mass independent isotopic compositions with the possible exception of water. Combined with theoretical and photochemical laboratory experiments, the mechanism by which these compositions are attained is now well understood. In the particular case of aerosol nitrate and sulfate, these highly specific isotopic signatures are particularly powerful. It has now been established that the mass independent isotopic composition is acquired from ozone and in part, hydrogen peroxide, both of which have been isotopically characterized by direct measurement. These measurements, in conjunction with laboratory photochemical and chemical kinetic models provides chemical transformation and transport information not attainable by single isotope ratio measurement or, in fact by any other measurement. These measurements in the present day atmosphere are capable of 1) quantifying the homogenous versus heterogeneous oxidative pathways and 2) the absolute percent contribution of ozone and hydrogen peroxide as oxidants. Such measures are of particular importance in defining long-range transport, chemical transformation, and radiative forcing in climate models.

Measurements of sulfate and nitrate in ice core samples are particularly powerful. Recent investigations have demonstrated how the oxidative capacity of the planet varies on time scales ranging from half yearly, to 100,000 year plus. This is particularly insightful given that there is no other quantitative measure of these changes. In addition,

the measurements of multi sulfur isotopes in sulfate aerosols in ice core samples have now shown the effect of large-scale volcanism on the Earth's atmosphere, in particular ozone. Various aspects of the role of mass independent oxygen isotopic compositions in ice core samples will be discussed.