Geophysical Research Abstracts
Vol. 14, EGU2012-4679, 2012
EGU General Assembly 2012

Non-mass dependent isotope fractionation in Ozone

F. Robert (1) and P. Reinhardt (2)

(1) LMCM, UMR-CNRS 7202 — Muséum National d'Histoire Naturelle Case 52, 61 rue Buffon, F — 75005 Paris, Francerance (robert@mnhn.fr), (2) Laboratoire de Chimie Théorique, Université Pierre et Marie Curie, 4 place Jussieu, F — 75252 Paris, France

In clear contradiction with the usual isotopic fractionation (1) a non mass dependent fractionation of oxygen isotopes was reported (2) in the refractory minerals of the carbonaceous chondrites. Although this effect seems ubiquitous in the first solids at the origin of solar system oxides, its origin is still in debate. Another non-mass dependent isotopic effect was then reported for the oxygen isotopic composition of ozone produced in the laboratory (3) as well as in the stratosphere (4-5). Numerous interpretations of this effect have been proposed but no consensus has been reached up to now (6-7).

The generally accepted theory is based on a modification of the standard RRKM model of unimolecular dissociation (8) where a parameter η is adjusted for taking into account mass-independent effects without further assumptions. If this parameter is propagated to all mass dependent isotopic fractionation factors between the different isotopomers of ozone, most observations are then reproduced numerically. The aim of the present work is to propose a possible origin for η.

We will show that the quantum mechanical principle according to which identical isotopes can be treated as indistinguishable particles, may be at the origin of the isotope effect. The scattering of $O + O_2 \rightarrow O_3^* \rightarrow O + O_2$ is modeled in a thermal gas with an activated complex O_3^* that is eventually stabilized in the form of ozone, depending on its lifetime. In order to illustrate the consequences of this principle, all calculations were performed in classical mechanics for ^{16}O i.e. by neglecting the differences in the masses of the different isotopes.

For a given lifetime range, the averaged lifetimes for complexes formed by reactions involving distinguishable (such as $^{16}O + {}^{m}O^{n}O$) or indistinguishable (such as $^{16}O + {}^{16}O^{16}O$) isotopes cannot be strictly equal. We then ascribe the non mass dependent isotopic fractionation factor η to the ratio of these lifetimes. The experimental data obtained for ozone are reproduced astonishingly well with this hypothesis.

Since this effect is not restricted to ozone or to oxygen isotopes, it could have played a role in several isotopic anomalies found in meteorites.

References: (1) E. D. Young, A. Galy, H Nagahara H, Geochim. Cosmochim. Acta, 66, 1095, (2002). (2) R.N. Clayton, L. Grossman,T.K. Mayeda, Science, 182, 485, (1973). (3) M.H. Thiemens, J.E. Heidenreich III, Science, 219, 1073, (1983). (4) K. Mauersberger, Geophys. Res. Lett., 8, 935, (1981). (5) D. Krankowsky, P. Lmmerzahl, K. Mauersberger, C. Janssen, B. Tuzson, T. Rckmann, J. Geophys. Rs., 112, D08301, (2007). (6) Y.Q. Gao, W-C. Chen, R. A. Marcus, J. Chem. Phys., 117, 1536, (2002). (7) R. Schinke, P. Fleurat-Lessard, S.Yu. Grebenshchikov, Phys.Chem.Chem.Phys., 5, 1966, (2003). (8) Q. Gao, R.A. Marcus, Science, 293, 259, (2001).