O-02

Session 2) Fundamentals of Isotope Fractionation

Mass-Independent Isotope Fractionation in Plasma: Theory and Experiments

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Introduction: Although mass-dependent isotopic fractionation (MDF) is ubiquitously observed in 2-body chemical reactions, the first doubts on its general character appeared in 1983 with the 3 body reaction responsible for ozone [1] ($O + O_2 + X \rightarrow O_3 + X$ where X is the third body stabilizing the complex O_3*): equal relative variations in $^{17}O/^{16}O$ and $^{18}O/^{16}O$ were observed in ozone, in clear contradiction with MDF [2,3]. Although this mass-independent fractionation (MIF) effect was found to be not restricted to ozone [4], its physical origin is still an open question [5].

Theoretical proposal: According to a recent proposal [6], the lifetime ratio of two complexes is different from unity if their formations involve identical or non-identical isotopes. The MIF effect would result from the quantum mechanical requirement according to which, for identical isotopes, the two possible reaction channels (elastic scattering and particle exchange) have to be superposed (such as, for example: $^{16}O + {}^{16}O_2 \rightarrow {}^{16}O_3$*). Application of this principle in molecular dynamics calculations gives results in reasonable agreement with laboratory data for ozone.

Experimental: Because the model predicts different MIF patterns for each chemical element, our aim was to verify experimentally these predictions by studying the reactions $TiCl_4$-C_5Hx, $MgCl_2$-C_5Hx and H_2O-CH_4 (for Ti, Mg and O isotopes, respectively) in plasma. In these experiments, the carbonaceous grains and/or films condensed from the plasma on silicon wafer surfaces were analyzed by SIMS and NanoSims.

Results: Large MIF effects (up to 1000 ‰ for Ti and Mg and up to 100‰ for O) were observed [6, 7, 8]. The predictions of the MIF model developped for ozone were satisfied.

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