

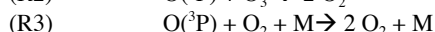
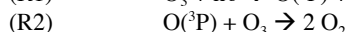
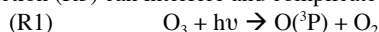
Experimental research on isotope effects in photodissociation of O₃

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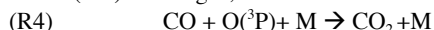
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Ozone (O₃) has a strong influence on the radiative balance and chemical processes in the Earth's atmosphere and also exhibits a very peculiar isotopic composition. It is highly enriched in both ¹⁷O and ¹⁸O and shows a clear offset from the mass dependent fractionation line (quantified as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 * \delta^{18}\text{O}$), i.e. it possesses excess ¹⁷O over what is expected based on ¹⁸O abundances. The O₃ formation reaction is the most prominent example for a reaction that leads to the formation of such mass independent isotope compositions. To what degree O₃ destruction reactions contribute to the isotopic anomaly in O₃ is still not fully understood. In particular, it has not been possible to isolate the isotope effects in the photolysis reaction (R1) from the subsequent reaction of O with O₃ (R2). In addition, the three-body recombination reaction (R3) can interfere and complicate interpretation.



Within the project INTRAMIF (Initial Training network on Mass-Independent Fractionation) we are investigating the isotope effect resulting from photodissociation of O₃. We attempt to suppress reaction (R2) and (R3) by using carbon monoxide (CO) as bathgas, which reacts with O(^3P) (R4).



In the experiments, O₃ is produced by electric discharge and exposed to different types of radiation with and without addition of CO. After reaction, the remaining O₃ is collected in a cold trap at the triple point temperature of nitrogen (63K). In order to measure the oxygen isotopes of O₃ using isotope mass spectrometry, O₃ is converted to O₂.

In this presentation we show first results of O₃ photodissociation with visible light, using CO as O(^3P) quencher.

Geochemical Modeling of Glass Alteration in Mg rich ground water

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Coupling interdiffusion, through a layer passivating the glass surface, with dissolution of this layer has been the objective of a glass alteration model named GRAAL (Glass Reactivity in Allowance for the Alteration Layer) [1]. It has been implemented within the CHESSE/HYTEC code. The interesting point is that GRAAL equations handle the nanometer scale interdiffusion phenomena through the passivating layer while the finite-element chemistry-transport code handles the centimeter scale transport through fluids. The model has been applied to many long term batch glass alteration experiments in Mg rich ground waters and various surface areas to solution volume ratios (S/V), following a work initiated in [1, 2]. Magnesium silicate precipitation has been proved to be a significant mechanism sustaining glass alteration. Magnesium silicate also consume hydroxide ions and its apparent solubility increases with the pH decrease. Glass alteration provides not only silica but also hydroxide ions required for magnesium silicate precipitation to go on. The strong coupling at work, visible through pH, Si and Mg variations as a function of time and glass S/V, illustrates the need for a geochemical model. Sensitivity studies on Si/Mg ratio in the magnesium silicate show that a precise knowledge of Si distribution between the depleted gel, the passivating layer, and the magnesium silicate is required for a precise prediction of pH and therefore glass alteration rate.

[1] Debure *et al* (2012) J. Nucl. Mater. 420, 347–361. [2] Jollivet *et al*. (2012) J. Nucl. Mater. 420, 508-518