Mass-independent fractionation of triple oxygen isotopes induced by hyperfine effect: The role of $(O_2)_2$ dimerization

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Thermal diffusion had been known to fractionate stable isotopes. However, Sun and Bao showed that mass-independent ^{17}O anomalies can be generated simply by subjecting O_2 gas in an enclosure to a thermal gradient[1,2]. By a method of exclusion, the authors proposed that a small defference in diffusion coefficient of gas molecules induced by nuclear spin is amplified during molecular collision. If the effect of nuclear spin (hyperfine effect) is indeed responsible for ^{17}O anomaly during thermal diffusion, it may play a role in gaseous nebulae discs and consequently in the puzzling triple oxygen isotope heterogeneity in solar system.

Since collision frequency is related to temperature, Sun and Bao's hypothesis would therefore predict that the θ ($=\ln\alpha^{17}O/\ln\alpha^{18}O$) will change with temperture continuously. Here we conducted a series of close-system experiments on O_2 diffusion along a thermal gradient with a temperature range from 78K to 1023K. It is found that, within the temperature range from 168K to 1023K, heavy isotopes are preferred in the cold end and the θs remain constant to be at ~0.48. However, at temperature pair of 78K/168K the fractionation exhibits an opposite trend in which heavy isotopes are enriched in the warmer end of 168K. In addition, the θ becomes 1.0. We suggest that the formation of O_2-O_2 dimer at 78K may be primarily responsible for the observed ^{17}O anomalies in Sun and Bao's and our experiments because spin-spin coupling accounts for ~15% of van der Waals forces to bind two O_2 molecules[3]. This hypothesis was further tested by applying an external magnetic field to hamper the dimerization of O_2. We found that in this case at 78K the ^{17}O anomalies are no longer observed. Thus, our results predict that thermal diffusion of CO would not generate a significant mass-independent ^{17}O anomaly.

[1] Sun and Bao, Rapid Commun. Mass Spectrom. 2011, 25, 20–24;
[2] Sun and Bao, Rapid Commun. Mass Spectrom. 2011, 25, 765–773;
[3] Aquilanti et al., Phys. Rev. Lett. 1999, 82, 69-72.