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Multiply-substituted isotopologues as tracers of geochemical cycles

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Multiply-substituted gas molecules, with more than one rare isotope (isotope clumping), are providing new tools for determining the provenance and evolution of gases of geochemical relevance. Methane and nitrogen serve as examples of the wide variety of problems addressed using these molecules. In the case of CH_4, rare isotopologues trace mainly processes of formation rather than substrates, while rare isotopologues of N_2 can act as robust tracers of origin through geological processing.

Studies of the methane mass-18 isotopologues, $^{13}CH_3D$ and $^{12}CH_2D_2$, show that in combination their relative abundances rival $\delta^{13}C$ and δD in information content, but are approximately orthogonal to these bulk isotope ratios. Microbially-assisted and abiotic methane formation produce gases with markedly low $\Delta^{12}CH_2D_2$ values (deviations from stochastic) as the result of drawing on different pools of hydrogen with distinctive D/H ratios. Correlations between $\Delta^{12}CH_2D_2$ and $\Delta^{13}CH_3D$ are indicative of specific formation pathways of "microbialgenic" methane. Methanotrophy also has tell-tale $\Delta^{12}CH_2D_2$ and $\Delta^{13}CH_3D$ signatures, with microbially-mediated anaerobic oxidation (AOM) and aerobic oxidation (AeOM) producing different trajectories in $\Delta^{12}CH_2D_2$ vs. $\Delta^{13}CH_3D$ space. AOM causes fractionation reflecting binding of methane to the catalyzing enzyme (Mcr) that varies with reversibility. Isotopologue fractionations attending AeOM are dominated by reduced masses along the reaction coordinate for bond rupture. The result is a set of new, powerful clues to the origin and processing of natural methane gases that are largely insensitive to different bulk isotope ratios, and so applicable to both terrestrial geochemical cycles and those elsewhere in the Solar System.

Discovery of an excess of $^{15}N^{15}N$ in air of nearly 20 ‰ has provided a unique tracer for N_2 in volcanic gases. Surprising results include the fact that $\delta^{15}N$, the traditional indicator of the provenance of N_2 in these gases, is deceptive, and fraught with degeneracies. By using $\Delta^{15}N^{15}N$ to identify air in magmatic gases, one can show that recycling of nitrogen in some arc settings is quantitative. This present-day relative isolation of nitrogen in air from the deep mantle requires a reevaluation of both the source of Earth's nitrogen and secular changes in the global nitrogen cycle.