A 'clumped-isotope' study of stratospheric CO_2 reveals a new atmospheric process

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The stable isotope composition of stratospheric CO_2 is a long-lived tracer of stratospheric photochemical processing. Although the stratospheric CO_2 isotopologue budget is thought to be governed primarily by the $O(^1D)+CO_2$ isotope exchange reaction, there is increasing evidence that other important physical processes may be occurring that standard isotopic tools have been unable to identify. Measuring the distribution of the rare 'clumped' isotopologue $^{13}C^{18}O^{16}O$, in concert with $^{12}C^{18}O^{16}O$ and $^{12}C^{17}O^{16}O$ abundances, provides sensitivities to these additional processes, and thus is a valuable test of current models.

We have discovered a large and unexpected enrichment in stratospheric $^{13}C^{18}O^{16}O$ originating from a process to which other long-lived stratospheric species are not sensitive. Air samples collected from the polar vortex, in particular, contain the highest $^{13}C^{18}O^{16}O$ proportions (reported as Δ_{47} values) ever observed in naturally-derived CO_2 samples. We show, through photochemical experiments, that lower $^{13}C^{18}O^{16}O$ proportions in the mid-latitudes are determined primarily by the $O(^1D)+CO_2$ isotope exchange reaction, which promotes a stochastic isotopologue distribution. In contrast, higher $^{13}C^{18}O^{16}O$ proportions in the polar vortex show correlations with long-lived stratospheric tracer and bulk isotope abundances (e.g., N_2O mixing ratio, $\delta^{18}O$, and $\Delta^{17}O$) opposite to those observed at mid-latitudes, and thus opposite to those easily explained by $O(^1D)+CO_2$. We believe the most plausible explanation for this meridional variation is either an unrecognized isotopic fractionation associated with the mesospheric photochemistry of CO_2 or isotopic exchange on polar stratospheric clouds (PSCs). This study demonstrates the utility of 'clumped-isotope' constraints for outstanding problems in carbon-cycle research.

^{53}Mn-^{53}Cr evidence for Allende chondrule formation at 4567.6 Ma

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We have recently suggested [1] that the current ^{53}Mn-^{53}Cr data for bulk carbonaceous chondrites imply that chondrules in them must also have formed early, given the logical necessity of forming chondrules first before accreting chondrites (we need "sand grains" first to form the cosmic "sandstone"). This simple temporal relationship is, however, at odds with the currently accepted chondrule ^{26}Al-^{26}Mg and some Pb-Pb ages, which at face value point toward 2-3 Ma younger ages. However, a younger chondrule age poses a serious dynamic problem for the early solar nebula, known as the "storage problem", namely, how could particles of CAI-size float in the protoplanetary disk for over 2-3 Ma until chondrules form, without facing head wind and spiralling into the Sun. Poynting-Robertson drag would efficiently remove the CAI-sized dust particles in the solar nebula in a timescale far less than 2-3 Ma.

Here, we present new ultra-high-precision ^{53}Mn-^{53}Cr data obtained for Allende chondrules and bulk carbonaceous chondrites that remove the classic "storage" problem. We show that the ^{53}Mn-^{53}Cr age of Allende chondrules is 4567.91±0.76 Ma, relative to the D'Orbigny age anchor, or 4567.12±0.83 Ma relative to LEW86010 anchor. Our data do not require chondrules in Allende to have formed 2 Ma after the beginning of the Solar System, as defined by the CAI age of 4567.60±0.36 Ma [2]. We further show that the slope and intercept for the bulk carbonaceous chondrites are indistinguishable from those of Allende chondrules. The bulk carbonaceous chondrite absolute ^{53}Mn-^{53}Cr age is 4567.61±0.67 Ma relative to the D'Orbigny anchor, or 4566.82±0.74 Ma relative to LEW86010 anchor.

[1] Moynier, Yin, and Jacobsen (2007) *ApJ*. **671**, L181-L183.
[2] B. Jacobsen *et al*. (2008) *EPSL*. **272,** 353-364.