DISEQUILIBRIUM OXYGEN CHEMISTRY IN THE SOLAR NEBULA. Robert N. Clayton, Enrico Fermi Institute, University of Chicago, Chicago, IL 60637 (r-clayton@uchicago.edu).

It has been proposed [1] that the anomalous isotopic fractionation of oxygen in chondrules and CAIs is the result of isotopic self-shielding in the photodissociation of carbon monoxide in the solar nebula. Photolysis of CO proceeds by a predissociation mechanism, in which each isotopomer absorbs in narrow energy bands, separated in wavelength due to the mass-dependent differences in vibrational energies. The young Sun was the source of ultraviolet radiation, and the self-shielding effect results from the much smaller depth of penetration of radiation of the wavelength absorbed by the abundant species, $^{12}C^{16}O$, compared to the depth leading to dissociation of the rare species, $^{12}C^{17}O$, $^{12}C^{18}O$, and $^{13}C^{16}O$ [2]. Thus, at depths into the nebula on the order of one magnitude of visual extinction, the production rates of atomic ^{17}O and ^{18}O exceed that of ^{16}O by a factor of about ten [3], and are approximately equal to one another. Incorporation of the rare-isotope-enriched reactive atoms into condensed phases leads to heavy-isotope enrichment in the products, with constant $^{17}O/^{18}O$ ratio, as seen in chondrules and exchanged phases of CAIs [4].

The slope-1 trend in the oxygen three-isotope graph is *prima facie* evidence of disequilibrium in the oxygen chemistry of chondrules and CAIs, as would be expected if photochemistry plays a significant role. Under these circumstances, the oxygen fugacity, an equilibrium property, is not defined. The *equilibrium* oxygen fugacity of a solar gas can be calculated from the thermodynamics and elemental abundances of hydrogen, carbon, and oxygen. The ratio of Ti^{3+}/Ti^{4+} in fassaite in some Allende CAIs is consistent with this value, corresponding to a very low oxygen fugacity, around IW-7 [5]. However, subsequent interaction with nebular gas implies an apparent oxygen fugacity several orders of magnitude higher [6]. This variation of oxidation state, along with the secondary enrichment in ^{17}O and ^{18}O in some CAI minerals, may be manifestations of the disequilibrium reactions of atomic oxygen derived from CO photolysis.

There are many examples of a rough correlation between the chondritic abundances of ferrous iron and the enrichment in ^{17}O and ^{18}O. At the level of whole meteorites, ferrous iron and heavy oxygen both increase in the order E < H < L < LL < R chondrites [4]. A correlation between olivine fayalite content and oxygen isotopic composition was found in Allende (CV3) chondrules [7]. Also in Allende, coarse-grained chondrule rims are always enriched in ferrous iron and in heavy oxygen relative to their underlying chondrules [8].

A striking example of oxygen disequilibrium is provided by the olivine matrix and dark inclusions in Allende, which have compositions of Fa_{40}-Fa_{60} coexisting with forsteritic olivine. Krot et al. [9] inferred a complex history involving hydrothermal alteration in a parent body, producing phyllosilicates, followed by metamorphic dehydration. However, the oxygen isotopic compositions of Allende matrix and dark inclusions lie exactly on the CCAM line defined by minerals from Allende CAI, strongly suggesting the derivation of oxygen from the same nebular source (Figs. 1 and 2). In an ion microprobe study of forsteritic olivine grains with fayalitic rims in Allende, Weinbruch et al. [10] found the rims to be consistently richer in ^{17}O and ^{18}O, and concluded that "these rims formed by condensation from an oxidized gas with higher $\delta^{17}O$ and $\delta^{18}O$".

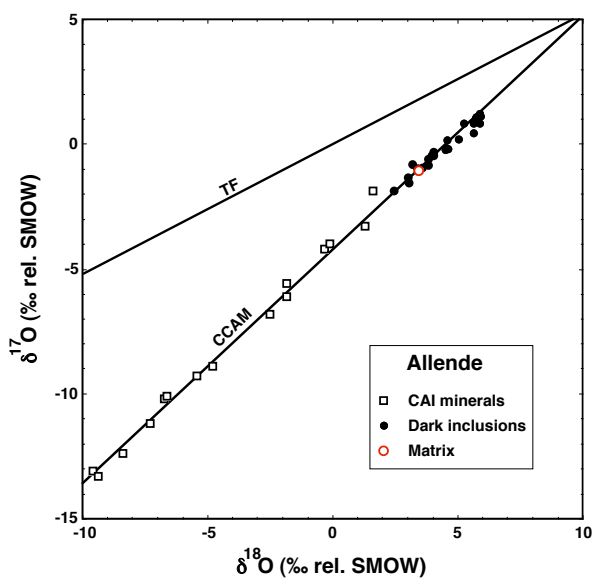

Fig. 1. Oxygen isotopic compositions of Allende CAI minerals, dark inclusions and matrix, showing exchange with a nebular gas reservoir enriched in ^{17}O and ^{18}O.

Enhancement of the dust/gas ratio in the solar nebula has often been invoked as a mechanism for increasing the oxidation state of the nebula, as is needed, for example, in order to account for the abundant ferrous iron in chondrites [11] . Fedkin and

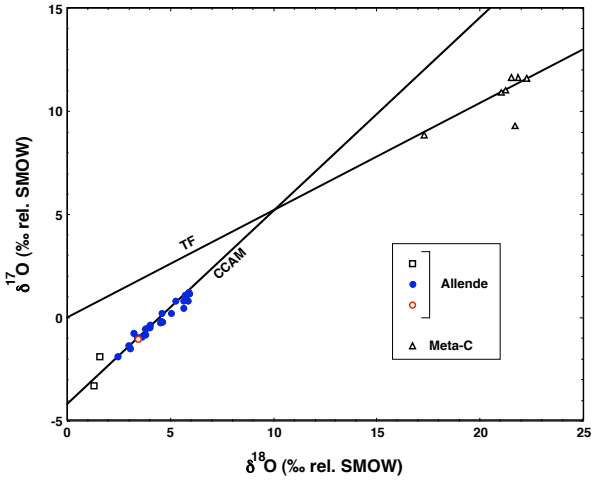

Fig. 2. A blow-up of the upper end of the line in Fig. 1, along with data from metamorphosed carbonaceous chondrites which have undergone hydration and dehydration.

Grossman [12] examined this mechanism and concluded that even a factor of 1000 enrichment in dust was inadequate to account for the ferrous iron content of unequilibrated ordinary chondrites by an equilibrium condensation process. Ebel and Grossman [13] also explored the effect of dust/gas enhancement on the possibility of liquid equilibrium condensates. They showed that a 1000-fold increase in the proportion of CI-like dust is sufficient to produce ferrous-iron-bearing melts, at a partial pressure of atomic oxygen of 5×10^{-14} bars. In the disequilibrium case, oxygen atom concentration from CO photolysis can exceed this value with only one percent dissociation, with a large heavy-isotope enrichment [3].

The association of anomalous oxygen isotope variations with oxidation-state variations in chondrules and CAIs suggests a causal connection, most plausibly the production of atomic oxygen by photolysis and its reaction with condensing melts and solids. This has important implications for the astrophysical site for the photochemical process. In the scenario described by [14], photolysis occurs in the pre-nebular molecular cloud, and in that presented by [15], it occurs in the outer surfaces of the solar nebula at a distance of several AU from the Sun. In both cases, the ^{17}O and ^{18}O atoms are trapped as water ice, bringing about the physical separation of ^{16}O-rich and ^{16}O-poor reservoirs, which subsequently lead to the observed slope-1 array in meteorites. Neither scenario provides any direct connection between the isotopic effect and the chemical processes of formation of chondrules or CAIs. In the X-wind model for accretion of the young Sun [16], chondrules and CAIs are thought to form at distances < 0.1 AU from the Sun, and to be ejected back into the nebular disk. This model also provides a mechanism for photolysis of CO in this same region of space [1].

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