

**OXYGEN ISOTOPIC EXCHANGE BETWEEN CARBON MONOXIDE GAS AND SILICATE MELT: IMPLICATIONS FOR THE EARLY SOLAR NEBULA.** J. S. Boesenberg<sup>1</sup>, E. D. Young<sup>2</sup>, I. Kohl<sup>2</sup> and S. W. Parman<sup>1</sup>. <sup>1</sup>Department of Earth, Environmental and Planetary Sciences, Brown University, 324 Brook Street, Providence, RI 02920 (joseph\_boesenberg@brown.edu). <sup>2</sup>Department of Earth, Planetary and Space Sciences, University of California, Los Angeles, 595 Charles Young Drive East, Box 951567, Los Angeles, CA 90095-1567.

**Introduction:** Oxygen is the most abundant element in the silicate portions of meteorites and asteroids. The Genesis mission determined the solar wind oxygen isotopic composition is  $\delta^{18}\text{O} = -58$ ,  $\delta^{17}\text{O} = -59$  [1] and this is assumed to be the starting composition of the solar nebula. However, meteorites (as well as asteroids and planets) have substantially heavier isotopic compositions. This implies that the oxygen isotopic compositions of planetary materials got progressively heavier during the evolution of the solar nebula.

There are essentially only two oxygen-bearing gas species in the hot, but cooling ( $\sim 1600^\circ\text{C}$  down to  $1000^\circ\text{C}$ ), early solar nebula that could have exchanged with the earliest solids: carbon monoxide and water vapor [2]. Carbon monoxide constitutes approximately 40-45% of the volume of the oxygen-bearing species over this temperature range, while water constitutes approximately 55% (at  $1600^\circ\text{C}$ ) to 43% (at  $1000^\circ\text{C}$ ) [2]. Yu et al. [3] shows that 50% exchange of the oxygen isotopic composition occurs between a small silicate sphere and an  $\text{H}_2/\text{H}_2\text{O}$  gas mixture at  $1400^\circ\text{C}$  after 5 minutes of melting at one atmosphere. They argue that at nebular pressures ( $\sim 10^{-2}$  to  $10^{-5}$  torr) 50% exchange would take  $\sim 10$  hours, depending on surface kinetics and exchange probability. This would extend the duration of possible chondrule formation and may be consistent with the textural and Fe-Mg zoning experiments of [4] and [5]. Boesenberg et al. [6] did similar oxygen isotopic exchange experiments using CO gas (instead of water vapor) and a IIAB chondrule analog at nebular pressures ( $10^{-3}$  torr) using a vacuum furnace. However, they [6] did not see exchange between gas and melt, only evaporation, giving the indication that CO might not exchange with silicate melt.

Upon further investigation, we concluded that the above results [6] were ambiguous and needed to be re-run using higher gas/rock ratios which would better record exchange. We have therefore conducted new exchange experiments at 1 atm, rather than under vacuum. We are testing exchange between carbon monoxide and a partially melted sample of Allende (CV3) to determine if a liquid/solid sphere does indeed exchange its oxygen isotopic composition with CO gas.

**Experimental Technique and Oxygen Isotopic Analysis:** A series of oxygen isotope exchange experiments were performed in a 1 atm, gas mixing furnace at Brown University, using unlabelled carbon monoxide

gas and a fine-grained (<45 microns) powdered sample of Allende. The experimental run details are listed in Table 1. The experimental Allende powders were compressed into 4mm pellets, weighed ( $\sim 35$ -40 mg), placed on Re wire loops and inserted into the hotspot of the furnace. A flow of carbon monoxide gas through the furnace was established 30 minutes prior to each experiment and was regulated using a high precision flowmeter. The charges were drop quenched into water at the end of each run. To determine the starting oxygen isotopic composition of the CO gas, one experiment involved inserting a small Zr metal sample into the furnace and oxidizing it with the flowing CO gas.

**Table 1. Experimental Runs**

Exp #	Sample	Conditions
1014	Allende	1500C, 6 hrs, vacuum, no CO
1009	Allende+CO	1500C, 24 hrs, one atm, 110 ml/min CO
1011	Allende+CO	1500C, 48 hrs, one atm, 100 ml/min CO
1008	Allende+CO	1500C, <66 hrs fail, one atm, 100 ml/min CO
1016	Zr metal+CO	1400C, 1 hr, one atm, 200 ml/min CO

After the experimental runs, the charges were split. Half was utilized for oxygen isotopic analysis and half for microprobe analysis (only partially reported here).

Oxygen isotopic analysis was performed at UCLA on a ThermoFinnigan Delta gas-source mass spectrometer using the laser fluorination technique of [7].

**Results:** The results of the experiments are plotted in Figure 1. The starting material for all of the experiments (except Zr metal) was average bulk Allende and plots at  $\delta^{18}\text{O} = 1.342$ ,  $\delta^{17}\text{O} = -2.778$ . Based on observation of the pre-ground chips, there were no large CAIs in the starting materials which might dramatically alter the oxygen isotopic composition.

Run 1014 was simply powdered Allende in vacuum for 6 hours with no CO gas. This experiment showed evidence of evaporation and plots on the heavy side of the starting material in a three oxygen isotope plot.

Run 1009, 1011 and 1008 are true exchange run products. These experiments were run at high temperature and 1 atm with a high carbon monoxide flow rate present. Experiment 1008 failed (fell off the holding Re wire) at some point during its run. It is suspected this experiment only ran a few hours in the hotspot, though it was only noticed at the bottom of the furnace after nearly 66 hours. Our interpretation is that this experiment only partially exchanged. Runs 1009 and 1011 plot above the terrestrial fractionation line at ap-

proximately  $\Delta^{17}\text{O} = 1.5$ . Terrestrial carbon monoxide plots at approximately  $\Delta^{17}\text{O} = 1.5$  and at  $\delta^{18}\text{O}$  values of  $\sim 5$  to 25, because of atmospheric processing [8]. In order to determine the  $\Delta^{17}\text{O}$  of the CO gas in the furnace, a piece of Zr wire was inserted into the hotspot and oxidized by the CO gas (Fig. 1). While having more  $^{16}\text{O}$  rich  $\delta$ -values, due to mineralogical equilibrium fractionation, the  $\Delta^{17}\text{O}$  of the Zr oxide is within error of runs 1009 and 1011. This suggests that experiments 1009 and 1011 have completely (or very nearly) exchanged with the CO gas.

Mineralogically, runs 1009, 1011 and 1008 consist of glass, olivine and metal/sulfide. Nearly all of the FeO in the experiments was reduced to Fe-metal because of the low oxygen fugacity imposed by the pure CO gas environment.

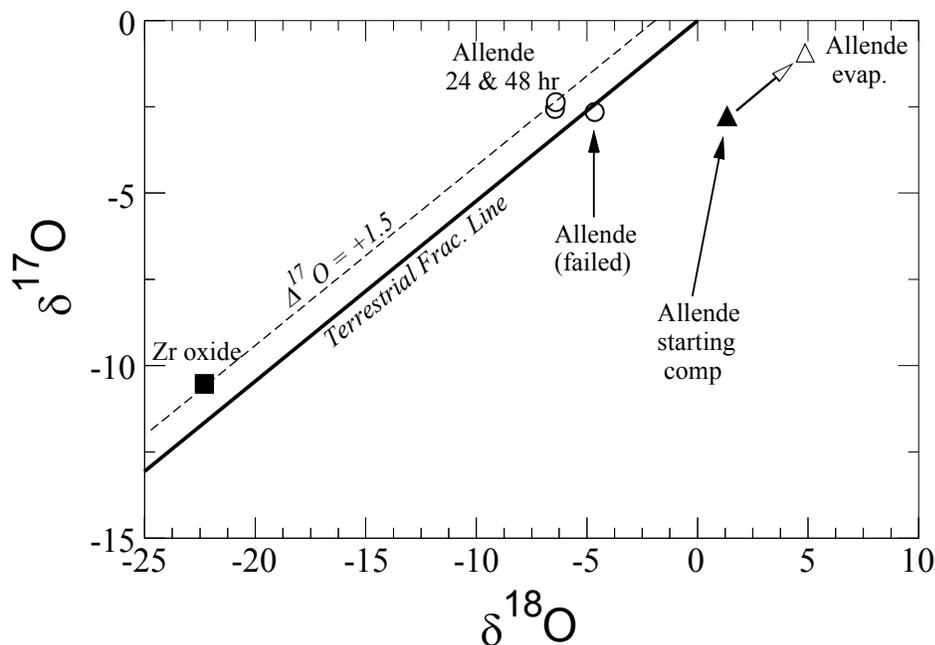
**Discussion:** These experiments demonstrate that exchange between CO and a silicate melt does occur. It is suspected that either longer durations or higher partial pressures of CO were needed in the experiments of [6], explaining why no exchange was observed.

The purpose of these experiments is both to confirm that exchange does occur and determine the oxygen isotopic exchange rates between CO gas and silicate melt. However, the 24 and 48 hour experiments (1009 and 1011) showed complete or nearly complete exchange with the CO gas, so exchange rates cannot be determined for these experiments. Experiments with lower CO flowrates will be run in the near future. Ideally, between 50 and 90% exchange is preferred for measuring exchange rates. In addition, the durations need to exceed the time necessary for the gas to diffuse

through the melt (otherwise something other than an exchange rate is being measured). Diffusion rates for chondrule and CAI melts are in the range of  $10^{-6}$  to  $10^{-7}$   $\text{cm}^2/\text{sec}$  [9] (i.e., experimental durations need to be hours to days depending on the run temperatures). In the near future, exchange rates between chondrule and CAI melts and CO gas will be determined.

Obtaining the oxygen isotopic exchange rates between CO and silicate melt are important because models utilizing mixing, photodissociation, or chemical isotope effects of the mass independent oxygen isotopic evolution of the nebula [10,11,12] rely on both the rates and pathways taken to transfer the heavy oxygen from gas to solid. If one assumes direct exchange using CO gas rather than an intermediary exchange path using water vapor, both the pathway and exchange rate will be altered. This is a critical measurement for the development and progress of these models.

**References:** [1] McKeegan K. et al (2011) *Science*, 332, 1528-1532. [2] Ebel D. S. and Grossman L. (2000) *GCA* 64, 339-366. [3] Yu Y. et al. (1995) *GCA* 59, 2095-2104. [4] Jones R. H. and Lofgren G. E. (1993) *Meteoritics* 28, 213-221. [5] Weinbruch S. et al. (1998) *MaPS* 33, 65-74. [6] Boesenberg J. S. et al. (2005) *MaPS* 40, A22. [7] Rumble D. et al. (1997) *GCA* 61, 4229-4234. [8] Rockmann T. et al. (1998) *Science* 281, 544-546. [9] Wendlandt R. F. (1991) *Contrib. Mineral. Petrol.* 108, 463-471. [10] Clayton R. et al. (1977) *EPSL* 34, 209-224. [11] Thiemans M. H. and Heidenreich J. E. (1983) *Science* 219, 1073-1075. [12] Young E. D. et al. (2008) *Reviews in Mineral. and Geochem.* 68, 187-218.



**Figure 1:** Three-oxygen isotope diagram showing exchange between Allende and carbon monoxide gas.