STABLE ISOTOPE ANALYSIS OF MOLECULAR OXYGEN FROM SILICATES AND OXIDES USING CO$_2$ LASER EXTRACTION

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Abstract

A laser-excited system for determination of the oxygen isotope composition of small quantities of silicate and oxide minerals was constructed and tested at JSC. This device is the first reported to use a commercially available helium cryostat to transfer and purify oxygen gas quantitatively within the system. The system uses oxygen gas instead of the conventional CO_2 for mass spectrometer analyses. This modification of technique permits determination of all three stable oxygen isotopes, an essential requirement for oxygen isotope analysis of meteoritic material. Tests of the system included analysis of standard silicate materials NBS 28 and UWMG2 garnet, six SNC meteorites, and inclusions and chondrules from the Allende meteorite. Calibration with terrestrial standards was excellent. Meteorite values are close to published values and show no evidence of terrestrial oxygen contamination. The one limitation observed is that, in some runs on fine-grained SNC matrix material, sample results were affected by other samples in the sample holder within the reaction chamber. This reemphasizes the need for special precautions in dealing with fine-grained, reactive samples. Performance of the JSC instrument compares favorably with that of any other instrument currently producing published oxygen isotope data.

Introduction

Oxygen isotope analysis of silicates and oxides, a technique developed by Silverman, 1951; Taylor and Epstein, 1962; and Clayton and Mayeda, 1963, has provided a wealth of information in igneous and metamorphic petrology, geochemistry of mineral deposits, meteoritics, and other fields. Interest in transport phenomena and nucleosynthetic processes has driven efforts to analyze small samples, leading to development of laser-fluorination devices that quantitatively release oxygen from milligram amounts of material. (Sharp, 1992). In most cases, the method of choice has been to liberate oxygen using a fluorinating agent such as fluorine gas (Taylor and Epstein, 1962) or bromine pentafluoride (Clayton and Mayeda, 1963) and convert the oxygen gas produced to CO_2, which is then analyzed mass spectrometrically.

Laser fluorination differs from conventional fluorination in that the fluorination system is attached directly to a mass spectrometer for "real time" analysis; and fluorination occurs in a small chamber in which laser energy is focussed on the sample so that the containment vessel is not exposed to the fluorinating agent at high temperature. The reason that most analysts convert oxygen to CO_2 before analysis is that CO_2 can be readily pumped and concentrated in liquid nitrogen cold traps whereas oxygen cannot. A particular disadvantage of performing isotopic analysis of oxygen using CO_2 gas is that ^{13}C (abundance approximately 1.1%) is collected in the mass spectrometer at nominal mass 45 ($^{13}C^{16}O^{16}O$) and masks isotopic variations in ^{17}O ($^{12}C^{17}O^{16}O$), which has an abundance of approximately .0375%. This does not pose a problem for analysis of terrestrial samples, which are isotopically homogeneous, that is, they show only chemical variations so that $^{17}O/^{16}O$ is always proportional to $^{18}O/^{16}O$. In contrast, the ability to analyze only abundances of ^{16}O and ^{18}O poses an unsatisfactory limitation on meteorite studies because meteorites are isotopically inhomogeneous, and this inhomogeneity offers critically important information about the origin of the solar system (Clayton 1993).

In collaboration with C. S. Romanek and R. A. Socki, I have developed and tested an apparatus for laser-excited mass spectrometric analysis of molecular oxygen in silicates and oxides in the stable isotope laboratory of Everett Gibson. The fluorination line is shown in Figure 1. A 25 watt CO_2 laser is used to heat the sample within a reaction chamber in the presence of a strong fluorinating agent. This procedure releases oxygen gas quantitatively from silicates and/or oxides by replacing it with a stronger oxidizing agent: fluorine. For example:

$$5SiO_2 + 4BrF_5 = 5SiF_4 + 2Br_2 + 5O_2$$
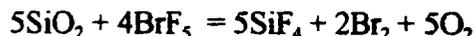
BrF_5 required in the reaction chamber (Fig. 1, RC) is fed into the system through the detachable cylinder R. After fluorination takes place in RC, a mixture of gases is present in the system, including O_2, excess BrF_5, SiF_4, Br_2, F_2, and trace gases. BrF_5, SiF_4, Br_2, and some trace gases are removed in a cold trap (T1) maintained at the temperature of liquid nitrogen. To the right of this trap, gas should be relatively free of strong oxidizing substances except sample oxygen. Some F_2 is carried over, and this is removed by reaction with KBr present in the vacuum line as indicated. The reaction involved:

$$F_2 + 2KBr = 2KF + Br_2$$
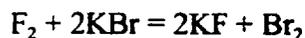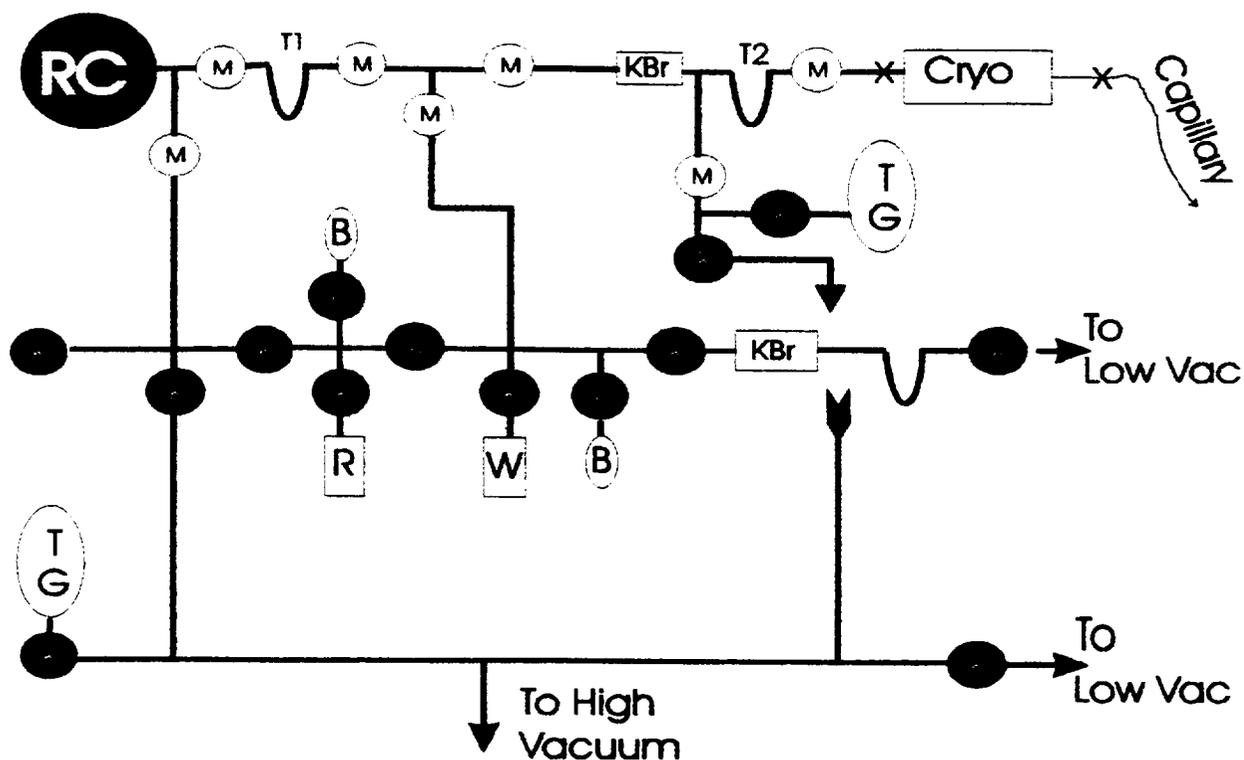
**Figure 1.-** Schematic of laser excitation system. RC: Reaction Chamber; Cryo: Helium Cryotrap; M:All-Metal Valves; K: Valves with Kel-F seats; KBr: KBr Traps for Fluorine; R: BrF$_5$ Reservoir; W: Waste collector; B: Bourdon Gauge: TG: Thermocouple Gauge.

produces Br$_2$ which is trapped in a second liquid nitrogen trap (T2). No Br$_2$, F$_2$, BrF$_5$, or H$_2$O should ever be allowed to pass beyond this trap. The gases Br$_2$, SiF$_4$, and excess BrF$_5$ are removed from the system by trapping them with liquid nitrogen in the cylinder labelled W.

An essential sample pretreatment step is to begin with one or more short (5 to 20 minute) fluorinations. This is because water vapor reacts to form HF, which is more corrosive than fluorine to 316SS tubing, copper gaskets and particularly BaF$_2$ windows:

$$5H_2O + 2BrF_5 = 10HF + Br_2 + {}^5/_2O_2.$$
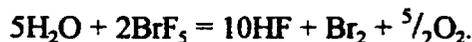
As the reaction indicates, water vapor is also a serious analytical contaminant.

The unique feature of the JSC system is that it uses a comercially available helium cryostat to collect oxygen gas for analysis. Oxygen is frozen out very effectively below 37° K,

whereas Br_2 and BrF_5 remain frozen at $100°$ K. The troublesome trace gas NF_3 (which has a breakdown fragment at mass 33 that interferes with ^{17}O measurements) remains frozen at $100°$ K. Thus, the procedure that has been developed is to cool the cryostat to $35°$ K, trap the sample in the cryostat and then raise the temperature to $100°$ K and release the collected sample, through a capillary leak, into a mass spectrometer (MAT 251).

The reason for building this system is to examine meteorites, particularly the SNC ("martian") meteorites. This type of analysis is a challenging task that has been accomplished by few laboratories in the world. Meteorite data that I collected is given in Table 1 and plotted in Figure 2. Units are $\delta^{18}O$ and $\delta^{17}O$ defined as permil (‰) variations from a standard: SMOW.

$$\delta^{18}O = 1000 \times [(^{18}O/^{16}O)_{Sample} - (^{18}O/^{16}O)_{SMOW}]/(^{18}O/^{16}O)_{SMOW}$$

$$\delta^{17}O = 1000 \times [(^{17}O/^{16}O)_{Sample} - (^{17}O/^{16}O)_{SMOW}]/(^{17}O/^{16}O)_{SMOW}.$$

For all terrestrial samples, to a good approximation,

$$\delta^{17}O = 0.52\delta^{18}O.$$

This is the equation for the "Terrestrial Fractionation line" shown in Figures 2 and 4, and it is the locus of oxygen isotope composition of all terrestrial oxygen reservoirs accessible to direct human observation (except the upper atmosphere). The implication is that these reservoirs are all well mixed. The sample analyses in Table I include two well-established terrestrial standards, NBS 28 quartz and UWMG 2 garnet. They also include meteorite material that spans over half the known variation in oxygen isotope composition of silicate minerals of the solar system. These constitute an excellent test of the capabilities of the JSC system. As Figure 3 shows, JSC data are consistent with accepted values for the some of the most diverse samples, inclusions in the carbonaceous chondrite meteorite Allende. The correlation of JSC values with "accepted" values reported by Clayton et al (1977) is excellent; there is no evidence of contamination with terrestrial oxygen.

Data for SNC ("martian") meteorites, plotted in Figure 4, show both the power and one of the limitations of the laser excitation method. The oxygen isotope composition of SNC samples plots on a line similar to, but distinctly displaced from, terrestrial samples as is shown in the figure. The least square regression line ($r^2 = .938$) through my data is:

$$\delta^{17}O = 0.50\delta^{18}O + 0.47.$$

The regression line through published analyses is:

$$\delta^{17}O = 0.53\delta^{18}O + 0.25.$$

Within the range of values of interest, these two equations are nearly identical, and there is little or no evidence of terrestrial contamination during an extremely humid summer.
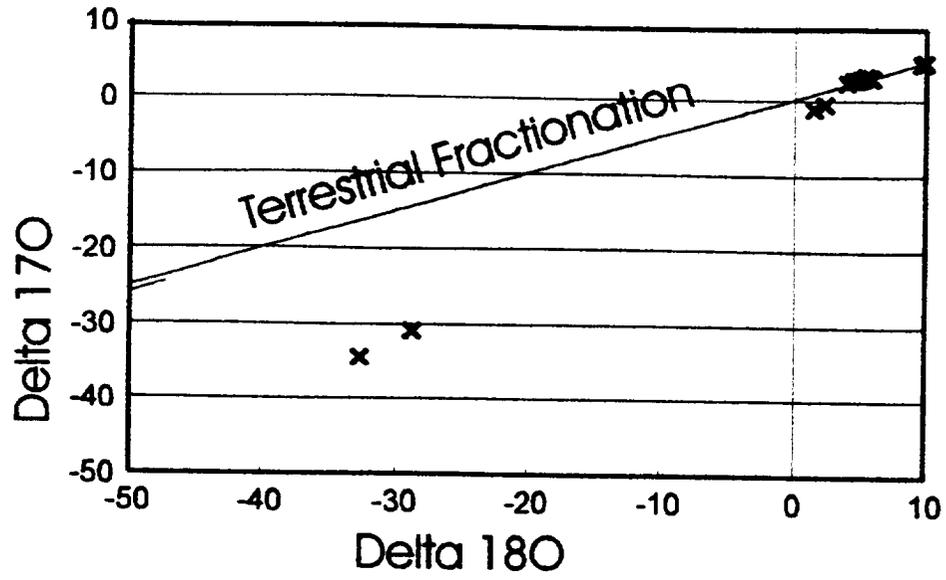
Figure 2.- Data generated with the JSC laser-excited system. Meteorite data diverge widely from terrestrial data. (Terrestrial samples from whatever source lie on the line labelled "terrestrial fractionation.")

Table 1.-

| Sample	Run #	$\delta^{17}O_{machine}$	$\delta^{18}O_{machine}$	$\delta^{17}O_{SMOW}$	$\delta^{18}O_{SMOW}$
NBS28	110	-8.42	-17.21	4.94	9.53
NBS28	111	-8.4	-17.22	4.96	9.52
NBS28	112	-8.32	-17	5.04	9.74
NBS28	114	-8.25	-16.97	5.11	9.77
Chassigny	115	-10.89	-22.68	2.44	3.91
LaFayette	116	-10.43	-21.56	2.91	5.06
79001B	118	-10.62	-21.97	2.71	4.64
Zagami	119	-10.6	-22	2.73	4.61
79001A	120	-10.53	-21.94	2.80	4.67
Chassigny	122	-10.59	-22.25	2.74	4.35
Chassigny	123	-10.57	-21.92	2.76	4.69
Chassigny	124	-10.45	-21.73	2.89	4.88
LaFayette	125	-10.35	-21.5	2.99	5.12
LaFayette	126	-10.06	-21.29	3.28	5.34
Allende Chondrule	128	-13.76	-24.31	-0.47	2.23
Allende Chondrule	129	-14.4	-25.1	-1.12	1.42
Allende Pink Inclusion	131	-47.25	-58.3	-34.41	-32.68
Allende Pink Inclusion	132	-43.71	-54.51	-30.82	-28.79
UWMG 2	133	-10.25	-20.95	3.09	5.69
UWMG 2	134	-10.31	-20.87	3.03	5.77
UWMG 2	135	-10.34	-20.92	3.00	5.72
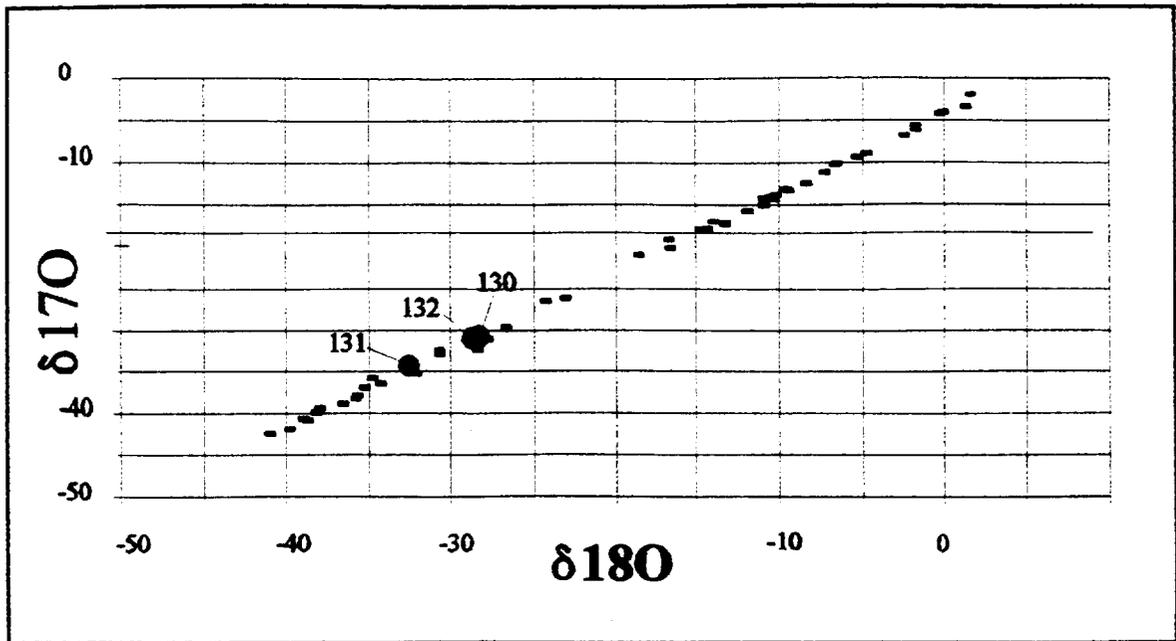
Figure 3.- Allende inclusion data. JSC data superimposed on literature data

The system limitation mentioned above shows up in repeat analyses of samples Chassigny and Lafayette. Although terrestrial contamination was not a problem, reproducibility of individual sample isotope compositions is not as good as predicted. Evaluation of the data strongly suggest that these samples (which are composed of extremely fine-grained and reactive material) contaminated each other within the sample chamber (where multiple samples were placed awaiting reaction). Clearly, with fine-grained meteorite samples special precautions will be required to obtain reproducible results.

The analyses reported here were of a size to produce 15 micromoles or more of oxygen gas. This is a normal sample size for laser analysis, but it does not challenge the limits of small sample analysis. The idea behind this choice of sample size was to test the precision of the system before attempting to work with extremely small samples. Some considerably smaller samples (about 5 micromoles of oxygen) were run in a small

secondary cryotrap. Preliminary results from these runs indicate that samples significantly smaller than those reported on here can be analyzed using the JSC instrument. This contrasts with devices using CO_2 conversion to produce samples for introduction into the mass spectrometer. These CO_2 systems may be unable to analyze relatively small samples because of the increased importance of carbon monoxide production at very low pressure.

Early results of the work reported here will be presentedat the 1995 annual meeting of the Geological Society of America (Romanek et al, 1995). A more detailed report (Perry, Romanek, Socki, and Gibson) is in preparation.
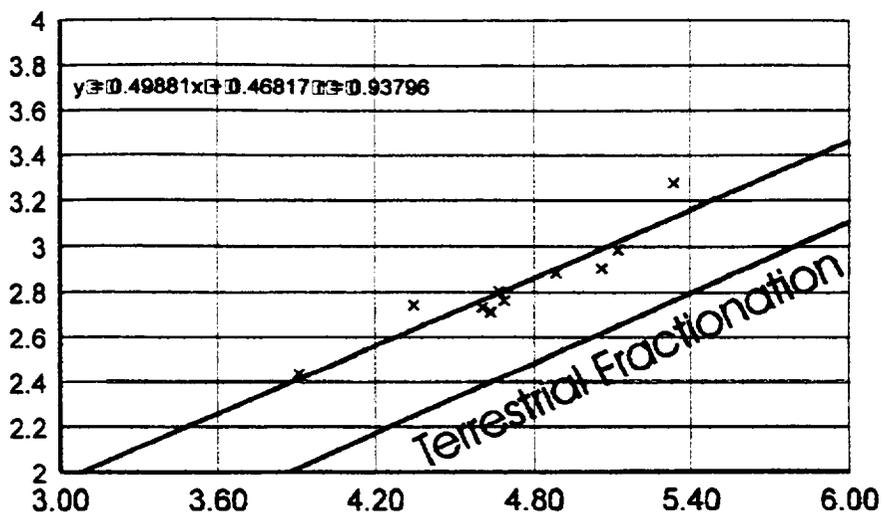
Figure 4.- SNC ("martian") meteorites. These are tightly grouped and fall slightly above the terrestrial fractionation line on a three isotope plot.

Conclusions

A system for laser excitation of oxygen in silicateand oxide minerals has been designed, built, and tested. This system incorporates a new design that depends on a helium cryostat to freeze oxygen and to release it into a mass spectrometer under precisely controlled conditions. Analyses of meteorites and terrestrial oxygen isotope standards indicate that the system is capable of precise analyses of small samples and that its performance compares favorably with that of any system currently in operation.

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