ANALYTICAL DEVELOPMENTS ON OXYGEN THREE ISOTOPE ANALYSES USING A NEW GENERATION ION MICROPROBE IMS-1280. N. T. Kita[1], T. Ushikubo[1], B. Fu[1], M. J. Spicuzza[1], and J. W. Valley[1], [1]Department of Geology and Geophysics, University of Wisconsin-Madison, 1215 W. Dayton St., Madison WI 53706-1692 (noriko@geology.wisc.edu).

Introduction: Oxygen isotopes in meteorites show a wide range of mass dependent and mass independent isotopic fractionations and provide a unique tool for studying the early evolution of the solar system (e.g., [1]). Ion microprobes were used to determine large mass independent ^{16}O enrichments (10-50‰) in CAIs and chondrules, and minerals in carbonaceous chondrites (e.g., [2-4]). However, studies of oxygen isotopic variations at the level of a few ‰ in the μm to sub-mm scale in meteorite samples are very limited [5-6] because of difficulties in analyzing low natural abundance ^{17}O and ^{18}O isotopes ($^{18}O/^{16}O \sim 2.0052 \times 10^{-3}$ and $^{17}O/^{16}O \sim 3.83 \times 10^{-4}$) with sufficient precisions.

Here we report the analytical developments to achieve sub‰ precisions on both $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios by using a new generation ion microprobe CAMECA IMS-1280 at the University of Wisconsin-Madison. Results of meteorite data have been reported as conference abstracts [6-10].

Analytical conditions: The analytical conditions were modified from [5]; (1) primary Cs+ ions (+10kV) were focused to obtain higher intensity for a given beam size (typically, Ip=2.5nA for 10μm dia.), (2) electron gun was used for charge compensation with homogeneous electron density over the 60μm×100μm oval area, (3) Manual Z-focus of the sample stage and automated X-Y recentering of secondary beam were applied before the each analysis, (4) transfer optics of ×200 magnification was applied that allow transmission of secondary ions ≥70%, (5) NMR (Nuclear Magnetic Resonance) probe was used for magnetic field control with stability better than 5ppm over 10 hours, and (6) Oxygen three isotopes were detected simultaneously in multicollection mode. A single 3 oxygen isotope analysis takes ~7min consisting of presputtering (~100s), automatic beam centering (~60s) and integration of oxygen isotopes (~200s). The entrance slit width is ~70μm and exit slit width for multicollector FCs for ^{16}O and ^{18}O are 500μm (Mass Resolving Power, MRP=2,200), while that for ^{17}O using monocollector is adjusted to 200μm to achieve MRP~5000. The effect of OH interference on ^{17}O is estimated from the tailing of ^{17}O mass spectrum at -0.0036amu, which is typically ~20ppm of the peak and thus the OH correction is insignificant for most analyses of anhydrous phases (OH/^{17}O<1).

Multicollection FC mode: We obtained high secondary ion intensities, typically from 2×10^9 cps for Ip=2.5nA (10μm dia.) to 7×10^9 cps for Ip=13nA (20μm). In these conditions, ^{17}O signals are in the range of 10^6-3×10^6 cps, high enough to use a FC detector with noise level better than ≤500cps for 100-200s integrations (S/N ratio better than 0.5‰). Under the same conditions, FC noise level is better than 0.1‰ for ^{18}O with intensity of $(0.4-1) \times 10^7$ cps.

With highly stable relative gain between three FC amplifiers, the reproducibility of San Carlos olivine standards is better than 0.2‰ and 0.5‰ (2σ) for $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios, respectively. The 8-15 analyses of unknown samples are bracketed by 8 standard analyses (4 analyses before and after). We apply the external errors of the 8 standard analyses to determine the uncertainty of individual sample analyses. Within 5mm of the center of the 1-inch sample holder, the measured isotopic ratios do not show measurable artifacts correlating with the XY positions of the stage. Fig. 1 shows an example of repeated measurement of KIM5 zircon standard [9] where the high primary beam intensity was applied. The step in δ-values at 21 hours is caused by a change in IMF for the new sample; $\Delta^{17}O$ is not affected by mass-dependent fractionations.
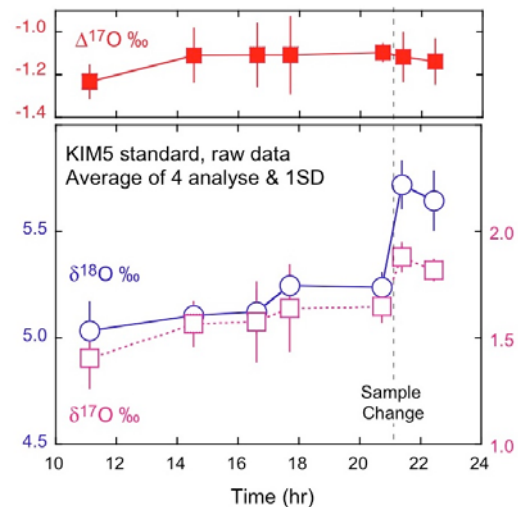

Fig. 1, Repeated analyses of KIM5 zircon standard [9]. The isotopic ratios were normalized to SMOW scale and shown as $\delta^{17}O$ and $\delta^{18}O$. The $^{16}O \sim 7 \times 10^9$ cps, allowing <0.2‰ precisions for both $\delta^{17}O$ and $\delta^{18}O$ measurements.

Multicollection FC-EM-FC mode: For 5µm diameter spot analyses, primary ion intensity was only 0.5nA. While ^{16}O and ^{18}O signals are detected by multicollector FCs, ^{17}O ions (~1.5×10^5 cps) are detected using an electron multiplier (EM) in pulse counting mode with low background level (<0.01cps). With this relatively high count rate, the EM detector gain would drift more than 1‰ after several analyses because of the aging of the first dynode. To avoid significant gain drift, the mono-collector was switched between EM and FC detectors every 14s and ^{17}O signals were collected for only 2s in each cycle. In this condition, the $^{17}O/^{16}O$ ratios of standard do not show any measurable drift through a day. The reproducibility of 0.5-1‰ (2σ) was obtained for both $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios, consistent with statistical errors.

IMF Correction: In order to evaluate the instrumental mass fractionation factor (IMF), we prepared a number of terrestrial standards including olivine, pyroxene, plagioclase, melilite, and spinel. Some are synthetic crystals (forsterite, åkermanite and gehlenite). However, it is not always easy to find mineral standards that are homogeneous in oxygen isotope ratio at the 0.1-0.2‰ level. First, we assess the homogeneity of potential standards ($\delta^{18}O$) by analyzing several ~mg sized fragments using via laser fluorination [11]. If samples are homogeneous at the 0.1‰ levels, ~20 randomly selected grains are mounted in epoxy resin for ion microprobe analyses to evaluate µm-scale homogeneity. When differences are small, the IMF is defined as the difference between measured ($\delta^{18}O)_M$ and true ($\delta^{18}O)_{VSMOW}$ obtained by laser fluorination;

$$\left(\delta^{18}O\right)_M = \left(\frac{(^{18}O/^{16}O)_M}{0.0020052} - 1\right)\times 1000 \quad (‰)$$

$$IMF = \left(\delta^{18}O\right)_M - \left(\delta^{18}O\right)_{VSMOW}$$

Through the course of study, we recognized that relative IMF between minerals is reproducible within analytical uncertainties (≤0.2‰). Most standards were mounted with San Carlos olivine to obtain a relative IMF. The measured IMF of San Carlos olivine is typically between 3-4 ‰. As shown in Fig. 2(a), plagioclase and pyroxene show strong matrix effects correlating with An and Wo contents, respectively, while olivine does not show measurable matrix effects for Fo_{100}-Fo_{60}. IMFs for other major silicate and oxide minerals as well as MPI-DING geological glass standards [12] are shown in Fig. 2(b). We observed IMF strongly correlated with SiO_2 and CaO contents among silicate minerals and glass standards. We obtained an empirical equation for IMF as a linear function of mo-

lar fractions of SiO_2, Al_2O_3, CaO, MgO, FeO, Na_2O and K_2O and applied this to estimate the IMF for glass in chondrules [8]. The difference between measured and calculated IMF for the glass standard was <0.5‰, within the limited range of chemical compositions.
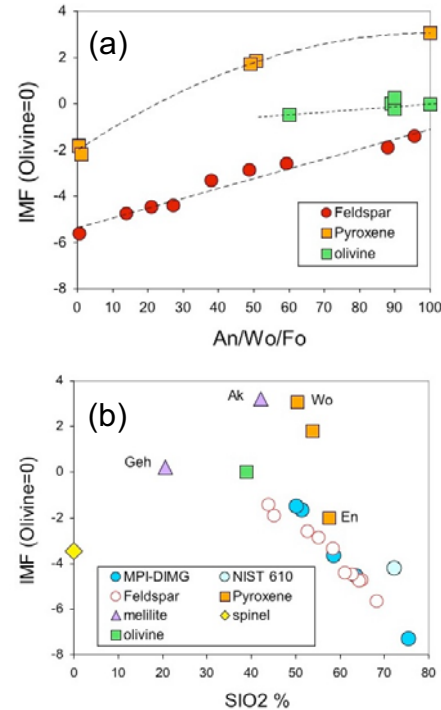

Fig. 2. IMF of mineral and glass standards relative to San Carlos olivine. (a) Matrix effect on mineral compositions. (b) Strong correlation of IMF with SiO_2 %.

Summary: Newly developed analytical techniques using the IMS-1280 ion microprobe allow us to determine accurate oxygen three isotope compositions at sub-permil levels from µm-scale areas in meteorite samples, which otherwise could not be determined. The technique is also applicable to sample return missions with a limited amount of samples, such as mineral grains from Stardust and Hayabusa missions to investigate oxygen isotope compositions of comets and asteroids.

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