Introduction: Analysis by ion microprobe can provide accurate and precise stable isotope ratios (±0.1-1‰) of pg to ng samples at 1-10 µm-scale in grain mount or thin section [1]. These capabilities cannot be matched by instruments on Mars, although robotic sample selection is important.

ALH84001: Secondary carbonate minerals in the Martian meteorite, ALH84001, have been intensely studied and variously interpreted. Several textural forms have been described including concentrically zoned “globules” (or concretions) with distinctive white magnesite rims, and “clots” of relatively homogeneous ankerite intergrown with glass and orthopyroxene (see [2]). The apparent continuum of Ca-Mg-Fe composition varying from near calcite to magnesite, X<0.2, have variable compositions [2]. Values of Mn are not continuous if Mn is considered and that δ18O, measured in situ from 30 micron spots by Cameca 4f ion microprobe, also correlates to texture (Fig. 1). Thus, there are at least two populations of carbonate. Globules were interpreted to form by aqueous precipitation at 20-190°C while clots may have formed by shock melting of globules [2].

Fig. 1. Carbonates in ALH84001. Globules, XCa <0.2, have variable δ18O from 3 to 27‰. Carbonate clots, XCa >0.4 have δ18O mostly from 3-7‰ [2].

Three oxygen isotopes have been measured by several studies of bulk silicate samples in Martian meteorites and consistently yield Δ17O = -0.3 [3]. Bulk analyses of carbonates have also yielded Δ17O values above the Terrestrial Fractionationation line (Δ17O=0), but values average 0.8±0.05‰, indicating that carbonates precipitated from fluids that exchanged with the Martian atmosphere and that the atmosphere is not in equilibrium with the silicate crust, attesting to the absence of plate tectonics and seafloor hydrothermal processes on Mars [4]. There have not been previous in situ analyses of Δ17O in Martian meteorites, in part because accuracy and precision were not sufficient to distinguish values from Earth from those on Mars, or Martian silicates from Martian carbonates.

Three-Oxygen Isotopes by Ion Microprobe: The Cameca IMS-1280 yields improved accuracy and precision for in situ analysis of δ18O and δ17O with a 15 µm spot [5]. After each analysis, 16OH was measured to correct for tailing under 17O (12-20ppm of 16OH). A series of carbonate standards were run to calibrate instrumental mass fractionation (IMF). SIMS analyses of carbonate were bracketed by analyses of orthopyroxene from ALH84001 (δ18O=4.99, Δ17O=0.32[3]), IMF in opx averages 0.03±0.13 permil (n=40, 1σ=0.02‰). Analyses were also made of terrestrial zircons, which were bracketed by analysis of the KIM-5 zircon standard (δ18O=5.09, Δ17O=0).

Results: Zircon analyses demonstrate the accuracy and precision of these in situ three oxygen isotope data. Values of Δ17O are 0 (by definition) ±0.11 (1σ, N=28, 1σ=0.02‰) for KIM-5 and -0.05±0.12 for 44 zircons with ages from 4.0 to 4.35 Ga (Fig. 2).

Values of δ18O range from 2.3 to 6.0 for carbonate in clots (Fig. 2b) and 13.9 to 24.6 in globules (Fig. 2a). As seen in previous studies, δ18O in globules increases with XMg [2]. Values of Δ17O average 0.46±0.20 (1σ) for clots, 0.61±0.36 for ankeritic domains of globules, and 0.96±0.16 for magnesite-rich domains including rims.

Discussion:
Terrestrial zircons. The detrital Hadean zircons are the only terrestrial materials that are similar in age to silicates and carbonates in ALH84001. There is no significant difference in Δ17O between KIM-5 which represents oxygen from the Earth’s mantle at ~0.1Ga and the Δ17O of Jack Hills (Western Australia) detrital zircons, which preserve values of oxygen isotope ratio from magmas that were contaminated by supracrustal oxygen at >4Ga in the Hadean [7]. Thus there is no evidence in these data for a secular trend in Δ17O on Earth for the mantle, crust, or hydrosphere.

Martian carbonates. Figs. 2 shows that the new in situ analyses of three oxygen isotopes from the Martian meteorite, ALH84001, are clearly distinct in Δ17O from those for terrestrial samples, proving that carbon-
ates did not originate on Earth. The average for all samples is close to that reported for bulk analyses [4]. The data are consistent with heterogeneity of ~0.5 permil in $\Delta^{17}$O within and among carbonates in ALH84001. This hypothesis is supported by the bulk analysis of our new in situ analyses. If carbonates are variable, this would confirm the hypothesis that there are multiple generations of carbonate formation with globules formed by low temperature aqueous precipitation [2].

Water in Martian carbonates. Bulk analysis of Martian meteorites shows significant H$_2$O contents with elevated D/H. In situ analysis of $\delta$D in ALH84001 carbonates yields values from +182 to 2092 permil, but the 60µm spot size was too large to test for zonation [8]. High D/H is confirmed by micro

Fig. 2. In situ ion microprobe analyses of $\delta^{17}$O vs. $\delta^{18}$O VSMOW in carbonates from globules ($\delta^{18}$O>13) and clots ($\delta^{18}$O<6) in ALH84001 (large blue squares) and from terrestrial zircons (small red triangles). Zircons with $\delta^{18}$O near 5 are the standard, KIM-5. All values above 6 permil are >4.0 Ga detrital zircons from the Jack Hills. 2a. shows all data. 2b. enlargement showing only data for carbonate clots in ALH84001 and zircons.

Fig. 3. Ion microprobe analysis of $\delta^{18}$O VSMOW vs. count rate on OH normalized to oxygen for carbonates in ALH84001. Carbonate globules ($\delta^{18}$O>13) contain significantly more OH than clots ($\delta^{18}$O<6).