

THE EFFECTS OF THERMAL METAMORPHISM AS RECORDED IN CO3.0 THROUGH CO3.2 CHONDRITES. S. B. Simon¹, S. R. Sutton^{2,3}, A. J. Brearley⁴, A. N. Krot^{5,6}, and K. Nagashima⁵. ¹Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131(sbs8@unm.edu). ²Dept. Geophysical Sci., The University of Chicago, Chicago, IL 60637. ³Center for Advanced Radiation Sources (CARS), The Univ. of Chicago. ⁴Dept. Earth and Planetary Sci., Univ. of New Mexico. ⁵HIGP/SOEST, Univ. of Hawai'i, Honolulu, HI. ⁶Geosci. Inst./Mineralogy, Goethe University Frankfurt, Germany.

Introduction: Even the least-altered chondrites show the effects of secondary processes on their parent bodies [e.g. 1,2]. It is important to understand these effects not only to better understand early planetary processes but also to recognize the resulting alteration of nebular materials, such as chondrules and refractory inclusions. We have compared properties of CO3.0 carbonaceous chondrites (ALHA 77307, DOM 08006) with CO3.1 chondrites (MIL 090025, DOM 08004) and a CO3.2 (Kainsaz). Here we combine published and new observations that document changes in mineralogy, mineral chemistry, O-isotopic compositions, valence states of Cr and Ti, and the coordination environment of Ti, giving an improved picture of the effects of the initial stages of metamorphism on the CO parent body as recorded in available samples.

Methods. Polished thin sections of the chondrites identified above were examined with the TESCAN LYRA3 scanning electron microscope at The University of Chicago and phases of interest were analyzed with a Cameca SX-50 electron microprobe. The oxygen isotopic compositions of phases in selected refractory inclusions were determined by secondary ion mass spectrometry (SIMS) with the Cameca ims-1280 ion microprobe at the University of Hawai'i according to the methods of [3]. Valences of Ti and Cr were determined by X-ray absorption near-edge structure (XANES) spectroscopy. XANES spectra were collected using the GSECARS X-ray microprobe in fluorescence mode, with a 1 μm X-ray beam. Valences of Ti were determined following the methods of [4] and are reported as values between 3 and 4, representing averages for the analytical volumes, with precisions based on spectral fitting uncertainties. The valence of Cr was determined using Fe-free glass standards with Cr^{3+} or Cr^{2+} as in [5]. For each analysis spot, for both Ti and Cr, spectra were collected at three or four different orientations and merged to minimize orientation effects. Average 1σ errors for valence measurements are ± 0.12 (Ti) and ± 0.05 (Cr).

Results. Observations and analytical results from the investigations are summarized below.

Secondary mineralization. Effects of hydrothermal alteration are seen in CO3.0 chondrites [1] but to a limited extent compared to higher petrologic types. In

DOM 08006 there is some replacement of Fe,Ni metal by magnetite in chondrules and matrix, and Fe,Ni-carbide-magnetite veins occur [6]. In addition to magnetite and phyllosilicates, CO3.1 chondrites, including DOM 08004, contain veins of fayalite in the matrix and fayalitic overgrowths on forsteritic olivine, with sharp contacts [1,2,6].

Cr and Ti valences. We previously reported valence results for ALHA 77307 and Kainsaz [7] which show that both Ti and Cr in olivine (isolated grains and in chondrules) are oxidized in Kainsaz compared to that in ALHA 77307. New data are now available for MIL 090025 (CO3.1) that are intermediate between those for ALHA 77307 and Kainsaz; thus, a clear trend of increasing oxidation, recorded by both Cr and Ti, is observed in the CO3 chondrites in the order ALHA-MIL-Kainsaz (Fig. 1). The proportions of Ti cations in tetrahedral sites in olivine are correlated with Ti valence in these samples (Fig. 2).

Oxygen isotopic compositions. Most CAIs in DOM 08006 (CO3.0) and Y-81020 (CO3.0) are isotopically uniform ($\Delta^{17}\text{O}$ from -25 to -20‰) within uncertainty of SIMS measurements ($2\sigma \sim \pm 2\text{‰}$) [6, 8, 9]. In contrast, CAIs in DOM 08004 (CO3.1) and Kainsaz (CO3.2) are isotopically heterogeneous [6, 8, 9]. The heterogeneity is mineralogically controlled: melilite and grossite are ^{16}O -depleted ($\Delta^{17}\text{O}$ up to 0‰) relative to hibonite, spinel, Al-diopside and forsterite, which have ^{16}O -rich compositions similar to CAIs in DOM 08006 and Y-81020. Oxygen isotopic compositions of grossite and melilite overlap with those of aqueously-formed magnetite in Y-81020 (CO3.0) [10] and magnetite and fayalite in MAC 88107 (CO3.1-like) [11], suggesting that melilite and grossite experienced O-isotope exchange with an aqueous fluid on the CO parent asteroid. The bulk $\Delta^{17}\text{O}$ values of CO3 chondrites also increase with increasing petrologic type [12, 13].

Discussion: The changes recorded by the progression from type 3.0 through type 3.2 CO chondrites include: oxidation of Fe, Cr and Ti; changes in Cr contents of ferroan olivine [14]; formation of secondary phases including fayalite, phyllosilicates, magnetite and Fe,Ni carbides; and O-isotope exchange. Assuming these changes resulted from fluid-assisted meta-

morphism, as previously inferred for CO chondrites [6,11], they indicate that the type 3.1 and 3.2 chondrites were altered at higher temperature, with higher volume diffusion rates, than type 3.0 chondrites. Diffusion rates were too slow under the CO3.0 alteration temperatures to induce the changes seen in types ≥ 3.1 chondrites. The fluid was very ^{16}O -poor compared to the nebular reservoir from which most refractory inclusions formed.

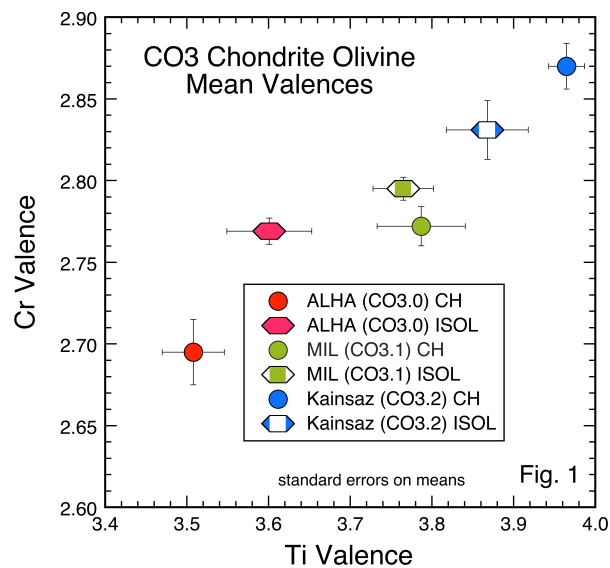


Fig. 1. Plot of mean Cr and Ti valences measured by XANES in olivine in ALHA 77307 (type 3.0), MIL 090025 (3.1), and Kainsaz (3.2).

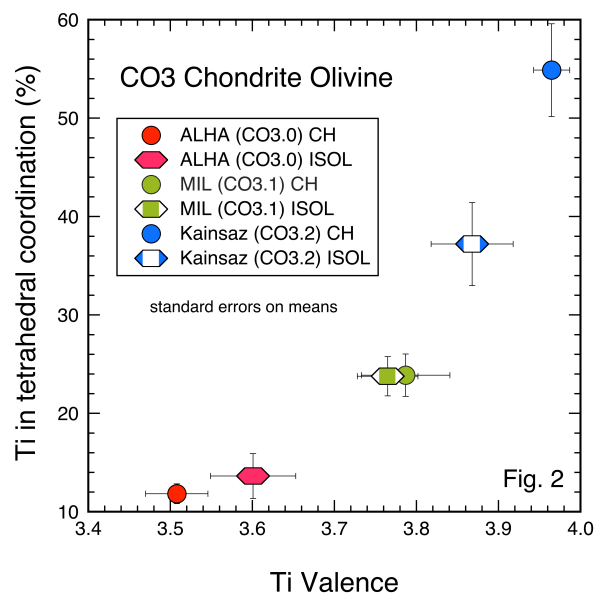


Fig. 2. Percentages of Ti cations in tetrahedral coordination vs. Ti valence state in chondrule (CH) and isolated (ISOL) olivine.

The Ti_2O_3 - TiO_2 buffer curve occurs at very low f_{O_2} , $\sim \text{IW}-5$, so trivalent Ti is not expected to occur in FeO-bearing silicates such as olivine and pyroxene. As Figs. 1 and 2 show, however, it is found in chondrule olivine, indicating that a) some chondrules had reduced precursors; and b) the valence of Ti is not easily reset, as Ti^{3+} survived chondrule-forming events in environments in which some Fe occurs as FeO. It is therefore not surprising that the limited extent of metamorphism experienced by CO3.0 chondrites caused little or no oxidation of Ti. The carbide-magnetite assemblages in them are thought to have formed by low-temperature reaction of Fe metal with $\text{H}_2\text{O}+\text{CO}$ fluid at low water/rock ratios [15], yielding $\text{Fe}_3\text{C} + \text{Fe}_3\text{O}_4 \pm \text{CO}_2$ [1]. Unlike type 3.0 chondrites, type 3.1 chondrites contain fayalite, indicating a relatively higher temperature environment, $\sim 100 - 300^\circ\text{C}$, based on the stability of fayalite [16]. In both ordinary [17] and CO chondrites, it is possible that oxidation occurred as heating continued and C contents decreased.

We have also seen previously that the proportion of Ti in tetrahedral sites in olivine in ordinary chondrites increases with petrologic type, with sharp increases seen between types 3 and 4 [18]. Here we see an increase from type 3.0 through 3.2 (Fig. 2). As in the ordinary chondrites, these increases are correlated with oxidation of Ti and may be a consequence of increases in $\text{Ti}^{4+}/\text{Ti}^{3+}$ ratios (Fig. 1), as Ti^{4+} can enter tetrahedral sites in olivine and Ti^{3+} does not.

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