RESPONSE OF Cr and Ti VALENCES TO THE ONSET OF METAMORPHISM IN CO CHONDRITES.

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Introduction: An important indicator of the pristinity of chondrites is the abundance and distribution of Cr in ferroan olivine chondrule phenocrysts. As first shown by [1], olivine in the least metamorphosed ordinary and CO chondrites has relatively high, uniform Cr_2O_3 contents. With increase in grade from 3.0 to 3.1, and standard deviations of analysis populations increase, and with further metamorphism through type 3.2, both Cr_2O_3 contents and standard deviations of analysis populations decrease. This relationship is a major diagnostic tool in the classification of low-grade chondrites, but the process that causes this behavior is not understood. Neither the valence of Cr in the olivine nor the phases that Cr redistributes into with the onset of metamorphism are known. Here we report the initial results of a study of Cr and Ti valences in olivine in two low-grade chondrites, ALHA77307 (CO3.0) and Kainsaz (CO3.2).

Methods: One polished thin section of each sample was mapped with a scanning electron microscope. Chondrules and isolated grains selected for study were analyzed by electron probe. Valences of Cr and Ti plus Ti coordination data were obtained 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. The valence of Ti was determined following the results of [2], who demonstrated that Ti K-edge XANES spectra of pure Ti^{4+}-bearing minerals fall into distinct valence-coordination clusters on a plot of pre-edge peak intensity *vs.* energy. The valence of Cr was determined using Fe-free glass standards with Cr^{3+} or Cr^{2+} as in [3]. For each analytical spot, spectra were collected at two to four different orientations and then merged to minimize orientation effects. Reported valences are averages for the analytical volumes and are between 2 and 3 for Cr and between 3 and 4 for Ti.

Results: As illustrated in Fig. 1, differences were found between ALHA77307 (ALHA) and Kainsaz and, within each sample, between chondrule olivine and isolated grains in the matrix. Valences of Cr tend to be reduced in ALHA chondrules relative to the isolated grains in that sample, but in Kainsaz, Cr is reduced in the isolated grains relative to chondrule olivine. Both Ti and Cr are reduced in ALHA chondrules relative to Kainsaz chondrules. Another difference is that subhedral to euhedral chromite grains 10-20 µm across are common inclusions in Kainsaz olivine and are rare in ALHA. In both samples a) the range of the valence of Ti in the chondrules is within the range of the isolated grains; and b) the range of Cr valence in the chondrules is wider than that in the isolated grains, extending to more reduced values in ALHA and to more oxidized values in Kainsaz (Fig.1). Proportions of Ti in tetrahedral coordination tend to be higher in Kainsaz olivine (21-58%) than in ALHA olivine (1-31%).

Discussion: There is evidence that during the early stages of metamorphism of ordinary chondrites, in which they were modified from type 3 to type 4, reduction of oxidized Fe occurred [4]. The present data, however, show no indication of reduction with increase in type from 3.0 to 3.2, and are difficult to explain in the context of a metamorphic sequence involving ALHA77307-like material as a precursor. Although some oxidation of Cr has occurred in Kainsaz [5], it is metal-rich, arguing against pervasive oxidation in its history. Alternatively, the relatively oxidized Cr valence in its olivine might result from diffusion, since mobility of Cr in Kainsaz is indicated by Cr-rich veins in olivine and the presence of chromite, although the details of such a process remain to be investigated.

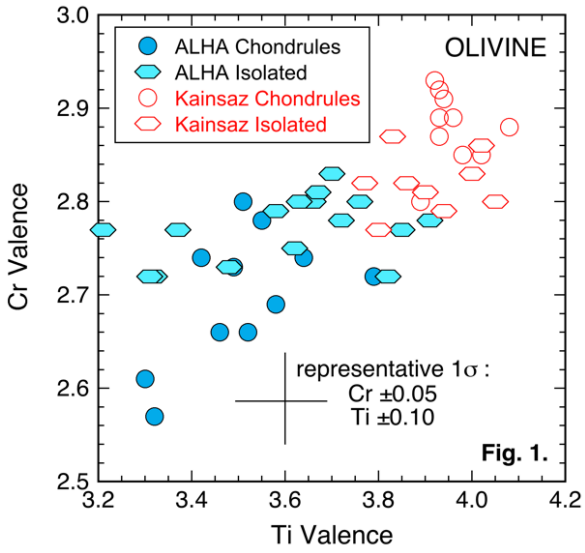

Fig. 1.

The clear presence of Ti^{3+} in ALHA chondrule olivine (average valence 3.51±0.13) supports inferences from similar findings in Semarkona [6] that at least some chondrules had reduced precursors and that Ti valence is not easily altered. In contrast, chondrule olivine in Kainsaz contains little to no Ti^{3+} (average valence 3.97±0.06).

References: [1] Grossman J. N. and Brearley A. J. (2005) *Meteoritics & Planetary Science* 40:87–122. [2] Farges F. et al. (1997) *Phys. Rev. B*, 56, 1809-1819. [3] Goodrich C. et al. (2013) *Geochimica et Cosmochimica Acta* 122:280-305. [4] Menzies O. et al. (2005) *Meteoritics & Planetary Science* 40:1023-1042. [5] Grossman J. N. and Rubin A.E. (1999) *LPS XXX*. Abstract #1639.[6] Simon S. B. et al. (2008) *LPS XXXIX*. Abstract #1352.