COMPLEXITIES OF INCLUSIONS IN EXTRATERRESTRIAL CHROME-SPINEL FROM THE JURASSIC REVEALED BY STEM-EDX. C. E. Caplan[1,2*], G. R. Huss[2], H. A. Ishii[2], J. P. Bradley[2], P. Eschbach[3], B. Schmitz[4,2], and K. Nagashima[2], [1]Department of Geology and Geophysics, University of Hawaiʻi at Mānoa, 1680 East-West Road, Honolulu, HI 96822, [2]Hawaiʻi Institute of Geophysics and Planetology, University of Hawaiʻi at Mānoa, 1680 East-West Road, Honolulu, HI 96822, [3]Electron Microscopy Facility, Oregon State University, 2900 SW Campus Way, Corvallis, OR 97331, [4]Department of Physics, University of Lund, P.O. Box 118, Lund SE-22100, Sweden. *caplance@hawaii.edu.

Introduction: As part of our study to determine meteorite infall over geologic time using remnant extraterrestrial chrome-spinels [1-3], we are studying silicate inclusions in the spinels as a means of classifying the parent meteorites. Awlmark and Schmitz [2] showed that fayalite (Fa) and ferrosilite (Fs) contents of inclusions of olivine and Ca-poor pyroxene, respectively, in chrome-spinels can help distinguish between meteorite types. Classification of chrome-spinels from ordinary chondrites is relatively straightforward using element and oxygen-isotope abundances, but it is difficult to discriminate between H, L, and LL chondrites using these parameters. Reliable Fa and Fs contents for inclusions would be valuable in the classification process.

We observed inclusions in 3 of 62 grains studied to date. We previously reported on two inclusions from one ordinary-chondrite chrome-spinel [4]. Unfortunately, the inclusions were not classifiable using Fa or Fs due to severe terrestrial alteration. Here we report on inclusions from another chrome-spinel grain. This grain is from either an L or LL chondrite, based on chrome-spinel element and oxygen-isotope abundances. Inclusions in this grain appear to have undergone only limited terrestrial alteration.

Experimental: Chrome-spinels for this study were recovered at Lund University from Spanish limestone; see [1] for methods. The grains were epoxy mounted at the University of Hawaiʻi (UH) in quarter-inch-diameter steel cylinders. The mounts were ground flat, polished using a series of diamond lapping papers, and carbon coated for analysis. Element abundances were determined using the JEOL JXA-8500F field emission electron microprobe at UH. . Oxygen-isotopes were determined using the Cameca ims 1280 at UH.

Using the UH FEI Helios 660 dual beam FIB-SEM at 15 kV, major- and minor-element abundances of inclusions were measured to identify olivine and pyroxene inclusions. Analyses before sectioning may have sampled not only the inclusion but also some of the surrounding chrome-spinel because the depth of the inclusions was unknown. Inclusion 1 was elongated in the plane of polishing with minor axis of 2.30 µm and major axis of 3.80 µm, and inclusion 2 was round with a diameter of 1.77 µm. A Pt protective layer was deposited over each inclusion before preparing standard FIB sections by 30 kV Ga^+ ion milling. The sections were FIB-polished at 5 kV to reduce amorphous kerf.

We used the UH FEI 80-300 kV Titan dual C_s-corrected and monochromated (scanning) TEM, capable of subnanometer-scale resolution, to image and analyze element chemistry at 300 kV. The pyroxene compositions of the inclusions (Fig. 2) were determined using a central box area, clear of edge alteration. Element maps (Fig. 1) were collected at 200 kV using the Oregon State University 80-200 kV Titan STEM with ChemiSTEM capability (4 EDX detectors for ~0.7 sr solid angle). Pixel sizes of 9 and 17 nm and total acquisitions of 30-45 minutes were sufficient to produce good signal to noise. Spectra from pixels in selected regions were summed, background-corrected and fit to extract element compositions.

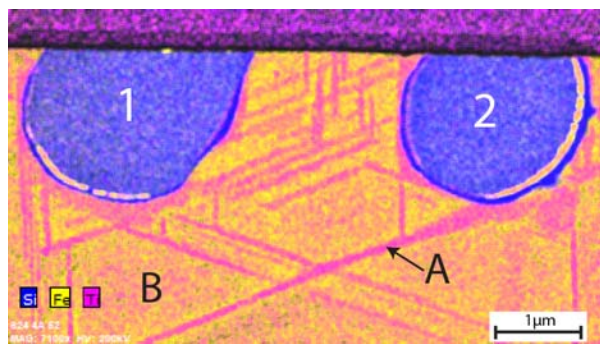

Figure 1: Overlaid STEM-EDX element maps of two pyroxene inclusions in chrome-spinel (blue=Si, yellow=Fe, magenta=Ti).

Results and Discussion: The inclusions in the FIB section are separated by ~ 2µm, rounded in shape, crystalline in structure, and rimmed with iron oxide (partial) and silica (Fig. 1). Inclusions 1 and 2 are orthopyroxenes with compositions of ~ $(Mg_{0.75}Fe_{0.20})SiO_3$ and ~ $(Mg_{0.75}Fe_{0.15})SiO_3$ (with trace amounts of Ti, Al, and Cr). The ferrosilite values are $Fs_{20.1}$ and $Fs_{17.6}$, respectively; inclusion 1 is L-chondrite-like and inclusion 2 is H-chondrite-like (Fig. 2). The difference in classification is likely invalid because they both originate from the same chrome-spinel grain, which is classified as coming from an L- or LL-chondrite. The most likely explanation is secondary alteration of the inclusions, probably at low temperature during their terrestrial history.

Both inclusions show a rim of Fe-oxide at the boundary with the spinel. Figure 3 shows a line scan of Fe content in inclusion 2 from the center of the inclusion into the surrounding chrome-spinel. The Fe content of the inclusion is generally constant until ~ 0.7 µm and then slowly decreases to form an Fe-depleted zone before the Fe rim. This depletion of Fe (and in some limited areas of surrounding chrome-spinel) suggests that at least some of the Fe in the Fe-oxide came from the pyroxene (and chrome-spinel).

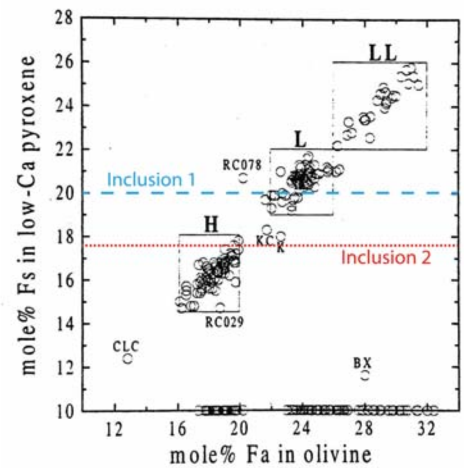

Figure 2: Fa vs. Fs plot (modified from [5]) for ordinary-chondrite silicates, with measured compositions of inclusions 1 ($Fs_{20.1}$) and 2 ($Fs_{17.6}$) overlaid.

The smaller size, the more-pronounced Fe oxide rim, and the zone of Fe depletion along the edge of inclusion 2 suggest that this inclusion did not retain its original composition. The pyroxene in this inclusion was probably originally more Fe-rich. Inclusion 1 shows a similar, but less extensive Fe oxide rim, and the hint of a similar Fe-depletion at the edge. It is likely that both inclusions started out with more-Fe-rich compositions consistent with an L-chondrite host, but that they were leached of Fe to different degrees resulting in different compositions.

The chrome-spinel surrounding the two silicate inclusions has exsolved into two regions (Fig. 1), with the exsolution pattern concentrated near the inclusions. A few exsolution bands reach ~3 µm below the inclusions, but the majority are visible in Figure 1. The region labeled A consists of bands relatively enriched in Ti and Cr, while the dominant spinel (Region B) has a more Fe, Mg, and Al rich composition. Table 1 shows representative compositions of the two regions.

Region	O	Mg	Al	Ti	Cr	Fe
A	51.67	1.00	3.55	3.52	29.91	10.33
B	51.57	1.63	3.91	0.75	28.01	14.13

Table 1: Compositions of the two regions (atomic %) measured by STEM-EDX. Region A is a spinel band, and Region B is the surrounding spinel.

Chrome-spinels are metamorphic minerals [6] and may have enveloped small amounts of pyroxene during their growth. A possible explanation for exsolution in spinel near the inclusions is strain development. During cooling from peak metamorphic temperature, the inclusions may have shrunk more rapidly than the chrome-spinel due to differences in thermal expansion or perhaps via a structural polymorph change in the pyroxene [7]. The change in relative volume would have produced a variable strain field around the inclusions that could drive exsolution of the Ti- and Cr-rich regions. The shrinkage of the pyroxene inclusions could also result in gaps around the inclusions that could permit water to enter and alter the pyroxene.

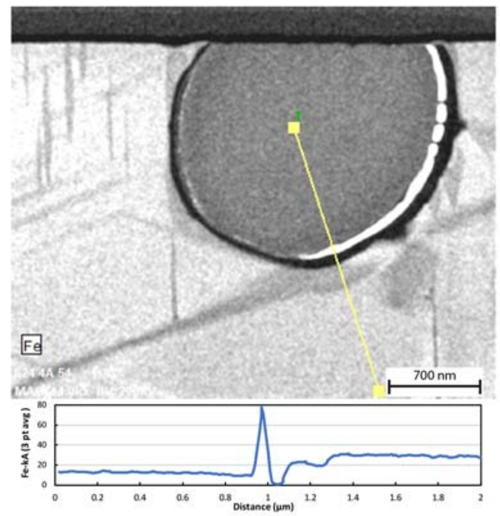

Figure 3: (Upper) Fe element map and (lower) Fe line scan on inclusion 2 show variation in Fe content from inclusion center to the surrounding chrome-spinel.

Conclusions: In this study, STEM-EDX analyses gave reliable inclusion compositions for host meteorite classification by removing the potential for analysis contamination by surrounding chrome-spinel. But the inferred classifications were inconsistent between the two inclusions. The section also revealed alteration rims on the inclusions. The alteration most likely caused variable Fe depletion of the inclusions, thus changing the inferred classification of the host meteorite. This work demonstrates that the use of silicate inclusion compositions in chrome-spinels as means to classify ancient ordinary chondrites must account for potential effects of alteration after the inclusions formed. We will continue to study inclusions in chrome-spinels in order to recognize and understand these effects.

References: [1] Schmitz, B. (2013) *Chem. der Erde,* 73:117-145. [2] Alwmark C. and Schmitz B. (2009) *GCA,* 73:1472–1486. [3] Alwmark C. et al. (2011) *MAPS,* 46.8:1071-1081. [4] Caplan C. E., et al. (2017) *MetSoc* LXXX, Abstract #6165. [5] Brearley A. J. and Jones R. H. (1998) *MSA*, 3-1:3-398. [6] Huss et al. (2006), *Meteorites and the Early Solar System*, 567-586. [7] Smith J. R. (1974) *Am. Min.* 59, 345-352. Supported by NASA grant NNX16AQ08G (GRH).