The purpose of this Electronic Annex is mainly to add a variety of figures that, due to considerations of length and/or color-reproduction costs, could not be included in the regular paper. We also provide here some additional discussion of the technique of using EPMA and stoichiometry to constrain Fe$^{3+}$ in NWA 5738 spinels.
Fig. EA-1. Macroscopic view of NWA 5738. Note many scattered patches of rust, mostly derived from Fe-metal, and the dark grey shock-glassy vein (diagonal from “southwest” to “northeast”) in the left-central portion of view.
Fig. EA-2. Macroscopic view of a small piece of NWA 5738. White object is 1 cm$^3$. 
Fig. EA-3. Backscattered electron (BSE) image of thin section NWA 5738-2, showing an area where the texture is mildly variolitic.
Fig. EA-4. Transmitted light, crossed-nicols view of “clouding” in a 170 µm wide view of the same NWA 5738-1 pyroxene seen in Fig. 10b. Note that the tiny “cloudy” exsolutions tend to show elongate shape, and consistent orientation relative to the host low-Ca pyroxene’s crystal axes. Portions of curvy microveins are seen as the much larger opaque grains in discontinuous trains within left half of the view.
Fig. EA-5. Compositions of NWA 5738 spinels on an Al-Cr-Ti ternary diagram. Fields shown for terrestrial spinels are from Moreno et al. (2001). The spread in Cr/Al ratio at the low-Ti end of the eucrite range, not apparent in the Mayne et al. (2009) data, is based on Yamaguchi’s (2000) field for low-equilibration (type 1-2) eucrites.
Fig. EA-6. BSE image of anomalous enclave along edge (right, black) of thin section NWA 5738-1. View is 0.25 mm wide.
Fig. EA-7. BSE mosaic-image of thin section NWA 5738-1, showing a fault surface (arrows) extending over 4 mm. The image is a composite of four high-resolution tiles along the fault, over a low-resolution backdrop. Large bright grain in upper right is a relatively equant-amorphous Fe-metal.
Fig. EA-8. Reflected-light photomicrograph of Kapoeta clast CF4 (acquired as preparation for the study of Warren et al., 1982). View is 5 mm across. Pyroxene laths are up to 2.4 mm long, plagioclase (darker grey) laths up to 1.3 mm long.
Fig. EA-9. Compositional diversity among unbrecciated and monomict-brecciated eucrites: Yb (incompatible) vs. Sc (mildly compatible with pyroxene). The overall trend is a loose positive correlation. NWA 5738 plots at the extreme high-Yb end of a horizontal subtrend (the “Stannern Trend”; cf. the very similar Fig. 7).
Fig. EA-10. BSE images of a glassy shock-melt vein in NWA 5738-6. The glassy groundmass is a medium grey, intermediate between the other two major components: pyroxene (light grey) and plagioclase (dark grey). Blacks are crack-voids, although minor silica is a grey only barely perceptibly lighter than black. Note rounded shapes of most of the entrained grains.
Fig. EA-11. (a) BSE mosaic-image of a shock-glassy vein in NWA 5738-8. This vein’s boundaries are jagged and in places indistinct, but its medium grey groundmass (of glass and devitrified glass) dominates the lower-central portion of this view. The vein gets thinner and angles rightward near the top of the view. (b) and (c) High-magnification BSE images of the shock-glassy vein in (a). Note rounded shapes of most of the entrained grains.
Fig. EA-12. BSE mosaic-image of a large pyroxene with many curvy microveins, which are uncommonly rich in Cr-spinel. (The same grain is featured in Figs. 12b and EA-4.) The main microvein phases in this locale are Ca-plagioclase (dark grey), Fe-olivine (light grey) and Cr-spinel (slightly lighter grey).
Fig. EA-13. NWA 5738 spinels: cation sums versus Fe$_2$O$_3$ implied by stoichiometry. Open symbols represent analyses that imply zero Fe$_2$O$_3$, but are arbitrarily plotted at 0.2 wt%.

Fig. EA-14. NWA 5738 spinels: approximate $f$O$_2$ versus Cr/(Cr+Al).
Fig. EA-15. Cross-nicols optical microscopic image of part of the Fe-metal vein of Fig. 13c. The metal and adjacent Fe-oxides appear as vaguely margined near-horizontal opaque, but this view clearly shows how the metal filled a fracture that cut through the middles of two large pyroxene laths (mostly green and blue; with their similarly oriented systems of augite lamellae, black). Note that the metal vein is truncated by the edge of the thin section (left).
Fig. EA-16. BSE image of “sawtooth” pyroxene (Figs. 18 and 19) and some of its enveloping Fe-metal (white). Fe-metal is uncommonly fresh in this area, but some Fe-oxide (light grey) is visible near lower left corner, along left edge of the pyroxene, and along edges of plagioclase (darkest phase). Note that two tongues of metal extend deep into the right side of the pyroxene, along boundary between primary low-Ca pyroxene and medium-Ca (now finely exsolved) pyroxene; and within the pyroxene are several inclusions of metal that may related to the lower of these tongues.
Fig. EA-17. BSE image-pair of an uncommonly large metal clump in NWA 5738-1: Images use two different brightness/contrast settings. Upper image is best for showing the relationship of metal (white) to slightly less bright phases, such as Fe-oxide, ilmenite, FeS; lower image better shows the distribution of the silicates, mainly pyroxene (medium grey) and plagioclase (dark grey, including the large grain, or half-grain, almost enveloped by the metal).
Fig. EA-19. BSE image-pair showing a metal clump of fairly typical size and shape in NWA 5738-1: Images use two different brightness/contrast settings. Upper image is best for showing the relationship of metal (white) to slightly less bright phases, such as Fe-oxide (mottled medium-grey; especially common at “bottom” of the metal) and ilmenite (arrows; equant grains to right of the metal); lower image better shows the distribution of the silicates, mainly pyroxene (medium grey) and plagioclase (dark grey), but also including silica (darker grey, along “southwest” margin of the metal).
Fig. EA-20. BSE image of a large, complex-shaped (and as-yet little studied) metal clump (white) in NWA 5738-2.
Fig. EA-21. BSE images of NWA 5738-5: In (a), note large metal clump in lower left and far smaller one in upper right. Metals are white, not to be confused with scattered very light grey additional opaques, mostly ilmenite. In (b), the large metal is seen to be intergrown with a variety of phases, mostly pyroxene but including apatite (arrows) and plagioclase (dark grey), of which some, but not most, has a Na-poor (secondary) composition.
Fig. EA-22. Results from direct WDS measurement of oxygen in Fe-oxides associated (as apparent weathering products) with Fe-metal in NWA 5738.

NB: Oxygen measured *independently* with WDS spectrometry.
Usage of EPMA/stoichiometry to estimate Fe$_2$O$_3$ in spinel

Among the many papers (e.g., Kamperman et al., 1996; Bosi et al., 2004) that have noted a need for caution in the application of EPMA/stoichiometry to measure Fe$_2$O$_3$ in spinel, probably the most detailed and insightful discussion is that of Wood and Virgo (1989). These authors emphasized that for stoichiometric spinels, inadequate analytical accuracy is far more worrisome than inadequate precision (and for major elements they based their precision estimate on count durations of only 5 seconds). Systematic errors, especially those related to the choice of EPMA correction method (e.g., ZAF), can strongly influence the implied Fe$^{3+}$ result.

As discussed by Wood and Virgo (1989) and Wood (1991), the elements with the greatest accuracy issues are light elements, mainly Mg and Al, for which correction factors for x-ray absorption (the “A” in ZAF) are especially large. The data evaluated by Wood and Virgo were for a set of 20 Al-Mg spinels, with Al$_2$O$_3$ ranging from 30 to 64 wt% and MgO ranging from 16 to 21 wt%. (In terms of molecular proportion, on average Mg and Al are nearly equal in these spinels; and Mg may be the bigger accuracy concern, because unlike Al, Mg has a cation valency far from the stoichiometric-spinel average of 8/3.) In contrast, the NWA 5738 spinels have Al$_2$O$_3$ no higher than 10 wt% and practically negligible MgO. Clearly, the accuracy concerns noted by Wood and Virgo (1989) are less severe in relation to the spinels of NWA 5738.

We do admit, due to the limited accuracy of EPMA, our derived Fe$_2$O$_3$ and f$O_2$ calibrations are approximate. But the method’s precision appears nonetheless adequate to define Fe$_2$O$_3$ and f$O_2$ being considerably higher in the secondary spinels than in the primaries; and to show that among the secondaries, Fe$_2$O$_3$ and f$O_2$ anticorrelate with temperature and with Mg/Fe (Fig. 16). We obtained our spinel analyses in two consecutive probe sessions, each with a subequal mix of primary and secondary spinels. Wood (1991) acknowledged that with suitable standards to assure accuracy, the EPMA/stoichiometry technique may be useful for oxygen thermobarometry. In the case of NWA 5738, the primary spinels are effectively internal accuracy-check standards, because all primary-igneous HED materials have f$O_2$ close to IW-1 (Gooley and Moore, 1976; Stolper, 1977; Hewins and Ulmer, 1984; Wadhwa, 2008). Moreover, relative f$O_2$ in comparison to the primary-igneous f$O_2$ is of greater concern to us than the absolute f$O_2$.

Kamperman et al. (1996) emphasized that many terrestrial spinels are apparently far from stoichiometric, i.e., they have abundant cation vacancies. In deriving our Fe$_2$O$_3$ results we assume that the NWA 5738 spinels are all stoichiometric. But if the NWA 5738 secondary grains are to varying extents nonstoichiometric, that itself would be noteworthy. Crystal site vacancies may develop due to a deviation in some intensive variable, such as pressure (but the scope for such variations is vastly lesser in an asteroid), or due to unusual cation valencies such as Cr$^{4+}$ or Mn$^{3+}$ (Kamperman et al., 1996). But such unusual valencies would by themselves imply a high f$O_2$. Bosi et al. (2004) found a strong correlation ($r = 0.998$) between vacancy content and Fe$^{3+}$ among nonstoichiometric spinels.

Among our 24 primary spinel analyses, the total range in measured cations/4O is 2.991 to 3.006, the mean (and median) is 3.002, and the standard deviation ($\sigma$) is 0.0041. Considering that these data were obtained from a set of broadly similar spinels from a single eucrite in consecutive probe sessions, there is nothing remarkable about that precision. For comparison, the data set of Mayne et al. (2009) for spinels from 25 different eucrites has $\sigma = 0.0048$ cations/4O; and Day et al. (2012) published data sets with $\sigma = 0.0042$ for 28 spinel analyses from ALH 77256, and $\sigma = 0.0035$ for 51 spinel analyses from MIL 07001 (both diogenites). Returning to our own data, among 35 secondary
spinel analyses, the median is 3.0162, and the total range is 3.007 to 3.024; i.e., 1.9 to 6.0 σ above the primary-spinel mean (Fig. EA-13). Ignoring the possibility of systematic bias-error (discussed below), our observed σ of 0.0041 cations/4O, in combination with the slope for the secondary-spinel data on Fig. EA-13, corresponds to a nominal 1-σ uncertainty in the implied Fe₂O₃ of 0.38 wt%.

True uncertainty for our Fe₂O₃ results is admittedly greater than this nominal 0.38 wt%, but probably not by some enormous factor. Lucas et al. (1988) compared results from determination of Fe₂O₃ in a set of spinels by the EPMA/stoichiometry-based approach against results obtained by Mössbauer spectroscopy. As noted by Wood and Virgo (1989), one problem with comparisons between Mössbauer and EPMA results is that heterogeneities such as lamellae of different spinels may be resolved by EPMA, but analyzed as mixtures in the larger samples used for Mössbauer. Lucas et al. (1988) were careful to choose their 5 spinel grains “on the basis of their freedom from inclusions and lack of alteration” (also, like the NWA 5738 spinels, these spinels are relatively poor in MgO, 11-13 wt%, and Al₂O₃, 6-23 wt%). These spinels yielded Mössbauer Fe₂O₃ results of 0.5, 2.6, 2.8, 3.6 and 8.9 wt%, and EPMA results in agreement to within 0.5, 0.03, 0.2, 1.0 and 0.3 wt%; i.e., on average, to within 0.4 wt%. Woodland et al. (1992) and Canil and O’Neill (1996) likewise reported fair-to-good agreement between Fe³⁺ as measured by Mössbauer and EPMA/stoichiometry, even for terrestrial mantle spinels.

Systematic EPMA analytical errors would generally have similar effect for analyses of both primary and secondary spinels, but conceivably some systematic bias-error affected only the secondary spinels. Bias-errors that would potentially, at egregious magnitudes, lead to 2 wt% of spurious Fe₂O₃ are: spuriously high FeO* (total Fe as FeO), or spuriously low Al₂O₃, Cr₂O₃ or TiO₂. Errors in FeO* have the greatest potential for Fe₂O₃ consequences. Both Al and Cr have cation valency (3) close to the average cation valency for any stoichiometric spinel (8/3), and moreover the NWA 5738 spinels are Al-poor. Ti has a valency far different from 8/3, but these spinels are generally not very Ti-rich, and there is no correlation between TiO₂ and implied Fe₂O₃ (Fig. 15). To be individually responsible for 2 wt% of spurious Fe₂O₃ in an average NWA 5738 spinel analysis, we find (by simple trial-and-error substitution of a range of alternative concentrations) that bias-errors would have to be 2.2 wt% for FeO, or 3.1 wt% for Al₂O₃, or 4.6 wt% for Cr₂O₃, or 1.20 wt% for TiO₂; or in terms of relative percentages, 5.3%, 48%, 11% and 13%, respectively. Errors this large would be considered appalling for any major-element EPMA, and here the systematic errors would have to arise between sets of broadly similar Cr-Fe-spinels analyzed in the same thin section (identical calibration, polish, carbon coat thickness, etc.). Conceivably systematic errors affect more than one of these oxides. For the case of say two oxides contributing equally to the net effect, the magnitudes of the required errors (half those cited above) would still be improbable, even individually (with the mild exception of FeO*: 2.7% relative), and more so as a required combination.

Conceivably, the data from the smaller secondary spinels might suffer from grain-boundary fluorescence. However, analyses from the centers of two outstandingly large secondary grains (15 × 5 µm and 11 × 5 µm) should be far less affected than other secondary-spinel analyses; yet the results from these locations are very typical of secondary spinel: 1.2 wt% Fe₂O₃ for the 11 × 5 µm grain and 1.7 wt% for the 15 × 5 µm grain. Conceivably, some minor element not analyzed would affect our results. But only a minor element with valency >> 8/3 could have any significant effect toward reducing apparent Fe₂O₃. Any divalent “missing” element (e.g., zinc) would, if added, only serve to enhance the apparent Fe₂O₃.
Kamperman et al. (1996) argued for direct measurement of oxygen by WDS spectrometry (i.e., the usual EPMA technique, except with a special crystal suited to the oxygen x-ray's wavelength; cf. our method for measuring oxygen in Fe-oxides, Fig. EA-22) as a means of improving the EPMA technique. However, a careful study by Herd et al. (2001) concluded that the Kamperman et al. (1996) technique “cannot be used to determine the Fe$^{3+}/\Sigma$Fe ratio of a spinel to an accuracy greater than is achieved by assuming stoichiometry.”

REFERENCES


