

PETROGRAPHY AND MINERAL CHEMISTRY OF SPINEL GRAINS SEPARATED FROM THE MURCHISON METEORITE; S. M. Kuehner and L. Grossman*, Dept. of the Geophysical Sciences, University of Chicago, Chicago, IL 60637. *Also Enrico Fermi Institute.

Ion microprobe measurements by Zinner and Epstein (1) revealed huge ^{13}C excesses in grains removed from Murchison acid residues which had been ashed in an oxygen plasma. SEM-EDX examination identified the grains showing this isotopic effect as spinel, chromite and Fe oxide, although other grains of the same phases from this material were found to contain normal carbon. Because of the possibility that the carriers of the excess ^{13}C are pre-solar grains, it is important to determine the chemical compositions of the spinel grains with anomalous carbon and whether the carbon resides in the crystal structure of the spinel, in inclusions within the spinel or in coatings on the surfaces of the spinel grains.

In order to explore the range of spinel compositions and the variety of inclusions within spinel grains in Murchison, we embarked upon an SEM and EPMA study of individual spinel grains which we hand-picked from the dense fraction of material obtained by freeze-thaw disaggregation of this meteorite. During hand-picking, these grains were identified as spinel on the basis of their pink, purple or red colors, high refractive index and, in some cases, octahedral shape. Included in this work are six grains whose preliminary descriptions were reported by MacPherson *et al.* (2), fragments of 12 other grains of which pieces were set aside for ion probe studies by Zinner and an additional ten unsplit grains.

Eighty-eight wavelength-dispersive analyses for Si, Ti, Al, Cr, V, Fe, Mn, Mg, Ni, Zn and Ca were obtained with a Cameca SX-50 electron microprobe, up to four for each spinel grain. In all cases, CaO, ZnO and NiO were below detection limits (0.015, 0.01 and 0.02 wt %, resp.), as was MnO (0.02) except for grain SP7. Cation sums range from 2.99-3.01 per four oxygen atoms. The spinel grains fall into three groups based mainly on their FeO contents: Group A (N=17)—0.22-1.64 wt % FeO; Group B (N=10)—5-10 %; and Group C (N=1)—11.0-12.8 %. These groups also differ in their natural colors as recorded during hand-picking: A—very pale pink to pinkish red; B—pinkish red to deep purplish red; C—red.

Because FeO contents are uniformly low and uncorrelated with Cr_2O_3 contents which range from 0.34-21.5 %, spinel grains in Group A are predominantly MgAl_2O_4 - MgCr_2O_4 solid solutions. Many are euhedral crystals or fragments thereof, 90-325 μm in maximum dimension. Four are particularly interesting in that they have a concentric or mottled chemical zoning pattern. One of these, SP5, (125 μm) has a 60 μm wide core containing 1.61 % Cr_2O_3 and a rim with 5.86% Cr_2O_3 . Although the core has a broadly idiomorphic shape, the core-rim contact is highly convoluted, with fingers of rim material penetrating 10-15 μm into the core and sometimes intersecting one another to form islands of core material. The mottled pattern of Cr_2O_3 -rich (8 %) and Cr_2O_3 -poor (4 %) regions in SP41 (250 μm) may be the result of sectioning through a core-rim interface. Zoned spinel grains contain 2-10 μm inclusions of anhedral Al-diopside, commonly associated with circular voids <5 μm in diameter. Pyroxene does not fill the voids but may form narrow (~2 μm) rims around the voids with undulose or flame-shaped contacts with spinel. The irregular shapes of the pyroxene inclusions suggest that they formed at the expense of spinel rather than as condensate crystals that were incorporated during spinel growth. The voids may be cross-sections of channelways through which gas

SEM & EPMA OF MURCHISON SPINEL
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was able to react with interior spinel to form pyroxene. Al-diopside and forsterite are the only phases found included within or attached to Group A spinel grains.

Although the range of Cr_2O_3 contents in Group B spinel grains, 5-25 %, is similar to that in Group A, the average Cr_2O_3 content, 15.9 %, is much higher than in Group A, 4.9 %. Among Group B spinel grains, FeO varies linearly with Cr_2O_3 up to ~10 % of each and then increases only slightly as Cr_2O_3 rises to 25 %, requiring increasing MgCr_2O_4 substitution above 10 % Cr_2O_3 . Complete overlap exists between Groups A and B in the contents of SiO_2 (<0.10-0.38 %), TiO_2 (<0.10-0.50 %) and V_2O_3 (0.10-0.45 %), except that one grain in Group B has higher V_2O_3 contents (0.44-0.46 %) than the highest found in Group A (0.36 %). Group B spinel grains are smaller (60-175 μm) than their counterparts in Group A and fewer of the former are euhedral than in Group A. Only two Group B spinel grains are chemically inhomogeneous, displaying a slightly mottled pattern due to variations in Cr/Al ratio as in Group A. Inclusions of other phases are uncommon in Group B spinel grains. One spinel (130 μm) is attached to an ~100 μm long olivine grain which, in turn, contains inclusions (<5 μm) of Cr-bearing spinel. Both phases contain inclusions of Fe-Ni metal.

Group C consists of a single euhedral spinel grain, SP7, ~120 μm in diameter. Only its high FeO and MnO (0.5-1.5 %) contents distinguish it from Group A and B. Three analyses define a unit slope on a plot of Fe cations *vs* Cr cations, indicating significant FeAl_2O_4 . SP7 has a mottled zoning pattern due to variations in both Fe/Mg and Cr/Al ratios and contains numerous Al-diopside inclusions. Unlike those in Group A spinel grains, however, these inclusions incompletely fill irregular voids up to 20 μm long and 10 μm wide. The remaining unfilled portions of the voids are in partial contact with spinel. Spinel-pyroxene contacts are sometimes convex toward the pyroxene, suggesting deposition of pyroxene in the voids rather than replacement of spinel.

The spinel grains observed in this work define three distinct chemical trends, implying that the three groups have different origins. Due to the method of recovery, little information is available about the textural setting of the spinel grains in each group. Determining the histories of the three groups will require locating examples of each *in situ* and studying their associated minerals, if any. MacPherson *et al.* (2) reported a Murchison hibonite being replaced by spinel containing 2 % Cr_2O_3 and 0.68 % FeO. Although this suggests an affinity between Group A spinel grains and refractory condensate phases, Fuchs *et al.* (3) reported four spinel grains with Group A compositions from less refractory forsterite inclusions in Murchison. Fuchs *et al.* also reported two types of Murchison spinel which we have not sampled: very FeO-rich (~25 %) and Cr_2O_3 -rich (~50 %) angular fragments and magnetite spherules, both in the matrix. In addition, spinel grains from a wide range of refractory inclusions in Murchison may belong to yet another group which we have not sampled, as they are extremely low in both FeO and Cr_2O_3 (2). All of these spinel compositions may be present in the residues studied by Zinner and Epstein (1). Models for the origin of the carbon isotope anomalies will be constrained by the group to which their host spinel grains belong.

References: (1) Zinner, E. and Epstein, S. (1986) LPS XVII, 967. (2) MacPherson, G. J. *et al.* (1983) GCA 47, 823. (3) Fuchs, L. H. *et al.* (1973) Smithson. Contrib. Earth Sci. 10.