PETROGRAPHY, COMPOSITION AND ORIGIN OF CHROMIAN SPINEL CRYSTALS SEPARATED FROM THE MURCHISON METEORITE; S.B. Simon[1] and L. Grossman[1,2], [1]Department of the Geophysical Sciences, [2]Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637.

Although most spinel grains in Murchison acid residues have large oxygen isotopic anomalies [1], spinel grains separated by freeze-thaw disaggregation, density separation and hand-picking have normal O [2] and Cr [3] isotopic compositions. Preliminary descriptions of the latter grains were given in [4]. Some are euhedral, others crystal fragments, most exceed 100 µm across and some are >200 µm in maximum dimension. They are clear, pink to deep red, are generally larger than spinel crystals found in Murchison CAI's or chondrules, and are intermediate in Cr_2O_3 and FeO contents between the virtually pure $MgAl_2O_4$ of the former and the Cr-rich spinel of the latter [5]. As they separated with no adhering material indicative of their immediate host, we know little of their petrographic setting in the meteorite. SEM and electron probe studies of zoning trends, analysis of inclusions in 45 spinels and comparison with *in situ* occurrences, however, allow us to constrain the origins of the grains.

Compositions. These spinels were divided into three groups on the basis of FeO contents [4]: Group A, 0.22-1.64 wt % (now, with additional analyses, up to 5%); Group B, 5-10%; and Group C, 11-12 % (now up to 17%). Group A has from 0 to 22 % Cr_2O_3, Group B 10-26 % and Group C 14-36 %. Electron probe data indicate that Cr substitutes for Al and Fe substitutes for Mg, independently of each other. Cr and V and Ti and V are positively correlated in all groups, but Fe and V are positively correlated only in Groups B and C.

Zoning. Several different zoning trends and patterns, defined by variations in Cr_2O_3 content, are exhibited by the grains: a) *patchy* (22 samples), with numerous islands, typically 10 µm (but up to 100 µm) across, of contrasting Cr_2O_3 contents distributed throughout the grain, or, in some cases, concentrated on one side. These grains have a mottled or patchy appearance in backscattered electron images. The shapes of the patches range from square to highly irregular with rounded boundaries. We have observed differences of up to 9 wt % Cr_2O_3 between patches in a single grain. In most cases, the high-Cr_2O_3 zones appear to enclose the low-Cr_2O_3 zones. In some grains, the silicate inclusions have aureoles around them but, in others, the inclusions cut across contacts between high- and low-Cr_2O_3 patches. There is also no clear relationship between cavities and the patches; b) *homogeneous* (11), with Cr_2O_3 contents ranging from 2-36 wt %; c) *gradational* (5), in which Cr_2O_3 varies smoothly (by as much as 10 wt %) across the grain, three with Cr_2O_3 increasing and two with Cr_2O_3 decreasing from core to rim; d) *chevron* (5), containing angular, sharply defined bands of different Cr_2O_3 content which are parallel to crystal edges in at least two cases. One grain has a Cr_2O_3-rich core, followed by a low-Cr_2O_3 zone and then a high-Cr_2O_3 zone. In the other four, the core is relatively low in Cr_2O_3, the layer adjacent to it is the most Cr_2O_3-rich one, and outward from this layer are as many as ten alternating bands of high and low Cr_2O_3 content superimposed on a general trend of decreasing Cr_2O_3; and e) *core-rim* (2), in which the grains have low-Cr_2O_3 (1-2 wt %) cores enclosed by high-Cr_2O_3 (5-6 wt %) rims with an irregular, embayed boundary between the two zones. In most of the grains, increases in Cr_2O_3 are accompanied by increases in TiO_2 and V_2O_3, but there is no systematic relationship with Mg/Fe.

Inclusions. Not all grains have inclusions. The most common is diopside with 12-20 wt % Al_2O_3 and up to 3.8% TiO_2. Except for SP6, which has a 10 µm-thick rind of Al-diopside, and SP23, which has an irregularly shaped ~50µm, pyroxene inclusion, the pyroxene inclusions are isolated, anhedral grains ≤10 µm across. Some are associated with voids, suggesting they may have formed *in situ* via reaction between spinel and Si-, Ca-rich fluid [4]. Five spinels occur with olivine (three with Fo_{99} and two with Fo_{95}). Two are patchy, two have chevron-type zoning and one is homogeneous. Spinel crystallized around olivine in four of these. In the other, spinel and olivine preceded Al-diopside. In at least two cases, Cr_2O_3 contents increase in olivine toward spinel contacts, from, *e.g.*, 0.43 to 0.55 wt %. Five Group A spinels have angular, 5-10 µm-sized glass inclusions. Four are patchy and one has chevron-type zoning. In four of these, the glass has 2-4 wt % MgO, 23-25% Al_2O_3, 48-53% SiO_2, 15-23% CaO and 0.4-1.8% TiO_2. These compositions are similar to those of glass inclusions in pyroxene-olivine inclusions [6] and isolated olivine crystals [7] in Murchison. In the fifth, the glass is Al_2O_3-rich (37 wt %) and SiO_2-poor (41%) relative to the others. Several spinels contain Fe-rich phyllosilicate, and one patchy spinel has ~10-µm inclusions of anorthite (or glass of anorthite composition).

In-situ occurrences. We searched 14 thin sections optically and by SEM, and found only a few Cr-bearing spinels. With one exception, these grains are smaller than the separated spinels, but all are within the composition range of the latter and may thus belong to the same families as those. The largest grain we found *in situ* is ~100 × 200 µm. It has patchy zoning with 22-26 wt % Cr_2O_3 and 5% FeO. It is subhedral, enclosed by anhedral olivine (Fo_{94}) crystals 100 µm across and, except along one broken edge, has a rim of an Fe-rich alteration product. The spinel also has olivine (Fo_{92}) inclusions, and one of the host olivine grains contains diopside (12 wt % Al_2O_3). Another patchy grain has 10-20 wt % Cr_2O_3 and ~1.5% FeO. It is anhedral, 34 × 24 µm, has crystallized around two grains of olivine (Fo_{95}), and has inclusions of (and is adjacent to) Al-diopside. This assemblage is attached to a subhedral, isolated olivine (Fo_{97}) grain (~90 × 60 µm) of the type proposed as condensates [7]. We found a 30 × 10 µm homogeneous spinel with 2.7 % Cr_2O_3 adjacent to an anhedral, isolated forsterite (Fo_{99}) crystal, and three homogeneous rounded spinels, ~10 µm across, with ~1 % Cr_2O_3 and 0.7% FeO enclosed in a single crystal of olivine (Fo_{99}). Another occurrence is a 200-µm diameter chondrule with coarse (170 × 100 µm), subhedral olivine (Fo_{99}) and finer (~30 µm), euhedral crystals of homogeneous spinel (2 Cr_2O_3) and olivine in a matrix of diopside (19 % Al_2O_3).

Discussion. In principle, spinel grains of the homogeneous, gradational, chevron and core-rim zoning types could have all crystallized from liquids. In such cases, Cr_2O_3 should decrease from core to rim because experimentally determined crystal/liquid D's > 100 in Fo-An-SiO_2 and Fo-An-Di [8]. The presence of a homogeneous spinel in the chondrule described above suggests that this type could form in chondrule melts, but the large sizes of separated spinels compared to those in the chondrule, and even to the sizes of whole chondrules, 300-400 µm [7], in Murchison, argue against this. Spinels with gradational zoning were also observed in Murchison chondrules containing mostly olivine ± mesostasis [5]. In these, spinel occurs as small (<50 µm), euhedral crystals of Fe-rich chromite, with Mg/(Mg+Fe) and Cr/(Cr+Al) decreasing from core to rim. Such chondrules could thus be a source for those separated spinels with gradational zoning in which Cr decreases outward, except again for an important difference in size and a major difference in composition. Spinel grains in the separates are unzoned with respect to Mg/(Mg+Fe), and have higher Mg/(Mg+Fe) (>0.55 *vs.* <0.40) and lower Cr/(Cr+Al) (<0.44 *vs.* ~0.7) than the chromite in Murchison chondrules. Although we have not found spinel grains of the core-rim zoning type in chondrules, it is conceivable that these spinels crystallized from a liquid. For these, however, a multi-stage origin is required. In one model, crystallization of low-Cr spinel crystals is followed by erosion and embayment of the crystals and later deposition of high-Cr mantles. Note, however, that the Cr zoning profile is inconsistent with the spinel/liquid D and that a chondrule melt seems inappropriate for such a complex history. Another model for core-rim spinels involves crystallization of low-Cr spinel crystals followed by a change in physico-chemical conditions favoring higher Cr/(Cr+Al) in the spinel, and incomplete exchange of Cr for Al by solid-state diffusion, leaving an irregular core-mantle boundary. Spinel grains with chevron-type zoning have not been found in chondrules but it is easy to imagine that their sharply defined, uniform layers that follow crystal outlines were produced by crystallization from a liquid. The multiple layers reflect complex histories, possibly involving repeated replenishment of Cr in the liquid or variations in temperature and/or f_{O_2}. It is difficult to imagine, however, how the multiplicity of physico-chemical changes implied by the number of zones in these spinels could have occurred in a chondrule melt or indeed in any igneous environment that existed prior to accretion of Murchison.

Each of these spinel types could have also formed by gas-solid condensation. The presence of significant amounts of FeO in these spinels would imply relatively low formation temperatures, if condensation occurred in a gas of solar composition. The presence, however, of inclusions of forsteritic olivine in one homogeneous spinel and in some of the chevron-type ones suggests crystallization of olivine prior to spinel, a sequence opposite to that expected from condensation in a cooling solar gas. Regardless of the gas composition, several reservoirs with different physico-chemical conditions would be required for a condensation origin for these spinels in order to account for the opposite Cr zoning trends in the gradational spinels, the different core and mantle compositions of the core-rim ones and the multiplicity of zones in the chevron-type ones.

It is unlikely that the grains with patchy zoning were ever molten. Crystallization from a liquid should result in unzoned or symmetrically zoned grains rather than crystals with irregularly distributed patches of contrasting composition. Four grains have glass inclusions, but these are so Ca-, Si-rich that they are not in equilibrium with spinel and cannot be parent melts. The observed textures are not the result of chance sectioning through an irregular core-rim boundary, as previously suggested [4]. Among our 45 grains, the ratio of core-rim spinels to patchy ones is 1:11. This ratio would be much higher if the suggestion of [4] were correct. It is unlikely that these grains are sintered aggregates, as this would require a source consisting purely of spinel grains with different compositions. The patchiness is not crystallographically controlled, as would be expected for exsolution. The patches in an *in situ* spinel grain have no spatial relationship with adjacent matrix, indicating that the patchiness predates accretion of Murchison. The patchiness is similar to the irregularly shaped, high-Ca islands in some terrestrial metamorphic garnets [9], and may represent incomplete equilibration by solid-state diffusion in which Fe and Mg have been homogenized but Cr and Al have not. The occurrence of a patchy spinel with a large, subhedral, isolated olivine grain supports a condensate origin.

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