'Normal' Fe-Mg-Al-Cr Spinel Minerals in Chondritic Stratospheric IDPs.

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Introduction: Spinel minerals with 'normal' structure are common in extraterrestrial materials and can form via a large range of processes including nebular condensation, crystallization from liquid melts and sub-solidus metamorphic reactions. Owing to their ability to accept a large range of cations in their crystal structures these minerals can be regarded as useful petrogenetic indicators which largely reflect their parental sources. In carbonaceous chondrites, for instance, multicomponent spinels present in Type 2 chondrules crystallized from silicate melts (droplets) rich in Fe, Cr, Mg and Al whereas nearly pure $MgAl_20_4$ spinels present in Type B CAIs formed in a nebular environment consistent with high temperature condensation of refractory minerals.

In this study we examine **non-magnetite, non-magnesioferrite** spinel minerals rich in Fe^{2+}, Mg, Al and Cr found in IDPs with the hope of shedding insight on how these minerals may have formed. Generally, it appears that many were formed in the interiors of IDPs via atmospheric entry heating (secondary spinels). Some of the spinels, however, cannot be explained by this mechanism and are more consistent with having their origins as high temperature nebular condensates (primary spinels). We use spinel compositions, textural relationships, mineral associations and comparison to spinels produced in heating experiments and those in other extraterrestrial materials to differentiate primary from secondary spinel minerals in IDPs.

Analytical Procedures: Spinel group minerals were studied in 15 individual chondritic hydrated and anhydrous IDPs. The IDPs were microtomed and placed on standard C-coated TEM grids. Chemical data were obtained from EDX spot analyses on 19 spinel grains using a 120 KV JEOL 1200EX STEM. SAED patterns were collected on a few grains to confirm their spinel structures. 'Normal' spinel endmembers – $MgAl_20_4$-$FeAl_20_4$-$MgCr_20_4$-$FeCr_20_4$ – were calculated after Fe^{3+} determineration by charge balance. High magnesioferrite or magnetite spinels were not used in this study. In most spinels, the elements Mn and Ti were typically low in abundance and were not considered.

Due to their small sizes, spectra obtained from some spinel grains were actually composite spectra from overlaps with adjacent grains or host phases, particularly olivine. In a few cases where the overlaps were particularly severe, spectra from the 'host' phase was subtracted from the composite spectra to give an improved spinel analysis.

The results from the measurement of 19 individual spinel grains are plotted in the Mg-Al-Fe^{2+} ternary diagram. Solid solution fields for spinel-hercynite and Mg chromite-chromite are shown. In the figure, spinel analyses obtained from hydrated IDPs are shown as solid circles while open circles apply to spinels from anhydrous IDPs. Two circle sizes are shown for both hydrated and ahydrous IDPs; large circles indicate high measured Cr while small circles indicate low Cr contents. A capital letter 'P' is shown adjacent to the six IDP spinels that may have a primary origin (see below).

Spinel data obtained from pulse heating experiments on terrestrial saponite, Orgueil matrix [1] and Allende+coal and Fe-rich olivine+coal mixtures [unpublished data], (designed to simulate atmospheric entry conditions in IDPs), are also shown in the figure along with average spinel from Type 2 chondrules in carbonaceous chondrites [2]. The spinel field from Type B CAIs in carbonaceous chondrites is indicated by the elongated oval on the spinel-hercynite solid solution join.

Secondary Spinels: Thirteen spinels studied in nine IDPs are believed to have a secondary origin which were likely formed in-situ during atmospheric entry heating. These are shown in the ternary diagram as either open or solid circles without an adjacent letter 'P'; most plot in the interior of the ternary diagram and contain Cr contents above 15 wt%. These spinels are primarily mixtures of Mg, Fe, Cr and Al oxides, and are believed to be liquidus phases crystallized from localized partial melts within the IDPs as low temperature phases (probably phyllosilicates) were heated to melting during atmospheric entry. Typical sizes of these spinels are 50 – 100 nm and most are associated with Fe-rich olivines (or occasionally pyoxenes) and aluminosilicate glass and sometimes occur as inclusions in these phases. Nearly identical assemblages – Mg-Fe-Al-Cr spinel+Fe-rich olivine+aluminosilicate glass – were observed from pulse heating experiments on terrestrial saponites and Orgueil matrix [1] which were designed to simulate atmospheric entry heating conditions. Stepped He-release data obtained on many of these IDPs provide peak heating temperatures up to 960 °C [3].

Most of the secondary spinels are present in anhydrous silicate IDPs; three that plot on the Mg chromite-chromite solid solution line are all from a single hydrated IDP. From SEM photos, none of the IDPs show any significant external melt features. The data suggest that minor amounts of saponite or other low temperature minerals present in strongly heated IDPs may produce local melt pockets in the interior of the IDPs during atmospheric entry and then recrystallize as a multicomponent spinel mineral+Fe-rich olivine+Al-rich silicate glass. The spinel mineral compositions probably reflect the local melt chemistry and therefore significant differences in spinel compositions may occur even within a single 10 um IDP.

Primary Spinels: Six spinels studied (from 5 different IDPs) are candidates for having a primary origin, perhaps as nebular condensates. These six are labelled in the ternary diagram with a small upper case 'P' and have grain sizes up to 300 nm. Four were observed in hydrated silicate dominant IDPs (2 cronstedtite-rich IDPs and one saponite-rich IDP) and plot close to $MgAl_20_4$ spinel. Of these, two fall within the CAI spinel field for carbonaceous chondrites; one contains 20 wt% Fe and is similar in composition to Fe-rich spinel from fine-grained Type 2 inclusions in Allende with spinel FeO contents up to 23 wt% [4]. The three spinel-bearing HS IDPs cantain phyllosilicate minerals that appear relatively intact (7.1 – 7.6 A lattice fringes measured for cronstedtite and 11.3 – 11.6 A lattice fringes measured for saponite) even though measured peak atmospheric entry temperatures were relatively high. No evidence of Fe-rich olivines, characteristic of secondary assemblages, was observed. Cr contents were low in these spinels (0.9 – 1.9 wt%) consistent with spinels from refractory inclusions in carbonaceous chondrites [4]. Two anhydrous IDPs were found to contain Fe-free spinels; one plots near $MgAl_2O_4$ (and overlaps a secondary spinel from a hydrated silicate in the ternary diagram making it difficult to see). The other primary spinel plots as a large open circle about 1/3 of the distance between $MgAl_2O_4$ and $MgCr_2O_4$ indicating its Fe-free composition but higher Cr content (23.6 wt% Cr). It occurs in close contact with an aluminous Ti-bearing diopside (2.6 wt % Al; 0.5 wt % Ti). This spinel is similar in composition to spinel grains separated from the Murchison meteorite where FeO is predominantly low and Cr_2O_3 ranges up to 21.5 wt% [5].

Conclusions: Non-magnetite spinel minerals were found in 15 hydrated and anhydrous IDPs. Most of the spinels are believed to have formed in the interiors of the IDPs during atmospheric entry heating. The secondary spinels were often found poikilitically enclosed in or associated with Fe-rich olivine and aluminosilicate glass. Their multicomponent compositions – $MgO+FeO+Al_2O_3+Cr_2O_3$ – reflect crystallization from localized melts from low temperature minerals heated during atmospheric entry. Most of the secondary spinels were found in anhydrous IDPs. Six primary spinels were observed in 5 IDPs; all were characterized by high $MgAl_2O_4$ contents or high $MgAl_2O_4$ with either moderate Fe or Cr. These compositions are similar to spinels in CAI's from carbonaceous chondrites. Their $MgAl_2O_4$-rich endmember compositions and lack of associated Fe-rich olivines typical of secondary minerals, suggest that these spinels are good candidates to have their origins in a solar nebula environment.

References: [1] Joswiak, D. J. and Brownlee, D. E., *LPSC XXIX*, 1998. [2] Johnson, C. A. and Prinz, M., *GCA*, 893-904, 1991. [3] Nier, A. O. and Schlutter, D. J., *Meteoritics 28*, 675, 1993. [4] Brearley, A. J. and Jones, R. H., *Planetary Materials, Reviews in Mineralogy, Vol. 36*, J.J. Papike ed., 3-114. [5] Kuehner S. M. and Grossman, L., *LPSC XVIII*, 1987.

Mg-Al-Fe^{2+} Spinel Ternary Diagram