

CARBON AND OXYGEN ISOTOPIC COMPOSITIONS OF INDIVIDUAL SPINEL CRYSTALS FROM THE MURCHISON METEORITE; L. Grossman¹, A.J. Fahey² and E. Zinner².
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Following the ion microprobe discovery by Zinner and Epstein (1) of huge ^{13}C excesses in grains of spinel-group minerals from Murchison acid residues, Kuehner and Grossman (2) began a petrographic and chemical study of individual spinel crystals recovered from this meteorite by freeze-thaw disaggregation followed by heavy liquid separation. Splits of some of these crystals were set aside for ion probe isotopic measurements. The objectives of this study were to determine whether the association of anomalous carbon with spinel is an artifact of chemical processing or, if it is not, whether the anomalous carbon resides in inclusions within the spinel or inside the spinel structure itself. In the latter case, a pre-solar origin for the spinel would be indicated and the trace and minor element content of the spinel would be an important constraint on the physico-chemical conditions of its pre-solar formation location. Minor element data were discussed in (2). Here we report the ion probe isotopic results.

Fragments of each spinel crystal were pressed into gold foil along with NBS-21 graphite and Burma spinel as terrestrial standards. Carbon and oxygen isotopes were measured as negative ions in different runs at different mass resolving powers sufficient to resolve ^{13}C from ^{12}CH and ^{17}O from ^{16}OH , resp. Techniques have been described previously (3,4). Measurements on Murchison spinel grains were interspersed with measurements on terrestrial standards. Data are normalized by comparison to the standards and are expressed as $\delta^{13}\text{C}_{\text{PDB}}$, $\delta^{17}\text{O}_{\text{SMOW}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$. For carbon, errors are dominated by counting statistics and are much larger than those obtained from C-rich samples (3). The scatter resulting from many individual oxygen isotopic measurements of Burma spinel is shown in Figure 1. The average of these points was equated to the accepted value for Burma spinel (4), shown as the large circle in Figure 1, in order to normalize the Murchison spinel data. The oxygen isotopic composition of each Murchison spinel is the average of several measurements that were interspersed with those of Burma spinel or other Murchison spinel grains.

Carbon isotopic compositions were measured in 33 spots on 12 separate spinel crystals and are shown in Table 1. Although the $\delta^{13}\text{C}$ values of most spots are indistinguishable from normal, several crystals contain regions with significantly negative $\delta^{13}\text{C}$, but never $< -100\text{‰}$. While large ^{13}C excesses have been found in spinel grains from Murchison acid residue 2C10c (5) and in 20 out of 93 grains of spinel-group minerals in acid residue CF0c (1), we have not found a single spot in any of the 12 crystals of spinel-group minerals extracted from Murchison by freeze-thaw disaggregation that has such anomalous carbon ($\delta^{13}\text{C} > +300\text{‰}$). Quantitative chemical analyses of the grains studied in (1) are not available, but 68 are described as either "Mg-spinel" or "Cr-spinel". While the compositions of all 12 crystals analyzed in this work can also be described by these general terms (2), it is not known whether those in (1) that contain anomalous carbon belong to a restricted range of composition not represented in our population. Size is another possible difference between the spinel collections of the two studies. Our method of hand-picking spinel grains from density separates results in selection of the coarsest spinel crystals in the meteorite. The spinel grains of this study are 85-325 μm in largest dimension, with most lying in the range 100-150 μm . Some of these are fragments of even larger crystals. Although the grains studied by Zinner and Epstein (1) were only 10-30 μm in size, that collection probably includes grains produced by fragmentation during crushing, acid dissolution and oxygen ashing. It is likely, therefore, that the collection of spinel grains studied in (1) contains members of the population studied in this work but it is not certain that the latter are among those that displayed anomalous carbon in (1). Nevertheless, it is noteworthy that, to date, the only Murchison spinel grains reported to contain large ^{13}C excesses have been found in residues produced by acid dissolution. This fact leaves open the possibility that the spots of anomalous carbon isotopic composition are not contained within the spinel but, instead, became associated with the surfaces of the spinel grains during laboratory processing. If so, the exotic origin attributable to the isotopically anomalous carbon would not be applicable to its host spinel crystals.

Oxygen isotopic compositions measured on the same spots as the carbon isotopes are shown in a three-isotope plot, Figure 1, along with the oxygen isotopic composition of the spinel-rich acid residue 2C10c from (6). All

Murchison spinel grains in this study have $\delta^{18}\text{O}$ values between -10 and $+10$ ‰ and $\delta^{17}\text{O}$ between -5 and $+5$ ‰, and form a cluster of data points comparable in size to that exhibited by the scatter of measurements on Burma spinel. They plot in a restricted region of the three-isotope diagram, near the intersection of the terrestrial fractionation line with the unit slope mixing line for anhydrous phases from carbonaceous chondrites. Although the spinel grains plot near the opposite end of this mixing line from the spinel-rich acid residue 2C10c, the analytical uncertainties in their isotopic compositions are too large compared to the distance between the two lines in this region to determine whether the spinel grains lie on the terrestrial line or the mixing line or both. Previous ion microprobe data (4) for individual spinel grains from the Murchison acid residue CF0c, however, exhibit a much wider range of oxygen isotopic compositions from which it is clear that they plot along the mixing line. Those data also show that Murchison acid residues contain spinel grains with the same oxygen isotopic compositions as those in this study, as well as others with much lower $\delta^{18}\text{O}$ than those found here. Our work shows that the largest spinel grains in Murchison have the highest $\delta^{18}\text{O}$ values. Furthermore, it is unlikely that their oxygen isotopic compositions were derived from those spinel crystals with $\delta^{18}\text{O} = -40$ ‰ by exchange with an external reservoir of heavy oxygen, as they are much larger than those whose isotopic compositions are unchanged. This suggests that Murchison acid residues contain spinel crystals that originated in reservoirs of different oxygen isotopic composition from one another. This, however, cannot be the reason for the difference in carbon isotopic composition between the spinel crystals of this work and some of those from acid residues (1,5), as Zinner and Epstein (1) showed that large ^{13}C excesses are found in some CF0c spinel grains with $\delta^{18}\text{O} = -40$ ‰ and others with $\delta^{18}\text{O} = 0$ ‰ (1).
Refs.: (1)Zinner, E. and Epstein, S.(1987)Earth Planet. Sci. Lett. 84,359-368. (2)Kuehner, S.M. and Grossman, L.(1987)Lunar Planet. Sci. XVIII,519-520. (3)McKeegan, K.D., Walker, R.M. and Zinner, E.(1985)Geochim. Cosmochim. Acta 49, 1971-1987. (4)McKeegan, K.D.(1987)Science 237,1468-1471. (5)Niederer, F.R., Eberhardt, P., Geiss, J. and Lewis, R.S.(1985)Meteoritics 20,716-718. (6)Clayton, R.N. and Mayeda, T.K.(1984)Earth Planet. Sci. Lett. 67,151-161.

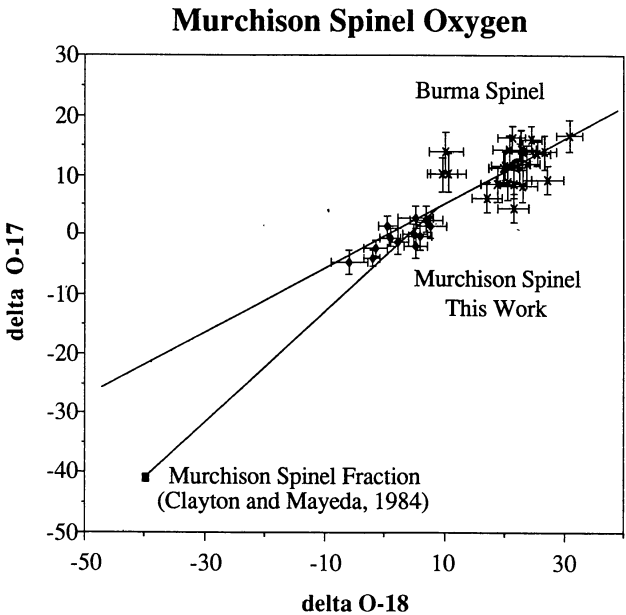


Table 1: Carbon isotopic composition of Murchison spinels

| Sample | $\delta^{13}_{\text{PDB}} \pm 2\sigma$ | C/O $^{\circ}$ (10 $^{-4}$) | Sample | $\delta^{13}_{\text{PDB}} \pm 2\sigma$ | C/O $^{\circ}$ (10 $^{-4}$) |
|--------|--|------------------------------|--------|--|------------------------------|
| Sp-21 | -18 \pm 31 | 1.75 | Sp-22 | -35 \pm 34 | 1.54 |
| Sp-24 | -17 \pm 15 | 10.5 | Sp-24 | +20 \pm 37 | 1.98 |
| Sp-27 | -54 \pm 18 | 1.55 | Sp-28 | -20 \pm 27 | 2.39 |
| Sp-28 | -32 \pm 47 | 2.21 | Sp-28 | -38 \pm 47 | 3.20 |
| Sp-29 | -76 \pm 88 | 0.29 | Sp-29 | -21 \pm 15 | 3.35 |
| Sp-30 | -8 \pm 39 | 1.39 | Sp-30 | +3 \pm 12 | 2.08 |
| Sp-30 | -8 \pm 41 | 1.29 | Sp-31 | -34 \pm 34 | 1.79 |
| Sp-31 | -1 \pm 26 | 1.83 | Sp-31 | -73 \pm 68 | 1.21 |
| Sp-31 | -20 \pm 49 | 1.74 | Sp-31 | -6 \pm 40 | 0.73 |
| Sp-31 | -44 \pm 17 | 1.01 | Sp-31 | -60 \pm 33 | 0.35 |
| Sp-31 | -31 \pm 57 | 1.34 | Sp-32 | +38 \pm 68 | 0.25 |
| Sp-32 | -35 \pm 10 | 7.05 | Sp-32 | -4 \pm 23 | 1.65 |
| Sp-32 | -34 \pm 178 | 0.38 | Sp-32 | -70 \pm 86 | 0.24 |
| Sp-33 | -17 \pm 92 | 1.20 | Sp-33 | -39 \pm 59 | 0.44 |
| Sp-34 | -50 \pm 21 | 1.63 | Sp-34 | -11 \pm 50 | 1.55 |
| Sp-34 | -96 \pm 47 | 0.95 | Sp-36 | -40 \pm 33 | 2.90 |
| Sp-36 | -89 \pm 62 | 0.79 | | | |