TRACE ELEMENT COMPOSITIONS OF SPINEL-RICH REFRACTORY INCLUSIONS FROM THE MURCHISON METEORITE; S. Yoneda[1], P.J. Sylvester[1,*], S.B. Simon[1], L. Grossman[1,2] and A. Hsu[3]. [1]Department of the Geophysical Sciences, [2]Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637, USA. [3]Illinois Math and Science Academy, Aurora, IL 60506, USA. *Present address: Research School of Earth Sciences, The Australian National University, GPO Box 4, Canberra, ACT 2611, Australia.

Abstract: Three spinel-rich, perovskite-bearing, pyroxene-rimmed, hibonite-free inclusions from the Murchison C2 chondrite have volatility-controlled, modified group II REE patterns. Two have high Eu/Yb ratios, two have small positive Ce anomalies and one has high refractory siderophiles for a group II inclusion. Two additional spinel-rich inclusions have subchondritic Ce/La ratios and negative Eu and Yb anomalies, the Eu anomalies being larger than the Yb ones. One of these inclusions is enriched in La relative to all HREE and the other is enriched in HREE relative to all LREE except La, possibly suggesting the presence of an ultrarefractory component in the latter. One hibonite-rich inclusion has a group III REE pattern with a negative Ce anomaly. A calcium dialuminate-bearing inclusion known to have crystallized from a melt at 2100-1800K has a modified group II REE pattern, rather than a pattern which would be predicted from the evaporation expected from such a droplet, *e.g.*, a group III or ultrarefractory pattern. Volatile element contents of these inclusions are among the lowest found in any refractory inclusions.

Introduction: Recent ion microprobe studies of refractory lithophiles in hibonite-bearing inclusions in C2 chondrites reveal a huge variety of volatility-controlled fractionations among these elements [1-4]. It is probable, however, that, among refractory inclusions in these meteorites, pyroxene-rimmed, spinel-rich, hibonite-free objects are at least as abundant as hibonite-bearing ones. The only trace element data reported for spinel-rich, hibonite-free inclusions come from ion microprobe studies of lithophile elements in Mighei inclusions [5,6]. Here we report preliminary INAA data on refractory lithophile and siderophile elements in splits of five hibonite-free, spinel-pyroxene inclusions in addition to two hibonite-bearing ones, all weighing between 3 and 11 μg and all newly collected from the Murchison C2 chondrite by freeze-thaw disaggregation followed by heavy liquid separation and hand-picking, as in [7]. The remaining fraction of each inclusion was made into a polished thin section and studied by SEM and EPMA.

M92B1, B3 and B7: These three inclusions are very similar to one another in mineralogy and petrography, all having a massive core of Mg-, Al-spinel with numerous, accessory perovskite grains (<5-10 μm) and a fluffy rim composed mostly of aluminous diopside. All three also have volatility-controlled, modified group II REE patterns (Fig. 1). These formed by condensation of the REE remaining in the gas after removal of the most refractory REE in an ultrarefractory condensate at a lower temperature than was the case for normal group II REE patterns [8-10]. This causes fractions of the most refractory of the LREE to be removed along with the refractory HREE, resulting in smaller LREE/HREE ratios and smaller fractionations among the HREE than is the case for normal group II patterns. Thus, La/Lu is 1.98±0.06, 3.98±0.26 and 1.16±0.04 and Tb/Lu is 0.51±0.10, 0.83±0.20 and 0.75±0.06 relative to C1 chondrites in B1, B3 and B7, respectively, compared to values around 50 and 20 in normal group II patterns [11]. Unusual features of the REE patterns include high Yb/Eu ratios in B1 and B3, 3.1±0.5 and 4.5±1.2, respectively, and small positive Ce anomalies in B1 and B7, with Ce/La of 1.56±0.03 and 1.21±0.03, respectively, all relative to C1 chondrites. The positive Ce anomalies are probably due to the fact that Ce is more volatile than La in a gas of solar composition, causing more of the Ce than the La to be left in the gas after removal of the refractory REE fraction in the earlier condensate [8]. The shape of the REE pattern of B1, including its positive Ce anomaly and its Eu/Yb ratio, is almost identical to that of spinel-perovskite nodule 2 of Mighei 3483-3-8 [5]. Enrichment factors for refractory siderophiles are uniformly low in B1 and B3, those for Ir being 0.115±0.003 and 1.75±0.03, respectively, relative to C1 chondrites, but are extraordinarily high for group II inclusions [12] in B7, with Ir=11.1±0.2 × C1.

M92B2, B5 and B9: These three inclusions differ in mineralogy and petrography from one another but are grouped together because of similarities in their REE patterns. B5 has the mineralogical and textural characteristics of the three spinel-rich inclusions discussed above. B9 consists of massive spinel but differs from the other spinel-rich inclusions in containing irregular grains (<5 μm) of accessory melilite in addition to perovskite and in lacking a pyroxene rim. B2 is composed of numerous plates of hibonite (~40 μm across) with minor perovskite. All three have REE patterns with affinities to group IIIs, *i.e.*, they have large negative Eu and Yb anomalies, with B2, B5 and B9 having Eu/Sm ratios of 0.15±0.04, <0.071 and 0.19±0.07, respectively, and Yb/Lu ratios of 0.094±0.006, 0.360±0.005 and 0.52±0.02, respectively, all relative to C1 chondrites (Fig. 2). Such patterns are thought to have formed by condensation of REE at a high enough temperature that the condensed fraction of Eu and Yb, the two most volatile REE, was considerably less than that of all the other REE [13]. Eu anomalies are larger than Yb anomalies in B5 and B9, a characteristic found in a minority of hibonite-rich samples [3, 14] but also found in the group III, spinel-rich inclusion Mighei 3483-3-4 [5]. In addition, all three of these inclusions have negative Ce anomalies, the Ce/La ratios of B2, B5 and B9 being 0.79±0.02, 0.49±0.01 and 0.37±0.02, respectively, relative to C1 chondrites. This may be due to a slightly higher equilibration temperature for these inclusions than is the case for normal group III inclusions, causing Ce, the next most volatile REE after Eu and Yb, to be incompletely condensed as well. Otherwise, B2 is the closest of the three to having a normal group III REE pattern, in that the other REE are approximately uniformly enriched at about 41 × C1 chondrites. In B9, however, La has a much higher enrichment factor, ~27, than all other REE which, except for Ce, Eu and Yb, have approximately uniform enrichment factors of ~15, relative to C1 chondrites. In B5, the enrichment factor for La, 54, is not only much higher than that for Ce but also than that for Sm, 36, suggesting that it may be incorrect to have inferred a negative Ce anomaly for this object based on the previously mentioned, low Ce/La ratio. Except for La, LREE are depleted relative to all HREE except for Yb, with enrichment factors varying from ~47 for Dy to ~61 for Lu, possibly due to the presence of an ultrarefractory component, as in [2]. In each of these inclusions, refractory siderophiles have uniform enrichment factors which are lower than those of most refractory lithophiles, that for Ir being 0.16±0.01, 1.24±0.02 and 2.93±0.04 in B2, B5 and B9, respectively.

M92B6: This is a spinel-, hibonite- and calcium dialuminate-bearing inclusion that appears to have crystallized from the outside of a molten droplet inward at extremely high temperatures [15]. Despite the fact that the temperature interval for crystallization of this object is so high, from at least 2100 to 1800 K, that the droplet would be extremely unstable with respect to evaporation in a low-pressure gas of solar composition, the REE pattern is neither group III nor ultrarefractory, patterns which could result from high-temperature evaporation, but instead is a modified group II, with C1 chondrite-normalized enrichment factors for LREE, Tb, Tm and Lu being ~35, 14, 23 and 2.4, respectively. Group II patterns were also found in all four calcium dialuminate-bearing inclusions from the Saharan meteorites investigated by BISCHOFF et al. [16]. As is usual in group II inclusions [12], refractory siderophiles are enriched in B6 much less than in most group I inclusions, Ir having an enrichment factor of only 1.1 relative to C1 chondrites.

Volatile Elements: As was also found by EKAMBARAM et al. [14] in their trace element study of refractory inclusions in Murchison, these objects have much lower concentrations of volatile elements than coarse-grained inclusions in Allende. Except for 1950 ppm Na in B3 and 28 ppb Au in B2, the Na concentrations of all inclusions studied here lie in the range of 265-640 ppm and the Au concentrations are all <4.3 ppb, placing them well within the field of coarse-grained inclusions from the reduced subgroup of C3V chondrites, the refractory inclusions with the lowest concentrations of these elements [17]. Despite the pervasive, low-temperature, parent-body alteration history alleged for C2 chondrites such as Murchison, such processes have had only a trivial impact on the volatile element contents of refractory inclusions in this meteorite.

References: [1] FAHEY, A. J. et al. (1987) *GCA* **51**, 329. [2] HINTON, R.W. et al. (1988) *GCA* **52**, 2573. [3] IRELAND, T.R. et al. (1988) *GCA* **52**, 2841.[4] IRELAND, T.R. (1990) *GCA* **54**, 3219. [5] MACPHERSON, G.J. and DAVIS, A.M. (1991) In *LPS XXII*, p. 841. [6] DAVIS, A.M. and MACPHERSON, G.J. (1992) *Meteoritics* **27**, 212. [7] MACPHERSON, G.J. et al. (1980) In *LPS XI*, p. 660. [8] MACPHERSON, G.J. et al. (1989) *Meteoritics* **24**, 297. [9] MAO, X.-Y. et al. (1990) *GCA* **54**, 2121. [10] SYLVESTER, P.J. et al. (1992) *GCA* **56**, 1343. [11] CONARD, R. (1976) M.S. Thesis, Oregon State University. [12] GROSSMAN, L. and GANAPATHY, R. (1976) *GCA* **40**, 967. [13] BOYNTON, W.V. (1978) In *Protostars and Planets*, p. 427. [14] EKAMBARAM, V. et al. (1984) *GCA* **48**, 2089. [15] SIMON, S. et al. (1993) This volume. [16] BISCHOFF, A. et al. (1992) *Meteoritics* **27**, 204. [17] BISCHOFF, A. et al. (1987) In *LPS XVIII*, p. 81.