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Joegoldsteinite: A new sulfide mineral ($MnCr_2S_4$) from the Social Circle IVA iron meteorite

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ABSTRACT

Joegoldsteinite, a new sulfide mineral of end-member formula $MnCr_2S_4$, was discovered in the Social Circle IVA iron meteorite. It is a thiospinel, the Mn analog of daubréelite ($Fe^{2+}Cr_2S_4$), and a new member of the linnaeite group. Tiny grains of joegoldsteinite were also identified in the Indarch EH4 enstatite chondrite. The chemical composition of the Social Circle sample determined by electron microprobe is (wt%) S 44.3, Cr 36.2, Mn 15.8, Fe 4.5, Ni 0.09, Cu 0.08, total 101.0, giving rise to an empirical formula of $(Mn_{0.82}Fe_{0.23})Cr_{1.99}S_{3.95}$. The crystal structure, determined by electron backscattered diffraction, is a $Fd3m$ spinel-type structure with a = 10.11 Å, V = 1033.4 Å^3, and Z = 8.

Keywords: Joegoldsteinite, $MnCr_2S_4$, new sulfide mineral, thiospinel, Social Circle IVA iron meteorite, Indarch EH4 enstatite chondrite

INTRODUCTION

Thiospinels have a general formula of AB_2X_4 where A is a divalent metal, B is a trivalent metal, and X is a –2 anion, typically S, but in some cases Se or Te. Some thiospinels are magnetic semiconductors and have been studied extensively by materials scientists. Synthetic $MnCr_2S_4$ is known to be a ferrimagnetic insulator (Menyuk et al. 1965; Darcy et al. 1968; Lotgering 1968; Plumier 1980; Denis et al. 1970) and recent single-crystal measurements have documented two different anomalies in heat capacity that correlate with magnetic phase transformations (Tsurkan et al. 2003). The complex behavior of thiospinel magnetism results from ferrimagnetic ordering of the Cr and Fe sublattices (Bertinshaw et al. 2014).

Joegoldsteinite is the first known natural occurrence of $MnCr_2S_4$. It is present as two 13–15 μm size subhedral inclusions in the Social Circle IVA iron meteorite. The meteorite itself was found as a single ~100 kg mass in Georgia, U.S.A., in 1926 during plowing (Buchwald 1975).

The IVA irons constitute the third largest "magmatic" iron-meteorite group; each magmatic group is modeled as having formed by fractional crystallization in the metallic core of a differentiated asteroid (e.g., Scott et al. 1996). IVA iron meteorites are fine octahedrites showing Widmanstätten patterns (Buchwald 1975). The bulk Ni concentrations range from ~60 to ~120 mg/g. Studies of the metallographic cooling rates in IVA iron meteorites have been controversial for several decades (e.g., Willis and Wasson 1978a, 1978b; Moren and Goldstein 1978). Relative to other magmatic irons, the IVA group has large depletions in S, Ga, and Ge (Wasson and Richardson 2001). The Ir-rich IVA samples are characterized by lower bulk Ir/Au ratios than comparable members of other iron-meteorite groups (Wasson and Richardson 2001).

The Mn-Cr thiospinel, joegoldsteinite, was approved as a new mineral by the International Mineralogical Association (IMA 2015-049) in August 2015. It was named in honor of Joseph (Joe) I. Goldstein (1939–2015), Distinguished Professor emeritus of mechanical and industrial engineering and former dean of the College of Engineering at the University of Massachusetts, Amherst. Before arriving at Amherst, Goldstein was the T.L. Diamond Distinguished Professor of Metallurgy and R.D. Stout Professor of Materials Science and Engineering at Lehigh University; he served as vice president for graduate studies and research and as director of Lehigh's Electron Optical Laboratory. Goldstein was well known for his fundamental contributions to research on iron meteorites, metallographic cooling rates, Fe-Ni phase equilibria, electron microscopy, and microanalysis.

SAMPLES AND ANALYTICAL METHODS

A polished thick section of Social Circle (TK 724) was made from a 2 × 3 × 5 mm size aliquot from the UCLA meteorite collection. It was examined in reflected light with an Olympus BX60 petrographic microscope and by backscattered electron (BSE) imaging using a VEGA Tescan SEM at UCLA and a Zeiss 1550VP field emission SEM at Caltech. Phases were analyzed by energy-dispersive X-ray spectroscopy (EDX) with the SEM and by a JEOL 8200 electron microprobe (EPMA) (WDS mode, 15 kV, 15 nA, focused beam mode using ZAF corrections) at UCLA. The chemical composition is shown in Table 1. A synthesized $FeCr_2S_4$ single crystal, grown by a chemical transport reaction method similar to that of Tsurkan et al. (2001), was used as a standard for S, Cr, and Fe measurements.

Single-crystal electron backscatter diffraction (EBSD) analyses at a sub-micrometer scale using methods described in Ma and Rossman (2008, 2009) were performed using an HKL EBSD system on the Zeiss 1550VP SEM at Caltech, operated at 20 kV and 6 nA in focused-beam mode with a 70° tilted stage and

TABLE 1. Analytical data for type specimen of joegoldsteinite

Constituent	wt%	Range	S.D.
S	44.3	43.6–44.7	0.4
Cr	36.2	35.7–36.5	0.3
Mn	15.8	15.4–16.0	0.2
Fe	4.5	4.2–5.2	0.3
Ni	0.09	0.02–0.13	0.04
Cu	0.08	0.05–0.11	0.02
Co	<0.03	–	–
Total	101.0		

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in a variable-pressure mode (20 Pa). The EBSD system was calibrated using a single-crystal silicon standard. The structure was determined and cell constants were obtained by matching the experimental EBSD patterns with structures of synthetic $MnCr_2S_4$ and daubréelite.

RESULTS

Petrography and mineral chemistry

Joegoldsteinite occurs as two subhedral inclusions, 13 and 15 μm in diameter, in Social Circle thick section TK 724 (Fig. 1). Physical properties were not measured because of the small grain size; however, they are likely to be close to those of daubréelite. Optical properties of joegoldsteinite were assessed in reflected light and compared to daubréelite grains that are adjacent to metallic Fe-Ni in the Aliskerovo and NWA 4704 IIIE iron meteorites (e.g., Breen et al. 2015). Both minerals have similar reflectivity and color. More accurate comparisons could be made if a single section were available that contained grains of both phases. Electron microprobe data indicate that the empirical formula (based on 7 atoms) is $(Mn_{0.82}Fe_{0.23})Cr_{1.99}S_{3.95}$; the general formula is $(Mn,Fe)Cr_2S_4$ and the end-member formula is $MnCr_2S_4$. The calculated density, based on the empirical formula, is 3.71 g/cm^3.

Joegoldsteinite is a thiospinel, the Mn analog of daubréelite ($Fe^{2+}Cr_2S_4$), and a new member of the linnaeite group. In joegoldsteinite and daubréelite, Fe and Mn probably have a 2+ valence and occupy the tetrahedral (A) sites. Chromium may have a 3+ valence and occupy the octahedral (B) sites. Because joegoldsteinite is $Fd3m$ spinel type, we do not think there is S-S bonding in the structure (a requirement if Cr were 2+; McCoy et al. 2014). It thus seems likely that Cr in both daubréelite and joegoldsteinite is located in the octahedral site; Cr^{3+} should thus be thermodynamically stable at a sufficiently high sulfur fugacity. It seems reasonable that enstatite chondrites could contain both Cr^{3+} and Cr^{2+} in different minerals. (Along with nearly pure forsterite and enstatite, some E3 chondrites contain oxidized mafic silicates, i.e., moderately ferroan olivine (Fa11) and low-Ca pyroxene (Fs18) grains (Weisberg and Kimura 2012).

Some tiny grains of joegoldsteinite associated with troilite (FeS) and niningerite [(Mg,Fe)S] were also observed in the Indarch EH4 enstatite chondrite (Fig. 2), but the grains are too small for accurate quantitative analysis by EPMA.

Crystal structure

The EBSD patterns match the cubic space group $Fd3m$ spinel-type structure (a = 10.11, V = 1033.4 Å^3, Z = 8) and give a best fit using the $MnCr_2S_4$ structure from Raccah et al. (1966) (Fig. 3), with a mean angular deviation of 0.40 to 0.45°. The cell parameters are taken from data for the matching phase in Raccah et al. (1966). X-ray powder diffraction data (Table 2, in angstroms for Cu$K\alpha_1$, Bragg-Brentano geometry) were calculated from the cell parameters of Raccah et al. (1966) with the empirical formula, using Powder Cell version 2.4.

DISCUSSION

Other Mn- and Cr-bearing phases in irons and reduced meteorites

The only known phases with detectable Mn in IVA irons besides joegoldsteinite are daubréelite (~0.2–0.8 wt% Mn) in Maria da Fé (this study) and orthopyroxene (~0.5–0.6 wt% MnO) and clinopyroxene (~0.5 wt% MnO) in Steinbach and São João Nepomuceno (Scott et al. 1996).

Social Circle contains a few Cr-rich phases in addition to joegoldsteinite; these include daubréelite ($FeCr_2S_4$), chromite ($FeCr_2O_4$), and possibly, brezinaite (Cr_3S_4) (Buchwald 1975). Additional Cr-rich

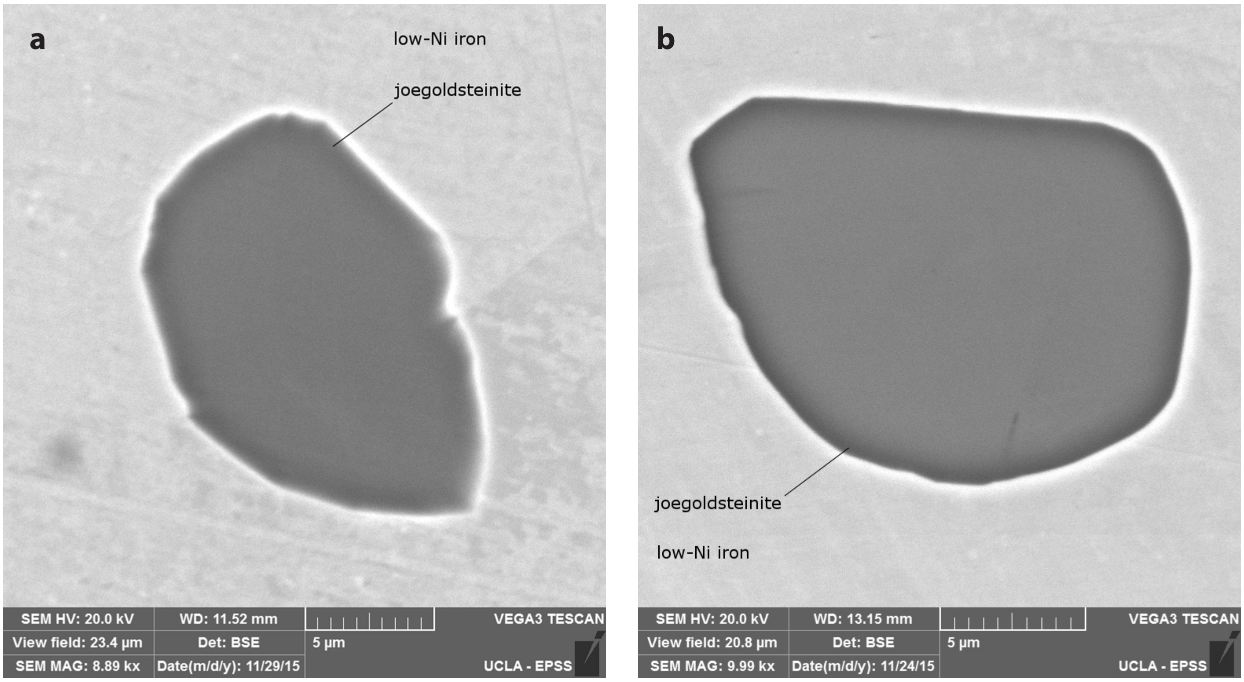

FIGURE 1. Backscattered electron (BSE) images showing two joegoldsteinite grains in Social Circle thick section UCLA TK 724.

phases reported in magmatic iron meteorites (but not in the IVA group) include carlsbergite (CrN) in several IIIAB samples and kosmochlor ($NaCrSi_2O_6$) in a few IIA samples (Buchwald 1975).

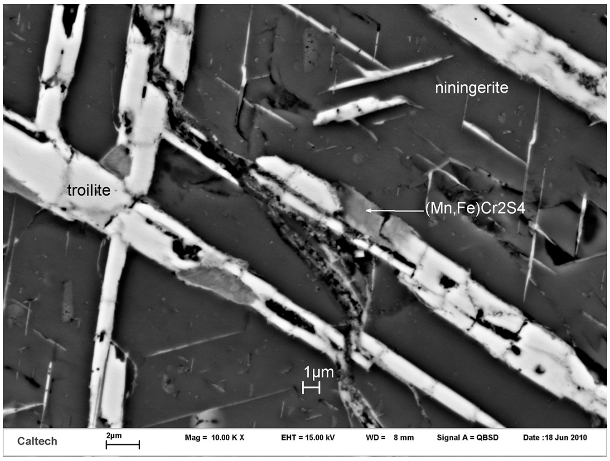

FIGURE 2. BSE image showing the $(Mn,Fe)Cr_2S_4$ phase in Caltech Indarch section ICM3.

Enstatite chondrites, such as EH4 Indarch (in which small grains of joegoldsteinite were found), formed under low f_{O_2} conditions. These rocks contain mafic silicates (predominantly enstatite, with minor forsterite in unequilibrated samples) with very low FeO, Si-bearing metallic Fe-Ni, and sulfide phases containing cations (e.g., Na, Mg, K, Ca, Ti, Cr, Mn, Fe) that partition mainly into silicates and oxides in more-oxidized assemblages (e.g., Keil 1968; Rubin and Keil 1983; Wasson et al. 1994). For example, sulfide in ordinary chondrites (OC), meteorites that are much more oxidized than enstatite chondrites, is Mn free (e.g., Williams et al. 1985; Rubin et al. 2002); Mn in OC occurs principally in olivine, low-Ca pyroxene, Ca-pyroxene, and chondrule mesostasis (e.g., Brearley and Jones 1998).

Additional Mn-bearing sulfides in enstatite chondrites (and related impact-melt rocks and impact-melt breccias) include daubréelite (with 0.7–4.0 wt% Mn), troilite (FeS: 0.02–0.39 wt% Mn), oldhamite (CaS: 0.18–1.3 wt% Mn), niningerite [(Mg,Fe)S: 6.1–12.9 wt% Mn], keilite [(Fe,Mg)S: 3.4–23.7 wt% Mn], rudashevskyite [(Fe,Zn)S: 1.6–3.6 wt% Mn], buseckite [(Fe,Zn,Mn)S, ~10 wt% Mn], browneite (MnS, ~62 wt% Mn) and pentlandite [$(Fe,Ni)_9S_8$: 0.66–1.1 wt% Mn] (Keil 1968, 2007; Lin et al. 1991; Britvin et al. 2008; Ma et al. 2012a, 2012b).

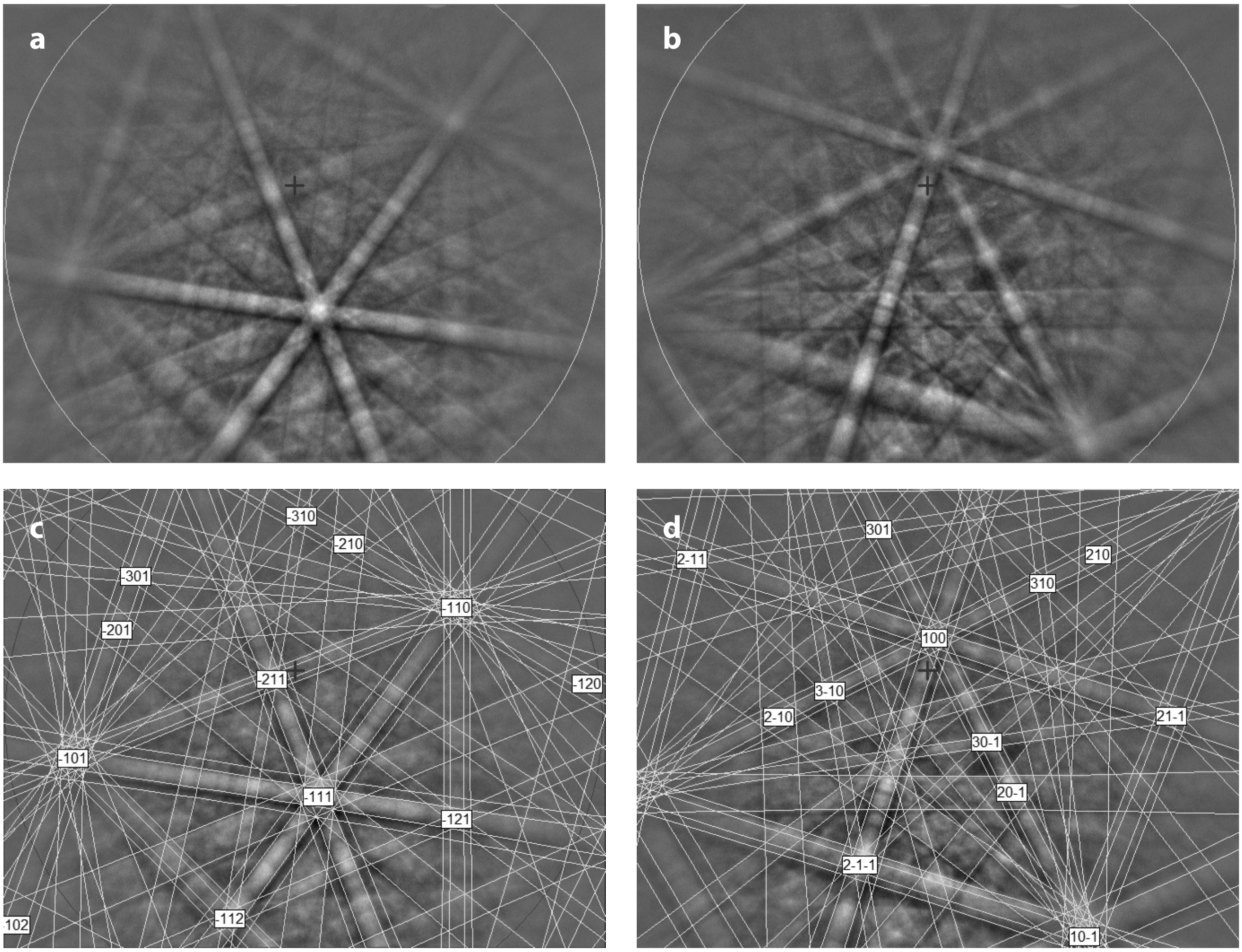

FIGURE 3. (**a** and **b**) EBSD patterns of the joegoldsteinite crystals in Figure 1, and (**c** and **d**) the patterns indexed with the *Fd*3*m* $MnCr_2S_4$ structure.

TABLE 2. Calculated X-ray powder diffraction data for joegoldsteinite ($I_{rel} > 1$)

h	*k*	*l*	*d* (Å)	I_{rel}
1	1	1	5.837	18
2	2	0	3.574	34
3	1	1	3.048	100
2	2	2	2.919	2
4	0	0	2.528	58
4	2	2	2.064	12
3	3	3	1.946	3
5	1	1	1.946	50
4	4	0	1.787	95
5	3	1	1.709	3
6	2	0	1.599	4
5	3	3	1.542	12
4	4	4	1.459	10
5	5	1	1.416	4
6	4	2	1.351	7
5	5	3	1.316	11
7	3	1	1.316	5
8	0	0	1.264	13
7	3	3	1.235	1
8	2	2	1.191	2
6	6	0	1.191	2
7	5	1	1.167	8
5	5	5	1.167	4
8	4	0	1.130	12
9	1	1	1.110	2
9	3	1	1.060	12
8	4	4	1.032	27
7	7	1	1.016	1
10	2	0	0.991	2
8	6	2	0.991	2
9	5	1	0.977	17
9	5	3	0.943	2
10	4	2	0.923	1
11	1	1	0.912	1
7	7	5	0.912	1
8	8	0	0.894	12
11	3	1	0.883	1
9	5	5	0.883	3
8	8	2	0.880	1
8	6	6	0.867	2
9	7	3	0.858	7
12	0	0	0.843	2
8	8	4	0.843	9
7	7	7	0.834	1
12	2	2	0.820	1
10	6	4	0.820	9
9	7	5	0.812	13
11	5	3	0.812	3
12	4	0	0.799	40

Shock effects

The presence of Neumann lines in Social Circle kamacite indicates that the sample was shocked to at least 10 kbar after cooling (Buchwald 1975). A later shock event caused widespread heating of the meteorite: (1) kamacite throughout the mass recrystallized, partially obliterating the Neumann lines (and forming "parallel ghost-lines"), (2) taenite and plessite fields partly decomposed and underwent minor spheroidization, and (3) troilite-metal eutectic shock melts formed (Buchwald 1975). It seems plausible that impact melting of the sulfide assemblages increased the Mn concentration in portions of the S-rich melts, facilitating the crystallization of joegoldsteinite.

After the formation of joegoldsteinite in Social Circle, a minor shock event caused shearing in the grain in the top image of Figure 1. Displacement by ~0.2 μm occurred along a kamacite grain boundary (also probably produced by shearing) running diagonally from SW to NE-ENE.

IMPLICATIONS

It has been shown that $MnCr_2S_4$ can transform from the spinel structure (where two-thirds of the cations are octahedrally coordinated) to the defect NiAs structure (where all cations are octahedrally coordinated) at temperatures of 1000 °C and pressures of 65 kbar (6.5 GPa) (Bouchard 1967). The high-pressure structure is reversible (Vaqueiro et al. 2001). Because of this structural reversibility, empirical observations of thiospinel minerals are unlikely to be useful for constraining the formation temperatures and pressures of asteroidal materials. Nevertheless, chalcospinels, thiospinels, and selenospinels have been used for geophysical studies because their phase transitions are good analogs for those of oxyspinel compounds. These are known to show phase transitions in high-pressure regimes (e.g., 29 GPa for $FeCr_2O_4$, Shu et al. 2007), while thiospinel transitions occur at lower pressure (e.g., 9 GPa for $FeCr_2S_4$, Amiel et al. 2011; and Manjon et al. 2014; Santamaría-Pérez et al. 2012).

It seems probable that additional occurrences of joegoldsteinite in enstatite chondrites and IVA irons could be identified by making Mn X-ray maps of enstatite chondrite thin sections and running EDS scans of sulfide grains in sections of iron meteorites. In enstatite chondrites, joegoldsteinite is most likely to be found in association with other sulfide phases; in IVA irons, it could be found as isolated crystals as in Social Circle or as parts of polymineralic sulfide assemblages.

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REFERENCES CITED

Amiel, Y., Rozenberg, G.K., Nissim, N., Milner, A., Pasternak, M.P., Hanfland, M., and Taylor, R.D. (2011) Intricate relationship between pressure-induced electronic and structural transformations in $FeCr_2S_4$. Physical Review B, 84(9), 224114.

Bertinshaw, J., Ulrich, C., Günther, A., Schrettle, F., Wohlauer, M., Krohns, S., and Deisenhofer, J. (2014) $FeCr_2S_4$ in magnetic fields: possible evidence for a multiferroic ground state. Scientific Reports, 4, 6079.

Bouchard, R.J. (1967) Spinel to defect NiAs structure transformation. Materials Research Bulletin, 2(4), 459–464.

Brearley, A.J., and Jones, R.H. (1998) Chondritic meteorites. Reviews in Mineralogy, 36, p. 3-1–3-398.

Breen, J.P., Rubin, A.E., and Wasson, J.T. (2015) Shock effects in IIIE iron meteorites: Implications for parent-body history. Meteoritics & Planetary Science, 50, Abstract 5083.

Britvin, S.N., Bogdanova, A.N., Boldyreva, M.M., and Aksenova, G.Y. (2008) Rudashevskyite, the Fe-dominant analogue of sphalerite, a new mineral: Description and crystal structure. American Mineralogist, 93, 902–909.

Buchwald, V.F. (1975) Handbook of iron meteorites, their history, distribution, composition, and structure. Center for Meteorite Studies, Arizona State University.

Darcy, L., Baltzer, P.K., and Lopatin, E. (1968) Magnetic and crystallographic properties of the system $MnCr_2S_4$–$MnInCrS_4$. Journal of Applied Physics, 39(2), 898–899.

Denis, J., Allain, Y., and Plumier, R. (1970) Magnetic behavior of $MnCr_2S_4$ in high magnetic fields. Journal of Applied Physics, 41(3), 1091–1093.

Keil, K. (1968) Mineralogical and chemical relationships among enstatite chondrites. Journal of Geophysical Research, 73(22), 6945–6976.

——— (2007) Occurrence and origin of keilite, $(Fe_{>0.5},Mg_{<0.5})S$, in enstatite chondrite impact-melt rocks and impact-melt breccias. Chemie der Erde, 67, 37–54.

Lin, Y.T., Nagel, H-J., Lundberg, L.L., and El Goresy, A. (1991) MAC88136—The first EL3 chondrite (abstract). Lunar and Planetary Science, 22, 811–812.

Lotgering, F.K. (1968) Spin canting in $MnCr_2S_4$. Journal of Physics and Chemistry of Solids, 29(12), 2193–2197.

Ma, C., and Rossman, G.R. (2008) Barioperovskite, $BaTiO_3$, a new mineral from the Benitoite Mine, California. American Mineralogist, 93, 154–157.

——— (2009) Tistarite, Ti_2O_3, a new refractory mineral from the Allende meteorite. American Mineralogist, 94, 841–844.

Ma, C., Beckett, J.R., and Rossman, G.R. (2012a) Buseckite, (Fe,Zn,Mn)S, a new mineral from the Zakłodzie meteorite. American Mineralogist, 97, 1226–1233.

——— (2012b) Browneite, MnS, a new sphalerite-group mineral from the Zakłodzie meteorite. American Mineralogist, 97, 2056–2059.

Manjon, F.J., Tiginyanu, I., and Ursaki, V. (2014) Pressure-Induced Phase Transitions in AB_2X_4 Chalcogenide Compounds. Springer Series in Materials Science, 189, 243 pp. Springer, Berlin.

McCoy, T.J., McKeown, D.A., Buechele, A.C., Tappero, R., and Gardner-Vandy, K.G. (2014) Do enstatite chondrites record multiple oxidation states? Lunar and Planetary Science, 45, Abstract 1983.

Menyuk, N., Dwight, K., and Wold, A. (1965) Magnetic properties of $MnCr_2S_4$. Journal of Applied Physics, 36(3), 1088–1089.

Moren, A.E., and Goldstein, J.I. (1978) Cooling rate variations of group IVA iron meteorites. Earth and Planetary Science Letters, 40, 151–161.

Plumier, R. (1980) The magnetic structure of sulfur spinel $MnCr_2S_4$ under applied magnetic field. Journal of Physics and Chemistry of Solids, 41(8), 871–873.

Raccah, P.M., Bouchard, R.J., and Wold, A. (1966) Crystallographic study of chromium spinels. Journal of Applied Physics, 37, 1436–1437.

Rubin, A.E., and Keil, K. (1983) Mineralogy and petrology of the Abee enstatite chondrite breccia and its dark inclusions. Earth and Planetary Science Letters, 62, 118–131.

Rubin, A.E., Zolensky, M.E., and Bodnar, R.J. (2002) The halite-bearing Zag and Monahans (1998) meteorite breccias: Shock metamorphism, thermal metamorphism and aqueous alteration on the H-chondrite parent body. Meteoritics and Planetary Science, 37, 125–141.

Santamaría-Pérez, D., Amboage, M., Manjón, F.J., Errandonea, D., Muñoz, A., Rodríguez-Hernández, P., Mújica, A., Radescu, S., Ursaki, V.V., and Tiginyanu, I.M. (2012) Crystal chemistry of $CdIn_2S_4$, $MgIn_2S_4$, and $MnIn_2S_4$ thiospinels under high pressure. Journal of Physical Chemistry C, 116, 14078–14087.

Scott, E.R.D., Haack, H., and McCoy, T.J. (1996) Core crystallization and silicate-metal mixing in the parent body of the IVA iron and stony-iron meteorites. Geochimica et Cosmochimica Acta, 60, 1615–1631.

Shu, J., Mao, L., Hemley, R.J., and Mao, H. (2007) Pressure-induced distortive phase transition in chromite-spinel at 29 GPa. Materials Research Society Symposium Proceedings, 987.

Tsurkan, V., Hemberger, J., Klemm, M., Klimm, S., Loidl, A., Horn, S., and Tidecks, R. (2001) Ac susceptibility studies of ferrimagnetic $FeCr_2S_4$ single crystals. Journal of Applied Physics, 90, 4639–4644.

Tsurkan, V., Mücksch, M., Fritsch, V., Hemberger, J., Klemm, M., Klimm, S., Körner, S., Krug von Nidda, H.-A., Samusi, D., Scheidt, E.-W., and others. (2003) Magnetic, heat capacity, and conductivity studies of ferrimagnetic $MnCr_2S_4$ single crystals. Physical Review B, 68(13), 134434.

Vaqueiro, P., Powell, A.V., Hull, S., and Keen, D.A. (2001) Pressure-induced phase transitions in chromium thiospinels. Physical Review B, 63(6), 064106.

Wasson, J.T., and Richardson, J.W. (2001) Fractionation trends among IVA iron meteorites: contrasts with IIIAB trends. Geochimica et Cosmochimica Acta, 65(6), 951–970.

Wasson, J.T., Kallemeyn, G.W., and Rubin, A.E. (1994) Equilibration temperatures of EL chondrites: A major downward revision in the ferrosilite contents of enstatite. Meteoritics, 29, 658–661.

Weisberg, M.K., and Kimura, M. (2012) The unequilibrated enstatite chondrites. Chemie der Erde, 72, 101–115.

Williams, C.V., Rubin, A.E., Keil, K., and San Miguel, A. (1985) Petrology of the Cangas de Onis and Nulles regolith breccias: Implications for parent body history. Meteoritics, 20, 331–345.

Willis, J., and Wasson, J.T. (1978a) Cooling rates of Group IVA iron meteorites. Earth and Planetary Science Letters, 40, 141–150.

——— (1978b) A core origin for Group IVA iron meteorites: A reply to Moren and Goldstein. Earth and Planetary Science Letters, 40, 162–167.

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