

SULFIDIZATION CONTEMPORANEOUS WITH OXIDATION AND METAMORPHISM IN CK6 CHONDRITES. T.J. McCoy¹, C.M. Corrigan¹, J. Davidson², D.L. Schrader³, and K. Righter⁴ ¹Dept. of Mineral Sciences, Smithsonian Institution, Washington DC 20560-0119 USA (mccoyt@si.edu) ²Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, DC 20015-1305, USA ³Center for Meteorite Studies, School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287 USA ⁴NASA Johnson Space Center, Houston, TX 77058 USA.

Introduction: As the most oxidized chondrites and a group of carbonaceous chondrites spanning the range of petrologic types [1], CK chondrites occupy an extreme in our understanding of the origin and evolution of chondritic parent bodies. With the proposed linkage of CV and CK chondrites [2] and the suggestion that differentiation of a postulated CV-CK asteroid could have differentiated to form a core and established a magnetic dynamo [3], CK chondrites are receiving considerable attention [e.g., 4-7]. Most of this attention has focused on the similarities between CK3 and CV3 chondrites [e.g., 4-6] and the origin of each [e.g., 7]. We have previously argued that melting of an oxidized core could produce a magnetite-sulfide core, rather than the more conventional metal-sulfide core [8]. In this work, we focus on CK6 chondrites to understand the origin of the most highly metamorphosed members of the group as representative of the material that might differentiate to form such an oxidized core.

Metamorphism: While early work [9,10] suggested peak metamorphic temperatures for CK6 chondrites of ~800-1000°C, [1,11] have suggested lower peak temperatures of ~750-800°C. Our analyses of high-Ca/low-Ca pyroxene pairs in CK6 chondrites yielded weighted temperatures of 755±38°C (weighted mean±2σ) for LAR 12265, 727±78°C for LAR 06636, and 745±26°C for LEW 87009 using the QUILF program [12]. The latter value is within uncertainty of the value (740±38°C) reported by [11] for LEW 87009.

Fe-Ti equilibration temperatures can also be determined from magnetite-ilmenite pairs. [1] determined temperatures for CK4-CK5,6 chondrites of ~300-650°C. These authors calculated a significant range of temperatures within individual chondrites (e.g., 413-658°C within the CK4 chondrite EET 99430), perhaps suggesting incomplete equilibration. Using the revision of [13], we calculate temperatures of 270-326°C for LAR 06636 and 423-460°C for LEW 87009, both CK6 chondrites. In addition to different Fe-Ti equilibration temperatures, magnetite-ilmenite pairs in these meteorites differ significantly in Cr₂O₃, with LEW 87009 containing ~2 times that in LAR 06636.

[1] argued that CK6 chondrites showed lower equilibration temperatures than type 6 ordinary chondrites, with two-pyroxene temperature for H6, L6 and LL6 chondrites ranging from 812-945°C [12]. Our results

suggest that within a single meteorite, magnetite-ilmenite Fe-Ti equilibration records significantly lower temperatures (~300-400°C) than two-pyroxene equilibration temperatures. When comparing two-pyroxene temperatures for CK6 and type 6 ordinary chondrites, while the CK6 chondrites record lower overall equilibration temperatures, the difference is in the range of 100-200°C, a smaller difference than suggested by [1].

Oxidation: Consistent with the presence of abundant magnetite, which is rare in most other meteorites, CK6 chondrites are the most oxidized meteorites. Magnetite-ilmenite pairs have yielded oxygen fugacities (*f*O₂) of 2.0 to 5.1 log units above QFM [1].

Magnetites in the CK6 chondrites LAR 06636 and LEW 87009 contain 1-5 μm wide ilmenite lamellae. To analyze these, we conducted traverses with ~0.7 μm spacing (Fig. 1) using the new JEOL 8530F microprobe at the Smithsonian Institution. The centers of the lamellae are stoichiometric ilmenite (Fe₂TiO₄). At the boundaries of this center region, areas enriched in Al₂O₃ are observed, likely reflecting coupled substitution of Fe³⁺Al³⁺ for Fe²⁺Ti⁴⁺. Ilmenite-magnetite pairs yield *f*O₂ of QFM+2.6 to QFM+2.7 for both LAR 06636 and LEW 87009, using the calibration of [14].

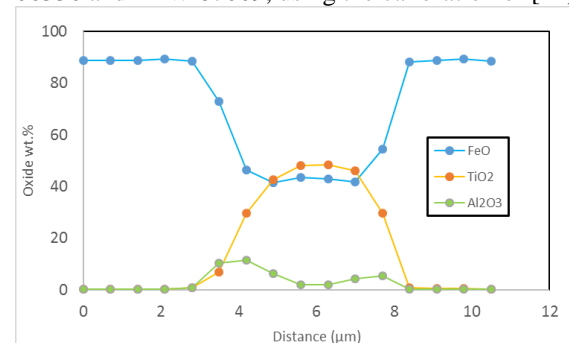


Fig. 1. Zoning profile across an ilmenite lamellae in magnetite in the CK6 LAR 06636.

Our derived values are at the lower end of the range determined by [1]. The data of [1], using the calibration of [14], yields *f*O₂ ~1 log unit lower, explaining part of the discrepancy. The remainder results from the analyses utilized. *f*O₂ calculated using the center analyses is ~2 log units than with the Al₂O₃-rich analyses (Fig. 1). Low Al₂O₃ analyses from [1] yield similar values of ~QFM+2.5. We suggest that this value accurately reflects the oxidation conditions experienced by CK6 chondrites.

The strongest evidence that oxidation occurred as a result of interaction with a fluid comes from oxygen isotopic disequilibrium ($\Delta^{17}\text{O}$) between olivine and magnetite in CK3 chondrites [7]. These authors suggested that olivine inherited its oxygen isotopic signature from the solar nebula, while the oxygen isotopic composition of magnetite reflects its formation by replacement of metal during interaction with a fluid. If we assume a simplified reaction of $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$ and ~10 wt.% magnetite in CK chondrites, ~4 wt.% H_2O is required for the reaction. This is more than typically argued for ordinary chondrites, but substantially less than for CM and CI chondrites. Thus, a portion of the thermal energy from ^{26}Al decay may have been required for melting of ice and reaction in CK chondrites, perhaps reducing energy available for thermal metamorphism and explaining the lower peak temperatures for CK chondrites compared to ordinary chondrites.

Sulfidization: Numerous authors have discussed the chemical composition of, and relationships between, sulfides in CK chondrites [e.g., 1,10,11]. During the course of this study, we observed a textural association between low-Ca orthopyroxene and sulfides not previously discussed (Fig. 2).

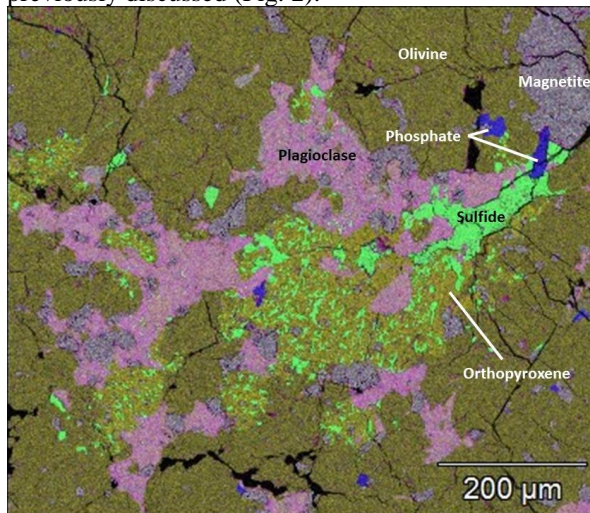
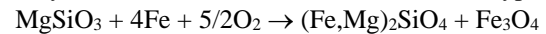


Fig. 2. Combined element map of LEW 87009 exhibiting finely dispersed sulfide within orthopyroxene.

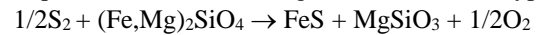
Within several CK6 chondrites, orthopyroxene occurs most frequently in this textural association with finely-dispersed sulfide. Grains of this type were analyzed for two-pyroxene equilibration temperatures and are remarkably uniform throughout the individual meteorite, suggesting formation during metamorphism.

The textural association may be indicative of a sulfidization reaction and we considered a number of possible pathways for formation of these phases. If formation of magnetite by alteration of metal from a fluid

also involved silicates, orthopyroxene could have been initially converted to olivine in a reaction of the type:

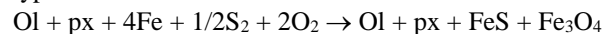


In this scenario, low-Ca orthopyroxene might form by subsequent sulfidization through a reaction of the type:



This reaction could explain the association between sulfide and orthopyroxene, although the production of orthopyroxene substantially more magnesian than olivine would then require subsequent metamorphism to drive silicate equilibration.

Alternatively, oxidation and sulfidization could have occurred concurrently, yielding a reaction of the type:



While the combined reaction explains the formation of both sulfide and magnetite, it offers no ready explanation for the co-occurrence of orthopyroxene and sulfides. It also does not offer a ready explanation for the fact that this texture seems restricted to CK6 chondrites. Thus, it seems more likely that oxidation was followed by sulfidization, but that both occurred during a prolonged period of metamorphism.

Implications: The interplay between oxidation, sulfidization and metamorphism is common in both chondrites [15] and achondrites [16]. Given the similar S concentrations in LEW 87009 compared to CK5-6 meteorites that lack evidence for sulfidization [17], sulfur was likely volatilized locally, as also suggested for ordinary chondrites [15]. The redistribution of sulfide increases sulfide abundances locally, with magnetite:sulfide ratios approaching the 50:50 magnetite:sulfide of the eutectic in the Fe-S-O system [18], perhaps allowing magnetite-sulfide melting that would mark the onset of formation of a highly-oxidized core.

References: [1] Righter K. and Neff K.E. (2007) *Polar Sci.*, 1, 25–44. [2] Greenwood R.C. et al. (2010) *GCA*, 74, 1684–1705. [3] Elkins-Tanton L.T. et al. (2011) *EPSL*, 305, 1–10. [4] Wasson J.T. et al. (2013) *GCA*, 108, 45–62. [5] Dunn T.L. (2016) *MAPS*, 51, 1701–1720. [6] Davidson J. et al. (2011) *42nd LPSC*, Abstract #1886. [7] Davidson J. et al. (2014) *MAPS*, 49, 1456–1474. [8] McCoy T.J. et al. (2015) *46th LPSC*, Abstract #2393. [9] Geiger T. and Bischoff A. (1991) *Meteoritics*, 26, 337. [10] Geiger T. and Bischoff A. (1995) *PSS*, 43, 485–498. [11] Schrader D.L. et al. (2016) *GCA*, 189, 359–376. [12] Anderson D. (1993) *Comput. Geosci.*, 19, 1333–1350. [13] Slater-Reynolds V. (2005) *MAPS*, 40, 745–754. [14] Ghiorso M.S. and Evans B.W. (2008) *AJS*, 308, 957–1039. [15] Lauretta D.S. et al. (1997) *EPSL*, 151, 289–301. [16] Rosenshein E.B. et al. (2006) *MAPS*, 41, 495–503. [17] Jarosewich E. (1991) *Meteoritics*, 25, 323–337. [18] Naldrett A.J. (1969) *J. Petrol.* 10, 171–201.