

Introduction. Magnesioferrite spinel grains are found in spherules at the Cretaceous/Tertiary boundary around the globe [1, 2], and are probably the most definitive and specific marker of that boundary [3]. One hypothesis is that they crystallized from silicate liquids which condensed directly from the initial, partially or completely vaporized plume resulting from the Chicxulub impact [4-7]. Here, this hypothesis is tested with a model of equilibrium condensation of such a 'fireball'. Using a condensation code developed to explore the stability of silicate liquids in dust-enriched nebular regions [8], we investigated the phase assemblages which condense from a plume of vaporized impactor and target lithologies, following realistic P-T paths. Recognizing that present understanding of plume interactions with an atmosphere is not profound, we also explored the consequences of mixing air into the plume. Results indicate that condensation of silicate liquid, followed by spinel crystallization from that liquid, could indeed have occurred in the Chicxulub fireball.

Technique. We modified the VAPORS code described previously [8, 9] to condense bulk compositions along fixed pressure-temperature (P-T) paths. VAPORS includes both the silicate liquid model and solid solution models embodied in the MELTS code of Ghiorso and Sack [10], but does not address ultra-refractory Fe-Mg-O liquids or the magnesiowüstite solid solution. The 18 elements H, C, N, O, Na, Mg, Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe, Co, and Ni are included here. The spinel solution model includes only Mg, Fe²⁺, Fe³⁺, Ti, Cr, and Al components, thus we do not address the Ni content (mean ~3 wt%) of the spinels observed at the K/T boundary [4]. The data and models are used here somewhat above the temperatures for which they were initially calibrated, rendering the results less quantitatively exact than might be desired.

The present calculations use initial fireball compositions based on results provided by Melosh (1997, pers. comm.) for the relative volumes of material vaporized by a 20 km/sec vertical impact, on a realistic target sedimentary rock and crustal lithology, of four dunite impactors of differing diameter and porosity, corresponding to runs number 1-4. Melosh estimated the vapors resulting from these impacts to have volume proportions of the components crust, water, sediment, and impactor as detailed in Table 1:

run	km	porosity	crust:water:seds:bolide
1	10	0	2.79 : 4.48 : 8.87 : 1.0
2	10	50%	0.95 : 4.96 : 9.83 : 1.0
3	20	0	2.70 : 0.61 : 2.75 : 1.0
4	20	50%	1.15 : 0.69 : 2.75 : 1.0

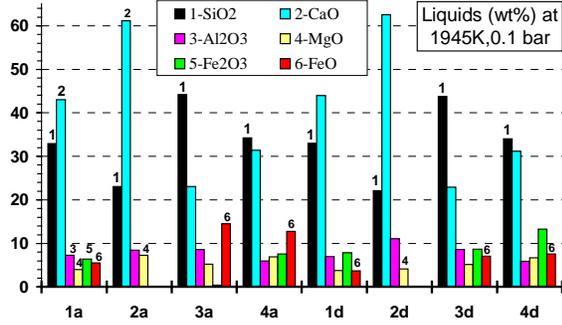
All these proportions are very similar to values recently published for these same cases [11]. Recent evidence strongly suggests that the Chicxulub bolide was of CV, CO or CR carbonaceous chondrite composition [12], and here CV chondrite [13] is assumed. Continental crust was taken as USGS granite G2 [14]. Proportions of carbonate and sulfate in pre-impact sediments have been a matter of some debate [11]. Here, the averages of stratigraphic thicknesses measured from two published sections [15, 16] of Pemex well Y4 were used, yielding volume fractions 0.568 calcite, 0.270 dolomite, 0.112 anhydrite, 0.036 sand, and 0.013 shale. The percentage of anhydrite in this result is markedly less than in [11].

Because air entrainment might occur in a fireball, runs were performed on bulk compositions 1-4 both with and without air admixtures. The air-free runs are labeled with an 'a', and those with an air/plume ratio of 2x 'd', for a total of 8 bulk compositions for runs 1a to 4d. Earth air was added so that the total number of atoms of air was twice the total number of atoms in the air-free bulk composition.

The P-T paths used here, kindly provided by Melosh [17; pers. comm.], were calculated for a distally located cell (#30), in an expanding sphere of hot dunite vapor with an initial internal energy of 71 MJ/kg. The same P-T path was used for all condensation scenarios reported here, because the path of a centrally located cell (#1) overlaps the P-T path of cell 30. Due to data considerations described in [8], calculations were limited to P < 1.0 bar, and T < 2400K. The (time since impact, P, T) coordinates run from (13.3s, 0.23b, 2354K) to (30.8, 0.0096, 1100), but depletion of the vapor causes runs to halt at intermediate T, usually close to the disappearance temperature of liquid, for reasons discussed in [8].

Results. Silicate liquid is the first condensate in all cases. Because sediment enriches the vapors in Ca, there is difficulty in using the 'MELTS' liquid model [10], which has CaSiO₃ as the Ca end-member [8]. The CaO-MgO-Al₂O₃-SiO₂ (CMAS) liquid model of [18], is ineffective used alone in Fe-rich systems. There is a high degree of consistency between the two models, as explored by [8], who also found that allowing both liquids to condense simultaneously yielded results close to those for condensation of the MELTS liquid alone, for compositions with Si/(Ca+½Mg+½Fe)>1. Here, CMAS liquids dominate by mass, and Fe, P, and Ti concentrate in MELTS liquids, making compositions far from that solution model's calibration range. Reported liquid compositions are the sum of the MELTS and CMAS liquids computed to condense simultaneously, as an

approximation to the actual propensities of the oxides to condense as liquid. Liquid compositions at the 1945K, 0.1bar step are illustrated in figure 1:



The oxygen fugacities of the vapor plumes are sensitive to sediment/(crust + impactor) ratios (e.g.-1a vs. 3a) and to admixed air (e.g.-1a vs. 1d). Even without adding air, these systems are much more oxidizing than has been speculated [3, 19]. The P^{tot} -T path, and f_{O_2} -T paths, are shown in figure 2:

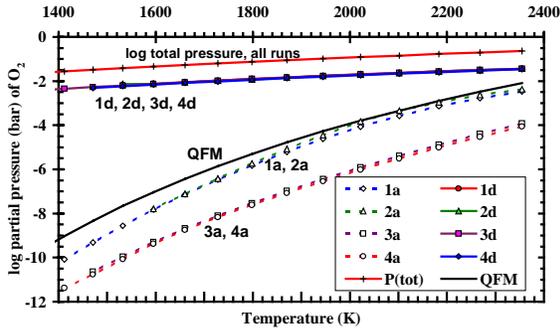
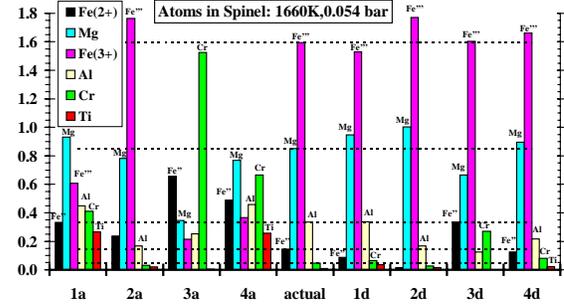


Table 2 documents the T steps (fig.2) at which metal, spinel, and major Ca-silicate (larnite Ca_2SiO_4 , melilite, hattrite Ca_3SiO_5 , or Ca-rich pyroxene) condense. Metal alloy always has Ni >75wt%, with Co<5wt%. Some Ni would, in a real vapor, condense as oxide in the spinel. The Ca- and Si-rich liquids crystallize to form silicates with decreasing T.

Tab.2	1	2	3	4
metal	a 2022 d 1595	a 2022 d<1595	a 2183 d 1870	a 2183 d 1870
spinel	a 2101 d 2022	a 2354 d 2267	a 1660 d 1798	a 1945 d 2022
Ca-Si phase	a 2022 b 2022	a 2101 d 2183	a 1532 d 1595	a 1595 d 1532

Cr-rich spinel condenses at a high temperature in every case. In the air-enriched, high f_{O_2} runs, Cr in spinel drops, and Fe^{3+} increases, with decreasing T, reaching the range observed in magnesioferrite spinels [2-4] in the basal K/T boundary clay. In air-free runs, this transition from Cr-rich to Fe^{3+} -rich spinel occurs at lower T. At the low f_{O_2} of runs 3a and 4a, spinels remain Cr-rich even to 1400K. In run 2a, the near-QFM f_{O_2} , and the lack of an alternative

Fe-bearing phase, cause this transition to occur above 1700K. In run 1a, liquid persists, and the transition occurs at a T ~200K lower. The cationic formulae of spinel calculated at the 1660K, 0.054 bar are illustrated, along with the mean of actual compositions reported by [2, 4; with $\text{Mg}=(\text{Mg}+\text{Ni}+\text{Mn})$] for comparison, in figure 3:



Discussion. These results strongly indicate that spinel would co-condense with Ca-silicate liquid and Ni-rich metal from the type of fireball expected from the Chicxulub impact. Spinel condensed from plumes with admixed air exhibit Cr-poor, Fe^{3+} -rich compositions similar to the magnesioferrite spinels in the K/T basal boundary clay spherules, as do relatively low-T spinels from air-free plumes resulting from some impactor characteristics. The authigenic Fe-hydroxide + clay of the spinel-bearing spherules could well represent severely altered glass and/or Ca-silicates, similar to those with which spinel is calculated to co-condense. Perhaps the Ni-rich inclusions reported by [20] are remnants of Ni-rich metal predicted to condense with spinel. Our results support the idea that magnesioferrite spinels in the basal K/T boundary clay formed by condensation from the vapor of the Chicxulub plume.

References. [1] Alvarez (1996) *GSA Spec. Pap.* 307, 141. [2] Smit & Kyte (1984) *Nature* 310, 403. [3] Gayraud *et al.* (1996) *GSA Spec. Pap.* 307, 425. [4] Kyte & Bostwick (1995) *EPSL* 132, 113. [5] Kyte & Smit (1988) *Geology* 14, 485. [6] Bohor *et al.* (1986) *EPSL* 81, 57. [7] O'Keefe & Ahrens (1988) *LPSC XIX*, 883. [8] Ebel & Grossman (1999) *GCA* (in rev.). [9] Ebel & Grossman (1998) *LPS XXIX*, Abs. #1421. [10] Ghiorso & Sack (1995) *Contrib. Mineral. Petrol.* 119, 197. [11] Pierazzo *et al.* (1998) *JGR* 103, 28607. [12] Kyte (1998) *Nature* 396, 237. [13] Wasson & Kallemeyn (1988) *Phil. Trans. R. Soc. Lond. A* 325, 535. [14] Flanagan (1967) *GCA* 31, 289. [15] Sharpton *et al.* (1996) *GSA Spec. Pap.* 307, 55. [16] Ward *et al.* (1995) *Geology* 23, 873. [17] Melosh and Pierazzo (1997) *LPSC XXVII*, 935. [18] Berman (1983), Ph.D., U.B.C. [19] Robin *et al.* (1992) *LPS XXIII*, 1161. [20] Doehne & Margolis (1990) *GSA Spec. Pap.* 247, 367.