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Nickel-rich magnesiowüstite in Cretaceous/Tertiary boundary spherules crystallized from ultramafic, refractory silicate liquids

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Abstract—We have found trace inclusions of Ni-rich magnesiowüstite within grains of magnesioferrite spinel recovered from Cretaceous/Tertiary boundary sediments from DSDP Site 596, South Pacific (23°51.20′S, 169°39.27′W) and DSDP Site 577, North Pacific (32°26.51′N, 157°43.40′E). Measured compositions of these inclusions range from $(Mg_{.85}Ni_{.11}Fe_{.04})O$ to $(Mg_{.74}Ni_{.09}Fe_{.17})O$. Coexisting magnesioferrite and magnesiowüstite can only crystallize from ultramafic, refractory, Mg-rich liquids with Mg/Si > 2 (atom ratio). Such liquid compositions cannot form as a result of fractional crystallization and are unknown to occur as a result of terrestrial igneous processes or meteoroid ablation. We infer that these minerals crystallized from liquid droplets that equilibrated with silicate vapor at high temperatures (probably >2300°C), resulting in fractionation of volatile SiO_2 from more refractory MgO. The most plausible source of this high-temperature vapor is in the fireball of the major impact event that terminated the Cretaceous.

1. INTRODUCTION

More than a decade ago, abundant spherules containing sanidine, glauconite, and magnetite (Smit and Klaver, 1981; Montanari et al., 1983) were first reported in Cretaceous/Tertiary (K/T) boundary sediments. They were cited as evidence that these sediments contained relicts of high-temperature, originally molten impact debris. However, these spherules were largely composed of authigenic phases that had replaced the original spheroidal materials (e.g., Montanari et al., 1983; DePaolo et al., 1983). Thus a considerable difference of opinion was expressed in the literature as to whether K/T spheroids were impact-derived (e.g., Smit et al., 1992a) or byproducts of biological (Hansen et al., 1986) or diagenetic (Izett, 1987) processes. Over the past decade there have been numerous reports of traces of high-temperature phases that appear to have survived diagenetic alteration. These include impact glass at K/T boundary sites in Haiti and northeastern Mexico (Sigurdsson et al., 1991; Smit et al., 1992b), rare clinopyroxene in spherules from DSDP Site 577, N. Pacific (Smit et al., 1992a), and magnesioferrite spinel from several sites around the world (e.g., Smit and Kyte, 1984; Kyte and Smit, 1986; Bohor et al., 1986; Jéhanno et al., 1992).

Not all of the K/T boundary spherules and associated high-temperature phases are necessarily derived from the same materials. Bohor and coworkers (Bohor, 1990; Bohor and Betterton, 1990, 1992; Bohor and Glass, 1995) and Smit et al. (1991, 1992a) have argued that at least two types of spheroidal debris occur in two distinct strewn fields. They are segregated by type between the two layers that occur in the K/T boundary unit at nonmarine sites in the Western Interior of North America (Pollastro and Bohor, 1993). One type of spherule is larger than the other, contains no magnesioferrite spinel, and is interpreted as originally composed of target-rock melt glass (Type 1 of Bohor and Betterton, 1990). These spherules have a restricted radial distribution around the putative impact crater in the Yucatán (Hildebrand et al., 1991; Sharpton et al., 1992). They occur as smectitic spherules with traces of glass in Haiti and Mexico. They are confined to the lower of the two boundary layers in the Western Interior (the kaolinitic layer) where they are mostly hollow, and they have been described in North Pacific Sites DSDP 577 and LL44-GPC3. The other spherules (Type 2 of Bohor and Betterton, 1990; microkrystites of Smit et al., 1992a) are globally distributed and in the Western Interior they are restricted to the upper, Ir-rich layer. This type of spherule displays textures interpreted as pseudomorphic after melt-crystallized phases (Smit et al., 1992a) and often contain magnesioferrite spinel. The larger, regionally distributed spherules have been interpreted to be microtektite-like glassy spherules that were distributed ballistically by the K/T impact. In contrast, the globally distributed crystallized spherules are described as formed from droplets condensed from an earth-girdling impact vapor cloud expanding above the atmosphere (Pollastro and Bohor, 1993).

In this paper we report analyses of high-temperature minerals found in K/T boundary sediments at DSDP Site 596, South Pacific (23°51.20′S, 169°39.27′W; Zhou et al., 1991) and a few analyses from a separate study of high-temperature phases from DSDP Site 577, North Pacific (32°26.51′N, 157°43.40′E; Kyte and Bostwick, 1995). At 65 Ma, DSDP Site 596 was located in the center of the ancestral South Pacific at ~45°S latitude, thousands of km from the nearest continental landmass (Schramm and Leinen, 1987) and ~10,000 km from the putative K/T impact structure in the Yucatán. The high-temperature minerals at this site are principally a magnesioferrite spinel, similar in composition to spinel found in K/T spherules at other sites around the world. Within this spinel we have found inclusions of a previously unreported oxide mineral, Ni-rich magnesiowüstite. This mineral has never been observed before in terrestrial sediments and its closest relation, periclase, is formed almost exclusively by high-temperature metamorphism of dolomites and magnesian limestones (Deer et al., 1992). We report here the composi-

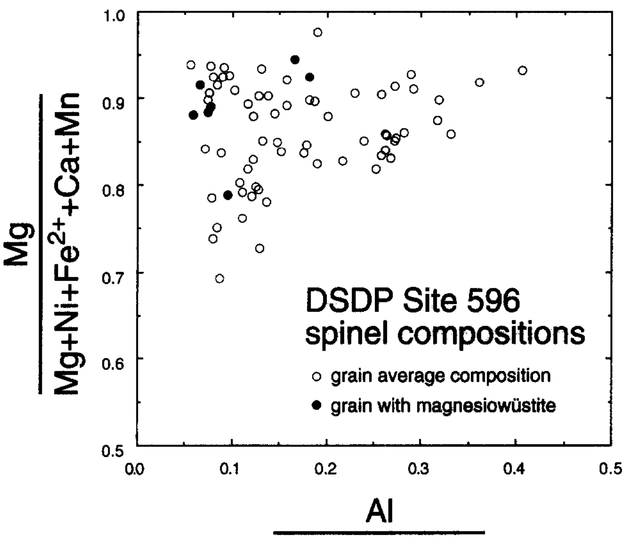

FIG. 1. Quantitative microprobe analyses of seventy-three grains, or aggregates of grains, of magnesioferrite spinel from K/T boundary sediments at DSDP Site 596 show a large range of compositions. Seven grains that contain inclusions of Ni-rich magnesiowüstite (filled circles) span a large fraction of this compositional range. One spinel-bearing spherule from DSDP Site 577 (577-3-9; Table 2, 3; Fig. 2e) with Ni-rich magnesiowüstite has magnesioferrite compositions similar to the most Al-rich sample measured at DSDP Site 596.

tion and discuss possible conditions of formation for this unique mineral occurrence.

2. SAMPLES AND PROCEDURES

Samples studied are mainly trace mineral extracts of pelagic clay sediment samples from the K/T boundary in DSDP Hole 596 which has a broad Ir anomaly centered at 20.1 m depth (core 3–4, 50 cm; Zhou et al., 1991). Clays were removed by centrifuging and biogenic and authigenic components were removed by dissolution in dilute HCl and etching for ~3 minutes in 25% HF. Most of the mineral residue consisted of opaque oxides (magnesioferrite), quartz, and feldspar. These grains were mounted for scanning electron microscope (SEM) examination including qualitative chemical analysis (EDX), mineralogy, and identification of shock features at the USGS in Denver. Initial results of this analysis were presented by Zhou et al. (1991) and mineralogic details by Bohor and Betterton (1991).

Selected grains of magnesioferrite were mounted in polished section and analyzed in a CAMEBAX model Cameca electron microprobe at UCLA. Typical operating conditions included accelerating voltage of 15 keV, beamsize of <1.5 μm, sample currents of ~12 nA, and counting periods of 20 s. Oxide and silicate standards and ZAF corrections were used. The magnesioferrite grains were analyzed for Mg, Al, Si, Ca, Ti, Cr, Mn, Fe, and Ni. Fe_2O_3 contents of the spinel were calculated assuming stoichiometry by the method of Finger (1972). This calculation occasionally yields slightly negative values for FeO, in which case FeO was recorded as zero. We report only analyses that totaled between 98% and 102% after correction for Fe^{3+}.

3. RESULTS

We obtained analyses on seventy-three different grains or aggregates of grains of magnesioferrite from DSDP Site 596. Although we attempted to obtain data on at least three points from each specimen, this was not always possible; a total of 193 point analyses were obtained. As at other K/T boundary sites (Smit and Kyte, 1984; Kyte and Smit, 1986), the principal spinel cations are Mg, Al, and Fe, with minor Ni and Cr. Although some grains were zoned, large areas suitable for detailed microprobe analyses were not abundant and details of the zoning were not explored. In a few samples we observed large ranges in the concentrations of Al and Cr. In the most extreme case, Cr_2O_3 concentrations varied from 0.8–6.0% while Al_2O_3 varied from 12.4–7.5% in a single sample. More typically, different analyzed points on a grain did not vary in composition by more than a few relative percent.

Average analyses for each grain or grain aggregate are plotted in Fig. 1. The fraction of Mg atoms in the divalent cation site ranged from 68–98%, Al in the trivalent site ranged from 5–41% and the fraction of the total Fe atoms in the divalent site ranged from 0–17%. The mean of 193 magnesioferrite analyses is given in Table 1, as are previously published data for three other K/T boundary sites (Kyte and Smit, 1986). For comparison, we also include analyses of spinel in spherules from a late Pliocene impact (Margolis et al., 1991) and spinel from meteoroid ablation debris, including fusion crust from the Allende (CV3) meteorite and cosmic spherules (Robin et al., 1992). The chemical formula of the average magnesioferrite composition at DSDP Site 596 can be estimated as $(Mg_{.88}Ni_{.06}Fe_{.06})O(Fe_{.83}Al_{.16}Cr_{.02})_2O_3$.

Within eight large (20–30 μm) magnesioferrite grains, we found inclusions of a new oxide phase that had not been iden-

Table 1. Mean composition and range of analyses on magnesioferrite grains from DSDP Site 596, compared to the compositions of spinel from three K/T boundary sites, late Pliocene impact spherules, and two types of meteor ablation debris.

	DSDP 596		DSDP 577[a]	LL44-GPC3[a]	Furlo[a]	Pliocene[b]	Allende[c]	cosmic[c]
	mean	range	N. Pacific	N. Pacific	Italy	Spherules	fusion crust	spherules
SiO_2	0.07	0.00- 0.58	0.12[e]	0.34[e]	0.02	1.07[e]	-	-
TiO_2	0.21	0.02- 0.54	0.32	0.76	0.51	0.29	0.10	0.20
Al_2O_3	8.49	2.52- 23.49	22.07	13.75	3.38	4.94	3.80	5.10
Cr_2O_3	1.03	0.00- 6.63	0.20	0.34	0.66	3.45	4.70	3.10
[d]Fe_2O_3	67.14	52.84- 75.07	53.42	60.62	68.44	66.21	64.10	62.20
FeO	2.01	0.00- 6.31	0.55	2.78	9.90	1.50	14.80	22.80
MnO	0.40	0.00- 1.20	0.58	1.13	1.15	0.67	0.10	0.10
MgO	17.96	13.60- 21.61	21.02	18.21	9.86	16.19	8.60	5.10
NiO	2.29	0.00- 5.45	1.41	1.40	5.48	4.55	3.80	1.40
CaO	0.50	0.00- 1.79	0.50	0.62	0.39	0.36	-	-
Total	100.10		100.19	99.95	99.79	99.23	100.00	100.00

[a]Data from Kyte and Smit (1986). [b]Data from Margolis et al. (1991). [c]Data from Robin et al. (1992). [d]Fe_2O_3 calculated from stoichiometry. [e]Some SiO_2 may be contamination from spherule matrix materials.

tified previously in K/T boundary sediments. These inclusions were found in regions up to ~10 μm in size, containing fine-grained (typically μm-sized) intergrowths of this phase with magnesioferrite (Fig. 2a–c). In each case, this phase was found to contain Mg, Ni, and Fe. Attempts to obtain quantitative analyses of its composition were inhibited by small grain size, and we were successful on only two samples (Fig. 2c,d; Table 2). All other attempts at analysis of this phase yielded similar results, but contamination by surrounding magnesioferrite were evident from variable (non-zero) Al_2O_3 concentrations, and low totals reflecting Fe_2O_3 from the matrix. We have chosen to call this phase Ni-rich magnesiowüstite, although another appropriate term might be Ni-rich ferropericlase. We prefer the former, however, as it implies an igneous, rather than metamorphic, paragenesis. In a separate study (Kyte and Bostwick, 1995), Ni-rich magnesiowüstite intergrowths within magnesioferrite grains have been observed in two spherules from K/T boundary sediments in DSDP Site 577, North Pacific (Fig. 2e).

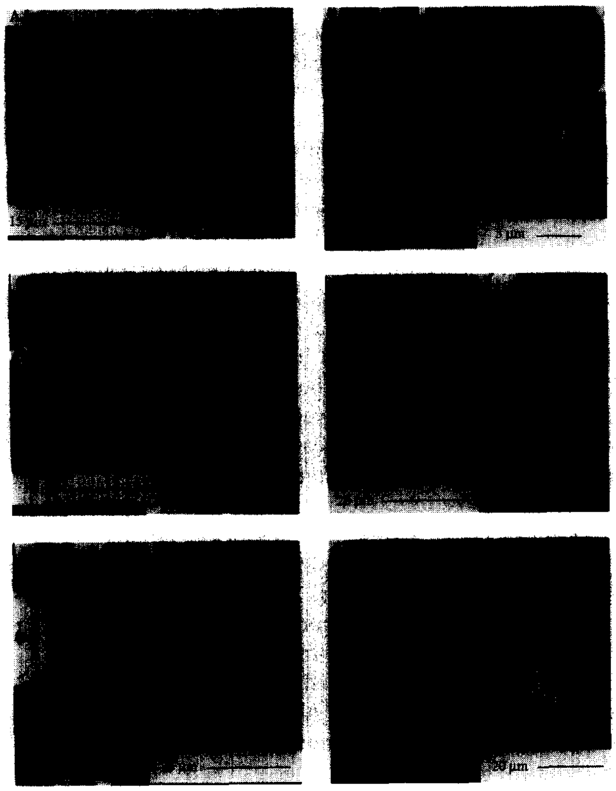

FIG. 2. Backscatter electron images of magnesioferrite spinel (bright grains) with inclusions of Ni-rich magnesiowüstite (arrows) and textures suggesting preexisting magnesiowüstite inclusions. (a) Spinel grain from DSDP Site 596 whose core is a fine intergrowth of spinel and magnesiowüstite. (b) Spinel grain from DSDP Site 596 with a circular patch of intergrown spinel-magnesiowüstite and two linear inclusions of magnesiowüstite. (c) Subhedral spinel grain from DSDP Site 596 (specimen 596-3,1) with a large inclusion of magnesiowüstite. (d) Spinel aggregate in which only one grain has a small inclusion of magnesiowüstite (specimen 596-2-14). (e) Portion of a spherule from DSDP Site 577 with several grains of spinel. One has an inclusion of magnesiowüstite (specimen 577-3-9) that also contains finely dispersed, submicron spinel. (f) Spheroidal aggregate of spinel that contains several oval patches of fine-grained spinel with voids. These textures are quite similar to those of spinel-magnesiowüstite intergrowths (a, b) and are common in other grains and aggregates from DSDP Site 596.

Table 2. Averages of microprobe analyses on Ni-rich magnesiowüstite and coexisting magnesioferrite spinel from DSDP Sites 596 and 577.

	Ni-rich magnesiowüstite			
Sample	596-1,3	596-2-14	577-3-9	577-5-30
SiO_2	0.28	0.47	0.02	0.18
TiO_2	0.01	0.00	0.02	0.05
Al_2O_3	0.03	0.38	1.88	0.32
Cr_2O_3	0.22	0.25	0.07	0.28
FeO	7.00	25.18	14.31	10.51
MnO	0.06	0.13	0.24	0.11
MgO	75.89	60.53	74.39	71.77
NiO	17.67	13.00	8.89	14.82
CaO	0.02	0.33	0.11	0.06
Total	101.18	100.27	99.94	98.08
	magnesioferrite spinel			
Sample	596-1,3	596-2-14	577-3-9	577-5-30
SiO_2	0.08	0.18	0.05	0.05
TiO_2	0.15	0.14	0.32	0.32
Al_2O_3	4.77	3.85	23.00	4.95
Cr_2O_3	1.82	0.76	0.13	0.88
Fe_2O_3	68.91	71.89	52.03	69.62
FeO	4.13	0.83	1.02	3.73
MnO	0.23	0.34	0.38	0.49
MgO	15.81	17.51	20.26	14.66
NiO	3.01	3.46	2.46	5.54
CaO	0.19	0.31	0.37	0.18
Total	99.10	99.27	100.00	100.43

Results of microprobe analyses of Ni-rich magnesiowüstite and coexisting magnesioferrite spinel for two grains from DSDP Site 596 and two spherules from DSDP Site 577 are given in Table 2. The magnesiowüstite in sample 577-3-9 was observed to contain submicron inclusions that appeared bright in backscatter electron images (high Z) and that are probably finely dispersed spinel (Fig. 2e). This has clearly contaminated the magnesiowüstite analyses which include 1.88% Al_2O_3, reflecting ~10% spinel. However, we include these data for completeness given the high Al_2O_3 of the coexisting spinel. Approximate chemical formulas for these four sets of coexisting Ni-magnesiowüstite and magnesioferrite spinel are listed in Table 3.

The divalent vs. trivalent cation composition of seven magnesiowüstite-bearing spinel grains from DSDP Site 596 are illustrated in Fig. 1. In the eighth grain containing Ni-magnesiowüstite, we did not obtain quantitative analyses on magnesioferrite or magnesiowüstite. Additionally, we have observed several other magnesioferrite grains with elliptical patches of fine-grained oxides and voids that are texturally similar to Ni-magnesiowüstite and magnesioferrite intergrowths (Fig. 2f). Given the tendency of periclase to alter rapidly to brucite (Deer et al., 1992), we consider it likely that these elliptical patches are regions where pre-existing Ni-magnesiowüstite has been weathered out of the sample or destroyed by our chemical leaching procedure. Although the Ni-magnesiowüstite has been observed in only 10% of the grains analyzed from DSDP Site 596 (seven out of seventy-three grains), it was probably considerably more abundant when these sediments were initially deposited.

4. DISCUSSION

Although all of our samples from DSDP Site 596 are individual grains of magnesioferrite spinel, we assume that they originally formed within silicate spherules (Type 2 of Bohor and Betterton, 1990 or microkrystites of Smit et al., 1992a) that were destroyed either by diagenetic alteration or our sam-

Table 3. Approximate chemical formulas for coexisting Ni-rich magnesiowüstite and magnesioferrite from DSDP Sites 596 and 577.

	magnesiowüstite	magnesioferrite
596-1,3	$(Mg_{.85}Ni_{.11}Fe_{.04})O$	$(Mg_{.80}Ni_{.08}Fe_{.12})O(Fe_{.88}Al_{.10}Cr_{.02})_2O_3$
596-2-14	$(Mg_{.74}Ni_{.09}Fe_{.17})O$	$(Mg_{.88}Ni_{.10}Fe_{.02})O(Fe_{.91}Al_{.08}Cr_{.01})_2O_3$
577-3-9	$(Mg_{.85}Ni_{.06}Fe_{.09})O$	$(Mg_{.91}Ni_{.06}Fe_{.03})O(Fe_{.59}Al_{.41}Cr_{.00})_2O_3$
577-5-30	$(Mg_{.84}Ni_{.09}Fe_{.07})O$	$(Mg_{.74}Ni_{.15}Fe_{.11})O(Fe_{.89}Al_{.10}Cr_{.01})_2O_3$

ple processing. This assumption is supported by the occurrence of spinel-bearing spherules at K/T boundary sites from Italy (Montanari et al. 1983, Smit and Kyte, 1984; Kyte and Smit, 1986), Spain (Doehne and Margolis, 1990), South Atlantic (Kyte and Smit, 1986), Haiti (Jéhanno et al., 1992), North Pacific (Kyte and Smit, 1986), and the Indian Ocean (Rocchia et al., 1992). Also, the relatively large range in composition we observe (Fig. 1) in Site 596 spinels leads us to infer that our specimens were derived from more than one, and probably several, different spherules. This is consistent with the fact that the spinel grains were taken from several stratigraphically distinct sediment samples (Zhou et al., 1991). Additionally, many spinel aggregates, particularly in the 50–100 μm size range, are spheroidal. In polished section, these spheroidal aggregates have considerable void space (Fig. 2f), but they are almost certainly the remnants of individual spinel-bearing spherules that have had their silicate fraction removed. The magnesiowüstite-bearing spinel in DSDP Site 577 samples was observed in silicate spherules that now consist largely of smectitic clays.

The spinel compositions at DSDP Site 596 fall along the trend noted previously at other K/T boundary sites around the world (Table 1). Kyte and Smit (1986) noted that spinel from North Pacific localities (DSDP Site 577 and LL44-GPC3) have higher Mg and Al contents than were found in spinel from Tethyan (Furlo, Italy) or South Atlantic sites (DSDP 524), and that all K/T boundary spinels are characterized by high Fe_2O_3/FeO ratios, indicative of crystallization under high oxygen fugacities. Recently, Kyte and Bostwick (1995) have shown that other Pacific K/T boundary sites (DSDP 576 and ODP 803 and 886) also fit this trend and that Pacific spinels are chemically and texturally distinct from those from nonpacific K/T sites or from cosmic spherules. There is considerable overlap in the range of compositions reported between these sites. None of the spinel analyzed from the Pacific K/T boundary sites have compositions closely similar to those reported in cosmic spherules or meteorite fusion crusts (Table 1), with large differences in the abundances of the major cations Fe, Al, and Mg. Also, Fe_2O_3/FeO ratios are an order of magnitude higher in Pacific K/T spinel than in meteoroid ablation products.

The specific processes which result in formation of K/T boundary magnesioferrite-bearing spherules are not well-defined, although it is clear that their formation is related to the accretion of extraterrestrial matter via impact. This is evident from the high Ir and Ni contents (e.g., Robin et al., 1993) of some spherules and their association with shocked quartz of terrestrial (target) origin (e.g., Zhou et al., 1991). Kyte and Smit (1986) suggested that these spherules could be derived from either impact melt, condensates of impact vapor, or projectile ablation debris. They favored the latter two, as these were most likely to experience high oxygen fugacities implied from the high Fe_2O_3/FeO ratios. Bohor and coworkers (Bohor and Betterton, 1990, 1992; Bohor and Glass, 1995; Pollastro and Bohor, 1993), noting the oxidized nature and global distribution of spinel-bearing spheroids, have also argued that they condensed from an impact vapor cloud.

In contrast, some researchers have argued that K/T spinel form by meteoroid ablation. Robin et al. (1992) showed that spinels in cosmic spherules and meteorite fusion crusts are also Ni-rich and contain a magnesioferrite component and they inferred that all formed under somewhat analogous conditions. They observed increasing Fe^{3+}/Fe^{2+} ratios from cosmic spherules through fusion crusts to K/T boundary spherules, and concluded that this increase in iron oxidation state reflected formation at different levels in the atmosphere. In a more recent study, Robin et al. (1993) reported the occurrence of irregularly-shaped spherules with magnesioferrite mainly around their rims in K/T boundary sediments from DSDP Site 577, North Pacific. These were considered to be analogous to irregular cosmic spherules formed by partial melting of meteoritic material during atmospheric ablation. Based on spinel textures and Ir concentrations, Robin et al. (1993) concluded that K/T boundary spinel-bearing spherules are ablation debris, derived from pure chondritic materials, and that they formed locally at each locality from multiple accretionary events. Although we cannot rule out the presence of some locally-derived ablation debris at some K/T localities, this ablation model fails to account for other data. These include the obvious dissimilarity in spinel compositions between known ablation debris and Pacific K/T spinel (Table 1). The observation that the compositions and textures of Pacific spinel represent a broad regional trend rather than a localized phenomenon (Kyte and Bostwick, 1995) is inconsistent with an ablation origin. Also, magnesioferrite is exclusively contained within the upper, fireball layer of the K/T boundary in the Western Interior of North America (Bohor and Foord, 1987), a unit which contains most of the Ir and continentally-derived shocked quartz. In addition the shocked quartz has been found at Pacific sites, including DSDP Site 596 in the South Pacific (Zhou et al., 1991) and DSDP Site 576 in the western North Pacific (Bostwick and Kyte, 1993), the latter being only ~500 km from DSDP Site 577. The size of the quartz grains fits the size-distribution pattern found worldwide by Bohor (1990). We find that these data are most consistent with globally-distributed impact debris from a single large-body impact and we find no reason to infer numerous small and localized accretionary events.

The fact that magnesioferrite-bearing spherules can form in impact ejecta was demonstrated by Margolis et al. (1991), who discovered magnesioferrite-bearing spherules associated with debris from an oceanic impact in the late Pliocene. Significantly, the late Pliocene magnesioferrite-bearing spherules are distinct from a more abundant vesicular impact melt that composes most of the late Pliocene impact debris. Both components have similar bulk chemical compositions, consisting of a mixture of the basaltic achondrite projectile and seawater salts from the oceanic target. The vesicular debris contains a more reduced Cr-spinel and euhedral zoned olivine (Kyte and Brownlee, 1985), whereas the magnesioferrite is found in glassy spherules. Since the Pliocene spherules contain salts from the oceanic target, they must have evolved within the impact ejecta and cannot simply be ablation debris that formed during atmospheric entry of the late Pliocene asteroid. Interestingly, the magnesioferrite spinel in the late Pliocene spherules has Fe_2O_3/FeO ratios essentially identical to those observed in Pacific K/T spinel (Table 1).

The occurrence of Ni-rich magnesiowüstite coexisting with magnesioferrite in some K/T components provides significant constraints on the composition of the precursor liquid droplet and possibly on associated impact vapor, as well as on the crystallization conditions of some spinel-bearing spherules. Its occurrence in K/T boundary spherules is indicative of crystallization from unusual silicate liquids that do not occur under conditions typical of the Earth's crust. The most relevant study of phase equilibria that includes magnesiowüstite and magnesioferrite is probably that of Muan and Osborn (1954), who investigated phase equilibria at liquidus temperatures in the system $MgO\text{-}FeO\text{-}Fe_2O_3\text{-}SiO_2$. This study predated the work of Eugster (1957), who first developed a method to control the oxidation potential in experimental runs. Muan and Osborn (1954) quenched melt charges that had been allowed to equilibrate at 1 atm with varying proportions of air, CO_2, and H_2. Even without direct control of the oxidation potential their results are nonetheless probably reliable, and, therefore, relevant to the origin of oxides in K/T boundary deposits.

A slice through the system $MgO\text{-}FeO\text{-}Fe_2O_3\text{-}SiO_2$ is illustrated in Fig. 3, showing the phase relations determined by Muan and Osborn (1954) for charges equilibrated with air. The magnesiowüstite field represents liquid compositions from which this phase would be the first mineral to crystallize. In similar projections representing higher oxygen fugacities, the magnesioferrite field would expand at the expense of olivine and magnesiowüstite; at lower oxygen fugacities it would contract. Chondritic compositions plot roughly in the center of this diagram, and the composition of CI chondrites is plotted as if all Fe were oxidized to Fe_3O_4 ($Fe^{3+}/Fe^{2+} = 2$; atom ratio). Unaltered chondrites are typically more reduced than this and contain varying proportions of Fe-bearing oxides, silicates, sulfides, and metal. CI chondrites are commonly the most oxidized chondrites (e.g., Jarosewich, 1990). Chondrites also contain significant amounts of Ca and Al oxides, but these are minor in abundance relative to Mg, Si, and Fe.

The phase relations in Fig. 3 show that it is impossible to crystallize magnesiowüstite from liquids with chondritic compositions or from less mafic liquids such as terrestrial magmas. A thermal divide extends across the olivine field in this system from forsterite (on the $MgO\text{-}SiO_2$ join), to the boundary between the olivine and magnesioferrite fields, and into the ferrite field. Fractional crystallization of less mafic liquids cannot evolve across this divide. In $MgO\text{-}FeO\text{-}Fe_2O_3\text{-}SiO_2$ space, only liquids with $(Mg + Fe^{2+})/Si$ atom ratios greater than in olivine (i.e., >2) can crystallize magnesiowüstite. During ablation of a chondritic body upon atmospheric entry, the first phase to crystallize from chondritic melt-droplets will be olivine (Fig. 3). As olivine crystallizes, the liquid composition evolves toward the magnesioferrite field until it intersects the boundary between fields where olivine and magnesioferrite crystallize together. The end result is that chondrite fusion crusts and chondritic cosmic spherules nearly always consist of zoned olivine, magnetite, and glass (Kyte, 1977; Blanchard et al., 1980). Magnesiowüstite has never been observed in chondritic meteorite fusion crusts or chondritic cosmic spherules, although wüstite (FeO) is common in Ni-Fe cosmic spherules (e.g., Blanchard, 1972) formed from metallic precursors.

Since fractional crystallization of silicate liquids cannot produce the high MgO/SiO_2 ratios necessary to precipitate magnesiowüstite, we suggest that the only plausible mechanism is by fractionation processes related to vaporization and/or condensation of ejecta during an impact event. Available data would appear to indicate that such vapor fractionation does not occur as a common result of meteoroid ablation. Chondritic cosmic spherules form by frictional melting, vaporization, and crystallization during atmospheric entry. Typical formation times are less than 10 seconds at temperatures typically <2000°C (Bates, 1986). These objects are known to be depleted in highly volatile elements such as Na, K, S, and Rb; presumably by vapor fractionation (Brownlee et al., 1983). They are also commonly depleted in Fe and siderophiles, apparently as a result of separation of immiscible silicate and metallic liquids during ablation. However, Mg/Si ratios cluster strongly around chondritic values. The only ablation spherules with high Mg/Si ratios (several percent of the total population) are also low in Al and are interpreted to have formed by melting of individual olivine grains (Brownlee et al., 1983). We note that Brownlee et al. (1983) conclude that Ca, Al, Ti-rich spherules recovered in stratospheric dust collections may be refractory residues of meteoroid ablation. However, because these particles are not known to contain magnesioferrite or magnesiowüstite, and are so rare that they are never reported in association with cosmic spherule collections or meteorite fusion crusts, we do not consider them to be a significant potential source of magnesioferrite and magnesiowüstite in K/T boundary sediments.

The relative volatilities of oxides in the system $FeO\text{-}MgO\text{-}SiO_2\text{-}CaO\text{-}Al_2O_3$ have been examined in laboratory experiments in which natural and synthetic chondritic liquids have been distilled under vacuum at temperatures of ~1500–2000°C (Notsu et al., 1978; Hashimoto et al., 1979; Hashimoto, 1983). These studies provide some insights into conditions that might be necessary for formation of liquid droplets that can precipitate Ni-rich magnesiowüstite and magnesioferrite spinel. However, we must note that there are two important limitations to these studies. First, they do not consider high oxygen fugacities clearly evidenced in K/T spherules by high Fe_2O_3/FeO in magnesioferrite spinel (Table 1). Second, vacuum distillation is an inherently nonequilibrium condition that is similar to meteoroid ablation, as opposed to evaporation/condensation within an impact vapor cloud

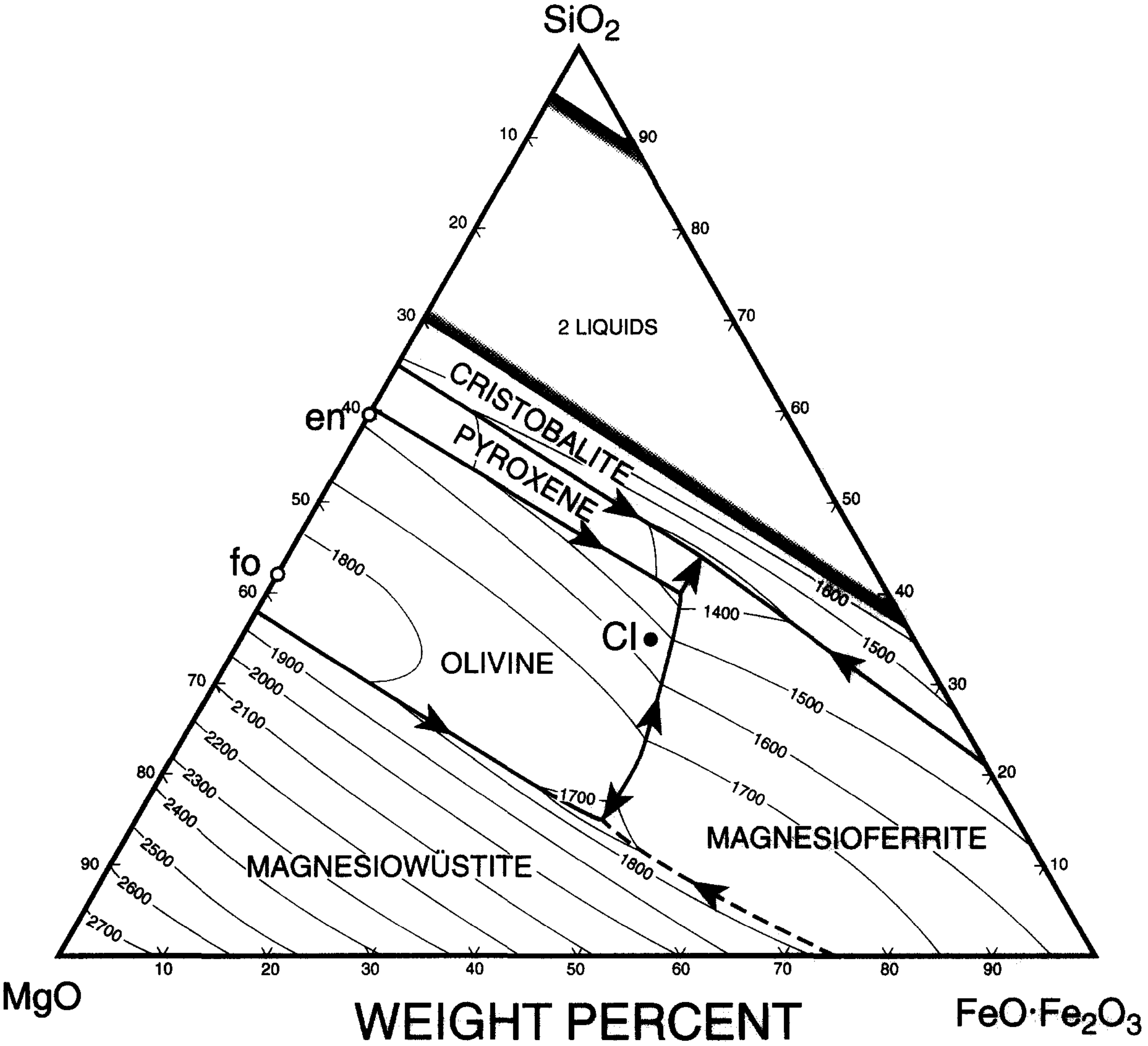

FIG. 3. Phase relations at liquidus temperatures in the system MgO-FeO-Fe_2O_3-SiO_2 for charges equilibrated with air at 1 atmosphere (adapted from Muan and Osborn, 1954). This is not a true ternary diagram, but a slice through a four-phase system. This figure illustrates that chondritic liquids (CI) cannot evolve by fractional crystallization to a composition with magnesiowüstite on the liquidus. They are separated from the magnesiowüstite field by a thermal divide that extends from forsterite into the magnesioferrite field.

where liquid and gas can interact and may approach equilibrium as pressures and temperatures change.

These laboratory experiments never produce magnesiowüstite-magnesioferrite because vaporization of chondritic liquids at ≤2000°C results in complete loss of FeO (at ~50% total mass loss) before any significant increase in the Mg/Si ratio (Hashimoto, 1983). Because SiO_2 is more volatile than MgO, Mg/Si atom ratios eventually increase from 1 – ~1.7. At this point CaO concentrations increase to the degree that this oxide interacts with silica in the liquid, causing a reversal of the relative volatilities of MgO and SiO_2, and decline of Mg/Si ratios until eventual total evaporative loss of MgO and then SiO_2.

Apparently, fractionation by evaporation/condensation can only evolve magnesiowüstite- and magnesioferrite-bearing liquids at temperatures significantly higher than this. With increasing temperature (i.e., >2000°C) the differences in volatilities between MgO and SiO_2 increase (Ackerman and Thorne, 1961; Muan and Osborne, 1965), while the difference in volatility between FeO and both these oxides decreases (Hashimoto, 1983). Hashimoto (1983) finds that at temperatures >2628°C, SiO_2 is more volatile than FeO. He estimates that at temperatures >2300°C the atomic ratio (Mg + Fe)/Si will be increased by vaporization. 2300°C would appear to be the minimum temperature at which MgO/SiO_2 ratios can increase to levels necessary for magnesiowüstite to be a liquidus phase, while sufficient Fe remains condensed to form magnesioferrite. This temperature is minimal compared to those that must occur within the vapor cloud of major impact event where peak temperatures exceed several thousand degrees (e.g., Jones and Kodis, 1982) throughout much of the early expansion of the impact fireball.

Compositions of magnesiowüstite, such as the $(Mg_{.85}Ni_{.11}Fe_{.04})O$ measured in one sample (Table 3), indicate that temperatures >2300°C were quite likely. In the pseudobinary system MgO-Fe oxides equilivalent to the MgO-FeO·Fe_2O_3 join in Fig. 3, the solidus temperature for $(Mg_{.85}Fe_{.15})O$ is ~2300°C (Muan and Osborne, 1965). Addition of NiO to this phase, and other oxides (e.g., SiO_2, CaO) to the liquid would lower the melting point of this phase significantly, but it probably precipitated at temperatures of at least 2000–2100°C. Clearly, initial formation of the liquid droplet it crystallized from could have been at much higher temperatures.

In the preceding discussion we have considered formation of these K/T spherules relative to chondritic materials because those are the materials involved in meteoroid ablation and that have been the subject of laboratory experiments. If the source of these droplets is an impact vapor cloud a wide range of precursor materials is possible, representing mixtures of both projectile and target components. Unfortunately, we can only speculate as to the composition of the vapor these spherules might have equilibrated with, since we do not even know the bulk composition of the spherules (only magnesioferrite and traces of magnesiowüstite have survived diagenetic alteration). However, we infer that spinel-bearing spherules contain a significant meteoritic component, as indicated by the relatively high Ni concentrations in the oxides and high bulk concentrations of Ir (Montanari et al., 1983; Bohor et al., 1986; Robin et al., 1993) and other Pt-group elements (Smit and Kyte, 1984) in the spherules. The meteoritic component derived from a chondritic impactor may be preferentially concentrated in specific regions of an impact vapor cloud (e.g., O'Keefe and Ahrens, 1982; Vickery and Melosh, 1990). Such regions would be the most likely to have initially high MgO contents and may be necessary for formation of these special liquids.

Finally, we note that textures of magnesiowüstite-magnesioferrite intergrowths could be interpreted to indicate that the bulk composition of the precursor liquid droplet may have evolved during crystallization. The magnesiowüstite is typically preserved where it is completely enclosed within the magnesioferrite (Fig. 2). We suggest that these textures may indicate that magnesiowüstite was the first mineral to crystallize. This would be consistent with the likely crystallization temperature of some magnesiowüstite at >2100°C. Textures suggest that magnesiowüstite was subsequently partially replaced and overgrown by magnesioferrite. This could indicate that magnesiowüstite was not a stable phase in the later stages of spherule evolution. This would be consistent with a sequence expected during condensation from a vapor cloud in which the earliest condensed liquids would be most refractory, but as the vapor cools, the bulk liquid evolves to a less refractory composition. Individual spherules may record their own distinctive crystallization and fractionation histories as temperatures and/or oxygen fugacities in the impact-produced vapor cloud changed.

5. CONCLUSIONS

The identification of Ni-rich magnesiowüstite in K/T sediments provides new clues and potentially important constraints on the formation of one component produced by the K/T event. Traces of magnesiowüstite were found in 10% of the magnesioferrite grains analyzed from DSDP Site 596 and textures suggestive of magnesiowüstite-magnesioferrite intergrowths (Fig. 2f) are much more abundant, suggesting that this phase was common in many spinel-bearing spherules from this site. The identification of magnesiowüstite in two spherules form DSDP Site 577, located 7000 km to the north of Site 596, proves that this is a widespread phenomenon, not just an odd, rare event restricted to sediments at one locality.

Nickel-rich magnesiowüstite can only crystallize from an ultrarefractory, MgO-rich liquid. This liquid cannot evolve by fractional crystallization of a chondritic melt or of a less mafic terrestrial magma. We suggest that this liquid can only form by fractionation related to vaporization or condensation during a major impact event in which volatility of SiO_2 results in liquids sufficiently enriched in MgO that magnesiowüstite can crystallize. This degree of fractionation of MgO relative to SiO_2 is never observed in meteor ablation debris and does not occur in laboratory experiments where vaporization is studied at temperatures ≤2000°C. Experimental studies indicate that this fractionation is only likely at temperatures >2300°C. This is only slightly above the temperature at which some of the more refractory magnesiowüstite probably crystallized.

Although we conclude that equilibration of liquids and gases in the vapor cloud of a major impact event is the most likely source of the magnesiowüstite-bearing spherules, our data do not significantly constrain whether these spherules are produced by partial vaporization of preexisting materials, or by condensation of impact-generated vapor. However, we favor the latter on the grounds that most of the projectile is probably vaporized during impact, and these spherules must contain a significant fraction of projectile material. This conclusion does not imply that all magnesioferrite-bearing spherules must form from similar, ultrarefractory liquids. Clearly magnesioferrite does occur in chondritic cosmic ablation spherules (Robin et al., 1992) and basaltic spherules from an oceanic impact in the Pliocene (Margolis et al., 1991). More to the point, we have now identified a new mineral phase in K/T boundary sediments that likely can only form under the special conditions found in the evolving vapor cloud of a major impact event.

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