Thermal decomposition pattern and particle size estimation of iron minerals associated with the Cretaceous–Tertiary boundary at Gubbio

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Abstract–Mössbauer studies of the samples from the Cretaceous–Tertiary (K-T) boundary layer at Gubbio, Italy show that iron appears mainly in two phases, magnetically ordered hematite and a paramagnetic silicate phase. The average particle size of hematite is estimated to be in the range of 16 to 27 nm from transmission electron micrographs and lack of a Morin transition. The hyperfine magnetic field at the iron nucleus is observed to be somewhat less than that of bulk hematite, which may be explained by collective magnetic excitation. Stepwise heating up to 1000 °C shows a decomposition pattern of the paramagnetic phase, which suggests it to be a tri-octahedral layer silicate. The iron-bearing phases found in the bulk sedimentary K-T boundary material are different from those found in the spherules separated from this material indicating that the redox conditions changed rapidly after the impact, becoming more oxidizing during the period these bulk phases were formed.

INTRODUCTION

The end of the Cretaceous period 65 Ma is marked by some catastrophic geological events, which resulted in mass extinction of many life forms on Earth, including the dinosaurs. The layers of sedimentary rocks deposited at the Cretaceous–Tertiary (K-T) boundary period have been studied extensively to ascertain the nature of these events and their aftereffects on the geochemical and climatic conditions leading to this mass extinction (for a review, see Sutherland, 1994; Bhandari, 1998). The K-T boundary in marine sediments appears as a distinct 1–2 cm thick chocolate-colored layer in most places. Worldwide attention was drawn by the findings of Alvarez *et al.* (1980) that the K-T boundary layer at several European sites including Gubbio, Italy contain anomalously high iridium content, several hundred times higher than the neighboring non-K-T boundary layers. The presence of high Ir, which has a very high abundance in extraterrestrial objects compared to the Earth's crust, strongly support occurrence of an impact of a bolide (~10 km in diameter) on the Earth resulting in severe climatic stress leading to the mass extinction. Later observations of shocked quartz (Bohor *et al.*, 1984), nickel-rich spinels (Robin *et al.*, 1992), and an identifiable impact crater (Sharpton *et al.*, 1996), *etc.* provided further evidence in support of the impact event. Shukolyukov and Lugmair (1998) have shown that the $^{53}Cr/^{52}Cr$ ratio in the K-T boundary layer has the same value as carbonaceous chondritic meteorites

and distinguishably different from other meteorites or terrestrial samples, implying that the bolide had a formation chronology similar to carbonaceous chondrites.

The hypothesis that has emerged is that a large meteorite collided with the Earth, a large amount of material from the bolide as well as the Earth's surface vaporized, part of the ejecta fell back following the ballistic kinematics and part, the plume, would have gone exoatmospheric, followed by condensation and fallback into the uppermost layers of the terrestrial atmosphere, finally settling out after global circulation; thereby, becoming the uppermost component of the K-T boundary layer. The large abundance of iron in the meteorites, as well as terrestrial rocks, implies that iron should be one of the dominant species in the vapor plume and the ejecta fallout. A variety of iron-bearing minerals would have formed depending on the thermal and chemical conditions and a study of iron mineralogy is expected to help in characterizing the ambient geochemical environment.

A large amount of work has been done on the spherules separated from the K-T boundary layer, as these are supposed to have been formed due to solidification of molten droplets of minerals formed in the hot ejecta and hence represent primary impact material (Montanari, 1991, and references herein). Smit and Kyte (1984) have studied magnetic microspherules separated from the K-T boundary samples and found that the main contents of such spherules are magnetite and magnesioferrite grains, which contain Ni, Al and other trace

elements besides iron. Worm and Banerjee (1987) examined the magnetism of magnetic microspherules extracted from the K-T boundary layers from Petriccio (also a part of the Gubbio formation), and of the bulk sample itself. They have shown that magnetite is the main contributor of the sharp anomaly in magnetic susceptibility across the K-T boundary. Kyte and Bostwick (1995) have also investigated the systematics of Fe^{3+}/Fe^{2+} ratio in the magnesioferrite extracted from a number of K-T boundary sites. However, relatively few reports are available on the gross iron mineralogy of the K-T boundary (Thorpe *et al.*, 1994). Mössbauer spectroscopic studies of samples from a number of K-T boundary sites (Wdowiak *et al.*, 1994, 2001; Armendarez *et al.*, 1998; Bhandari *et al.*, 2002) revealed that the K-T boundary layer sediments themselves contain nanosized iron minerals, mainly goethite and/or hematite. The concentration of these nanophase iron minerals correlates with the iridium enhancement (Bhandari *et al.*, 2002), indicating that their formation is not due to common terrestrial weathering processes but is related to the impact event. This observation also supports the idea of a common source for iridium and the oxide/oxyhydroxide nanophases as suggested by Wdowiak *et al.* (2001).

While K-T boundary layers from American and Asian sites showed superparamagnetically relaxed Mössbauer spectra at room temperature giving clear evidence of nanosized iron minerals, the Mössbauer studies of the Italian K-T boundary sites showed a well-developed six-line pattern corresponding to hematite with hyperfine magnetic field (HMF), somewhat smaller than the standard value. Such a temperature-dependent reduction of HMF at the site of ^{57}Fe has been seen in nanoparticles of magnetically ordered iron phases and can be explained in terms of collective magnetic excitation, where the magnetic moment of the single domain particle fluctuates around an easy axis of magnetization but is not able to flip to another easy direction (Mørup *et al.*, 1980). We have estimated the particle size of the hematite present in the Gubbio K-T boundary sample using transmission electron microscopy (TEM), a lack of Morin transition and temperature-dependent reduction of HMF. Beside the magnetically split six-line pattern, the Gubbio (Italy) K-T boundary sample shows a very prominent paramagnetic doublet. Wdowiak *et al.* (2001) have proposed, on the basis of x-ray diffraction and Mössbauer spectroscopy, that this paramagnetic phase could be due to the phylliosillicate mineral illite. To achieve further insight into the nature of this paramagnetic iron complex at the K-T boundary site at Gubbio, we have studied its thermal alteration behavior up to 1000 °C, as well as its solubility in different acids using Mössbauer spectroscopy.

SAMPLE DETAILS AND
EXPERIMENTAL METHODS

Fresh sediment samples from the well-documented K-T boundary section of Gubbio, at Bottaccione, were collected

after removing the immediate surface from the exposed sections. The K-T boundary at Gubbio section is sandwiched between limestones and consists of a thin (1–2 cm) chocolate-colored band, which shows an abrupt iridium enhancement increasing from <50 to 5200 pg/g in the boundary layer (Alvarez *et al.*, 1980). Iron concentration also increases abruptly to 5.4% in this layer from a value of <0.5% in adjacent layers. In the present work, sediments from the iridium-rich K-T boundary layer, as well as away from the iridium-rich layer, were analyzed to understand the nature and variation of iron phases across the boundary.

The absorbers for Mössbauer spectroscopy were prepared by pressing finely ground powders in a 12 mm diameter copper ring and fixing the open ends with transparent tapes. The spectra were recorded using a conventional constant acceleration Mössbauer spectrometer with ^{57}Co in Rh matrix as the Mössbauer source. Calibration spectra with natural iron foil were taken before and after each measurement. The zero velocity channel was determined by locating the point of mirror symmetry (folding point) in each spectrum, using a standard algorithm. Data were analyzed by fitting an appropriate number of discrete doublets and sextets with Lorentzian peaks using a least-squares code. In case of magnetically split sextets, the quadrupole splitting is calculated by the equation $QS = [(v_1 + v_6) - (v_2 + v_5)]/2$, where v_i is the velocity corresponding to the ith peak. The typical uncertainties in the isomer shift and quadrupole splitting are ~0.04 mm/s, whereas that for the HMF is ~0.1 Tesla. The relative areas under different component spectra have an uncertainty of ~5%.

RESULTS

Mössbauer Spectra of Raw Samples

The Mössbauer spectra of the K-T boundary layers at different temperatures are shown in Fig. 1. The Mössbauer parameters deduced from the discrete fitting are given in Table 1. As seen from Fig. 1, each of the Mössbauer spectra is a superposition of a well split sextet and a strong ferric doublet and a weak ferrous doublet. The Mössbauer parameters match well with those reported by Wdowiak *et al.* (2001). The sextet has been assigned to hematite. Several magnetically ordered phases, such as magnesioferrite (Kyte and Bostwick, 1995), magnetite (Worm and Banerjee, 1987) and goethite (Montanari, 1991), have been reported in the spherules of Gubbio K-T boundary. The representative Mössbauer parameters of these phases obtained from literature are given in Table 2, for reference. No peaks associated with these phases were seen in the Mössbauer spectra of Gubbio K-T boundary samples.

Apart from the sextet, two doublets are evident in the spectrum at 295 K. One of these is a small ferrous component (relative area ~6%) and the other is an intense doublet, with isomer shift 0.34 mm/s and quadrupole splitting 0.60 mm/s. These parameters may correspond to a variety of iron phases
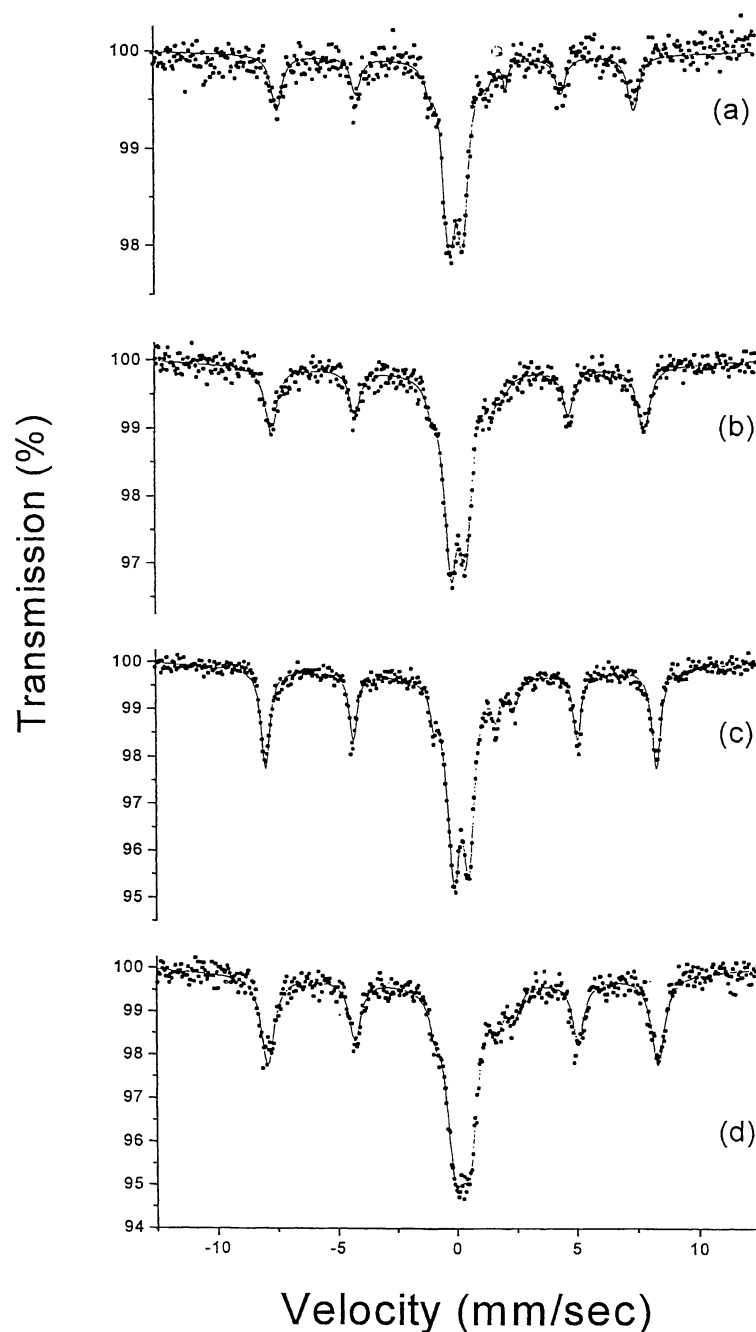
FIG. 1. Mössbauer spectra of the Gubbio K-T boundary samples at (a) 435 K, (b) 380 K, (c) 295 K, and (d) 100 K.

such as Fe^{3+} in clay minerals, layer silicates, hydrated minerals, pyrite, illite, *etc.* The Mössbauer parameters of such minerals are also listed in Table 2. As the temperature is lowered from 295 to 100 K, no significant reduction in the relative area of the doublet occurs, establishing that the doublet is not due to superparamagnetic hematite. Wdowiak *et al.* (2001) have reported spectra of Italian K-T boundary samples down to 12 K whereas the doublet still persists. In order to get further insight into the origin of this doublet (termed here phase-A), we heated this sample in air at various temperatures and studied its thermal

decomposition pattern by Mössbauer spectroscopy. We also treated the samples with HCl, HNO_3 and HF and carried out Mössbauer studies of the residues.

Acid Treatment to the Samples

The behaviour of paramagnetic minerals, when treated with various acids, can be used to identify or exclude the types of minerals present. For example, sulphide minerals, such as pyrite, dissolve in dilute nitric acid; whereas, sulphate minerals

TABLE 1. Mössbauer parameters of Gubbio K-T boundary samples after different treatments.

Sample	Temperature (K)	Doublet phase	IS (mm/s)	QS (mm/s)	B (T)	Relative area (%)
Raw	435		1.03	2.57		3
		A	0.22	0.55		60
			0.22	−0.18	46.4	37
	380		1.02	2.15		5
		A	0.26	0.61		55
			0.28	−0.22	48.4	40
	295		1.13	2.78		6
		A	0.34	0.60		53
			0.37	−0.22	49.9	41
	100		1.15	2.72		7
		A	0.36	0.55		47
			0.40	−0.20	51.4	46
Diluted HNO$_3$ treated	295	A	0.31	0.60		61
			0.36	−0.20	50.5	39
Diluted HCl treated	295	A	0.28	0.62		55
			0.36	−0.20	50.5	45
Concentrated HNO$_3$ treated	295	A	0.32	0.59		58
			0.39	−0.22	50.5	42
HF treated	295	very small absorption				
Heated at 400 °C	295	A	0.32	0.68		35
		B	0.31	1.41		17
			0.37	−0.20	50.8	48
Heated at 500 °C	295	A	0.23	0.94		28
		B	0.34	1.42		32
			0.37	−0.26	50.5	40
Heated at 600 °C	295	B	0.35	1.42		53
			0.37	−0.16	50.6	47
Heated at 800 °C	295	C	0.23	0.83		34
			0.35	−0.24	50.0	66
Heated at 1000 °C	295	C	0.27	0.70		34
			0.35	−0.18	49.9	66
	100	C	0.28	0.75		35
			0.41	−0.20	51.9	65
	12	C	0.25	0.75		41
			0.37	−0.24	52.2	59

Abbreviations: IS = isomer shift, QS = quadrupole splitting, B = hyperfine magnetic field.

dissolve in dilute hydrochloric acid. Boiling in concentrated nitric acid dissolves ferric hydroxides, while hydrofluoric acid reacts strongly with the silicates. Considering these dissolution properties, the following acid treatments were performed on the Gubbio samples: (a) treated with dilute HNO$_3$ for several hours, stirring at regular intervals. Filtered and the residue washed with distilled water several times and dried. (b) Similar treatment as in (a) but with dilute HCl. (c) Boiled in concentrated HNO$_3$ for 15 min and filtered. The residue was washed with distilled water and dried. (d) Similar treatment as in (c) but with HF.

Figure 2 shows Mössbauer spectra of these acid-treated samples, recorded at room temperature. We see that neither

TABLE 2. Mössbauer parameters of some iron minerals at room temperature.

Mineral	Site	IS (mm/s)	QS (mm/s)	B (kOe)
Magnetic minerals				
Magnesioferrite*	Tetrahedral	0.37	−0.08	523
	Octahedral	0.49	0.17	537
Magnetite†	Tetrahedral	0.26	−0.02	490
	Octahedral	0.67	0.00	460
Hematite†		0.37	−0.20	517
Goethite†		0.37	−0.52	382
Silicates				
Calic Amphliboles†	Fe^{3+}	0.38	0.65	−
Kaolinites†	Fe^{3+}	0.36	0.51	−
Montmorillonites†	Fe^{3+}	0.35	0.54	−
Nontroite†	Fe^{3+}	0.36	0.66	−
Coquimbite#		0.39	0.60	−
Glauconite‡	Fe^{3+}	0.32	0.50	−
Illite§	M(2)	0.36	0.59	−
	M(1)	0.41	1.16	−
	Fe^{2+}	1.13	2.74	−
Illite§ heated at 225 °C	M(2)	0.38	0.66	−
	M(1)	0.43	1.17	−
	Fe^{2+}	1.12	1.11	−
Illite§ heated at 700 °C	Oxide	0.67	0.02	454
	Fe^{3+}	0.48	1.02	−
	Fe^{2+}	1.05	1.05	−
Sulphides				
Pyrite†	Fe^{3+}	0.30	0.60	−
Marcasite†	Fe^{3+}	0.27	0.51	−
Ferihydrite†	Fe^{3+}	0.35	0.52	−
Lepidocrocite†	Fe^{3+}	0.37	0.53	−

Abbreviations: IS = isomer shift, QS = quadrupole splitting, B = hyperfine magnetic field.
*Hamdeh et al. (1994).
†Burns (1993).
‡Kotlicki et al. (1981).
§Saproschenko et al. (1980).
#Pankhurst et al. (1986).

the magnetic phase (sextet) nor the paramagnetic phase (doublet) are significantly altered by the first three treatments (a), (b) and (c). The relative area of the central doublet (Table 1) varies only slightly due to these treatments. This indicates that sulphide (like pyrite), sulphate or hydroxide minerals are not present in significant amounts. On the other hand, the HF treatment (d) has drastically changed the composition of the sample. The Mössbauer absorption is greatly reduced, indicating that the paramagnetic complex has reacted with HF to form soluble compounds. This indicates that the paramagnetic component in the Mössbauer spectra of Gubbio K-T boundary samples is due to a silicate mineral.

Thermal Decomposition of the Doublet

Raw samples were heated in air at 400, 500, 600, 800 and 1000 °C, for 10–15 h. The Mössbauer parameters of these heated samples are given in Table 1. In all the spectra of the heat-treated samples, a single sextet with the Mössbauer parameters similar to the raw sample was obtained. However, significant changes occurred in the doublet parameters. Figure 3 shows the portions of these spectra from velocity −2.5 to +2.5 mm/s to illustrate the changes in the doublet phase. The third and fourth lines of the sextet are also visible in the spectra. The phase-A doublet decomposes at ~400 °C and a new phase (phase-B), with isomer shift ≈ 0.32 mm/s and QS ≈ 1.42 mm/s, appears. This component increases at the expense of the original doublet, as the heating temperature is increased and the process appears to be complete at 600 °C, where the original doublet nearly vanishes. Table 1 shows that the relative area of the magnetic segment remains largely unchanged up to 600 °C. This implies that the paramagnetic phase-A present at the K-T boundary, after decomposition between 400 and 600 °C, generates another paramagnetic phase (phase-B). As the sample
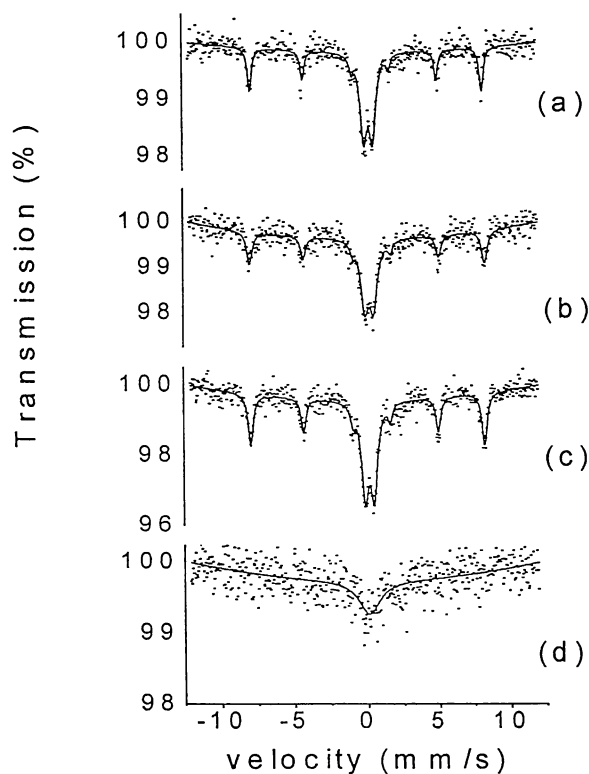
FIG. 2. Mössbauer spectra of the residues after treatment with (a) diluted HNO_3, (b) diluted HCl, (c) concentrated HNO_3 and (d) HF recorded at 295 K.

FIG. 3. Mössbauer spectra of the samples heated at different temperatures and recorded at 295 K.

is heated further to 800 °C and then 1000 °C, phase-B also decomposes. A part of it becomes magnetically ordered and another part appears as yet another paramagnetic phase (phase-C), with isomer shift ≈ 0.25 mm/s and QS ≈ 0.75 mm/s. Interestingly, the magnetic part formed from the decomposition of the phase-B has almost identical Mössbauer parameters as the raw sample and no new sextet appears in the spectra of the samples heated at 800 or 1000 °C. Thus decomposition of phase-B results in the same compound (hematite) as in the raw sample.

As the phase-B decomposes, the abundance of hematite, as well as of phase-C, increases. To check if the phase-C itself is a superparamagnetic hematite phase, Mössbauer spectra of samples heated at 1000 °C were recorded at low temperatures. The spectra recorded with this sample are shown in Fig. 4. From the visual comparison of the spectra and the Mössbauer parameters given in Table 1, we see that the doublet has become broad at low temperatures, but the relative areas of the magnetic and doublet portion remain roughly the same as that at room temperature. This indicates that the decomposition has resulted in a new paramagnetic phase (phase-C), which is stable at least up to 1000 °C.

Off-Boundary Samples

To see the variation in iron phases across the boundary, we have recorded the spectra of samples away from the boundary
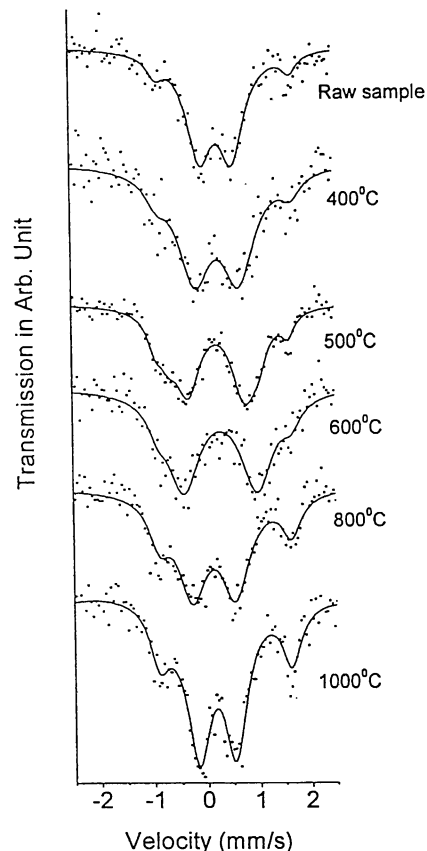
layer at Bottaccione. As expected, the Mössbauer absorption is very small, showing very low concentration of iron-bearing minerals in the carbonate sequence. The results indicate that the concentration of iron was abruptly and for a short time enhanced at the K-T boundary, in an otherwise low-iron-containing continuous depositional sequence and that the iron compounds found at the K-T boundary were most likely formed in the impact-created chain of processes and not due to common terrestrial processes, such as weathering.

DISCUSSION

The Mössbauer spectra of the raw sediments, their acid residues and the heated samples provide some indication of the nature of the iron minerals present at the K-T boundary layer.

Particle Size Estimation of Hematite

Goethite appears as the prominent magnetically ordered iron phases at most of the American/Asian K-T boundary sites and it shows up as a superparamagnetic doublet at room temperature in the Mössbauer spectrum. This implies that the particle size is of the order of few nanometers across. Such
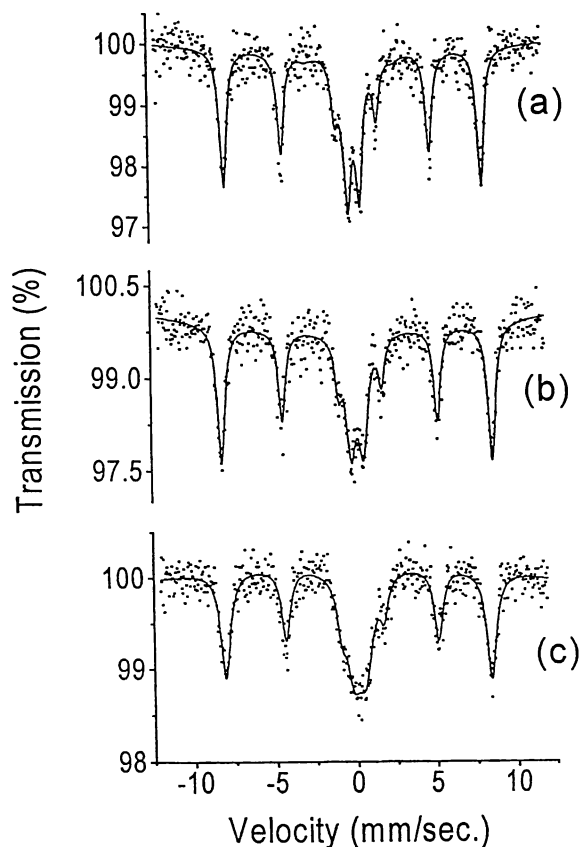
FIG. 4. Mössbauer spectra of the sample heated at 1000 °C and recorded at (a) 295 K, (b) 100 K and (c) 12 K.

$$\frac{B_{eff}}{B_0} = 1 - \left(\frac{k}{4KV_p}\right)T$$

where B_{eff} is the measured HMF, B_0 is the HMF corresponding to the bulk particles, K is the magnetocrystalline anisotropy constant, and V_p is the average volume of the particles. This approximation is quite good for $kT/KV_p < 0.1$. Thus, a plot of B_{eff}/B_0 vs. T should be approximately a straight line, the slope of which can give the particle volume, if the anisotropy constant is known. Several studies have been made to obtain the anisotropy constant for hematite from the Mössbauer data and the suggested values range from ~1 to 60 kJ/m^3, making a direct determination of particle size from the measured HMF difficult (Mørup et al., 1980; Kündig et al., 1966; Hansen et al., 2000; Bødker et al., 2000). It appears to depend on the source of hematite, as well as the particle size.

An upper limit on the particle size of Gubbio K-T boundary hematite can be obtained from the observation that the quadrupole splitting of the hematite sextet remains negative down to 12 K (Wdowiak et al., 2001). Bulk hematite undergoes a magnetic transition from weakly ferromagnetic to antiferromagnetic at 260 K, as the temperature is lowered. This transition known as the Morin transition is easily detected in Mössbauer spectra as the quadrupole splitting is negative in the weakly ferromagnetic phase and positive in the antiferromagnetic phase. The transition temperature is reduced, as the particle size gets smaller (Muench et al., 1985; Nininger and Schroeer, 1978; Kundig et al., 1966). It is 150 K for particles 27 nm in size (Bødker and Mørup, 2000). The fact that Morin transition has not taken place down to 12 K in Gubbio K-T boundary hematite, shows that these particles are well below 27 nm in size. To get an idea of the lower limit, we recorded TEM micrographs of the finest particles in the samples. Figure 5 shows a representative micrograph at a magnification of 80 000. The sizes of these particles are around 16–20 nm. Thus, the hematite particles in the Gubbio K-T boundary are likely to be in the range of 16 to 27 nm.

Figure 6 shows the variation of B_{eff}/B with temperature, which does exhibit a linear decrease. Using average particle size of 21 nm, as estimated above, anisotropy energy constant K comes out to be 11 kJ/m^3 which is in the observed range of K values for hematite.

The Paramagnetic Silicate Mineral

As has been established by the acid-treatment studies of the Gubbio K-T boundary sample, the paramagnetic iron phase is a silicate mineral. Wdowiak et al. (2001) have suggested that it could be illite. Thermal decomposition of an iron-rich dioctahedral illite clay from Fithian has been investigated, using Mössbauer spectroscopy (Saporoschenko et al., 1980). Mössbauer parameters from this study are included in Table 2. The thermal decomposition pattern seen in Gubbio is quite
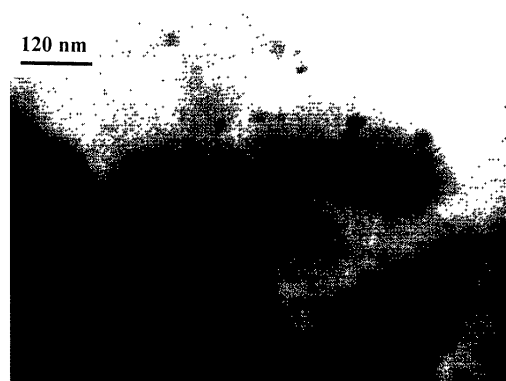
particles normally contain a single magnetic domain and the direction of magnetic moment of the particle rapidly flips among different easy axes of magnetization, due to thermal energy. Rapid flipping of magnetic moment causes zero effective HMF during the measurement time and hence, the usual six-line Mössbauer pattern collapses to a superparamagnetic doublet. In contrast, the Gubbio K-T boundary samples give a well-split sharp sextet corresponding to hematite, implying a particle size large enough to prevent rapid fluctuation of magnetic moments. However, the HMF at the iron nuclear site is considerably smaller than the standard value for hematite, at all the temperatures studied. This reduction may also arise due to the particle size effect. For particles of sizes not too small to allow rapid flipping of moments and not too large to force the moment to stay along the easy axis, the moment oscillates about the easy axis. This process, known as collective magnetic excitation, causes the effective HMF to reduce by a factor of $<\cos\theta>$, where θ is the instantaneous angle of magnetic moment with the easy axis. Mørup (1983) has deduced the dependence of effective HMF on the volume of the particle and the temperature, due to collective magnetic excitation. For low temperatures (T), this relation can be approximately expressed as

FIG 5. Transmission electron micrograph of Gubbio sample showing the smallest particles.

FIG. 6. Variation of B_{eff}/B_0 for the Gubbio K-T boundary hematite, with temperature.

different from, at least, this illite and resembles better with that of a trioctahedral 2:1 layered silicate. The basic structural unit of this group of silicates consists of a sheet of octahedrally coordinated cations, sandwiched between two identical sheets of linked $(Si, Al)O_4$ tetrahedra. Between these composite layers lie the interlayer cations, generally K^+ and/or Na^+. There are three octahedral sites per unit cell and iron, if present, occupies these sites. Each iron ion is then surrounded by four oxygen and two hydroxyl ions. Mica belongs to this 2:1 layered silicate group. When micas are heated, the hydroxil ions from the octahedral sites are converted to water molecules which are expelled out and this dehydroxylation process (occurring between 300 and 500 °C) causes a distortion in the octahedral symmetry, increasing the quadrupole splitting in Mössbauer spectrum to ~1.5 mm/s. The structure itself starts changing at around 800–900 °C, when it forms hematite (Tripathi *et al.*, 1978). In the present case, the thermal decomposition pattern of the paramagnetic phase is qualitatively similar, providing strong evidence that it belongs to the layer silicate group. However, the structural decomposition occurs somewhat early in the observed phase in Gubbio. Whereas in typical layer silicates in terrestrial soils the structural decomposition starts at 800–900 °C, in our case the decomposition is almost complete before 800 °C. This may be a result of the fine particle nature of this phase. In the terrestrial soil samples, the silicate phases are normally seen in micron-sized clay fractions. The silicate minerals observed at the K-T boundary at Gubbio may range in size from a few tens of nanometers, as is the hematite phase. This also explains the observation that hematite formed due to decomposition of this phase has similar reduced HMF value as the original hematite in the K-T boundary sample.

Different Redox Conditions During Sedimentation

As mentioned earlier, several workers have reported magnesioferrite and magnetite in the magnetic microspherules separated from the K-T boundary samples, from the Gubbio section. However, in the samples studied by us, which contain the bulk sedimentary material, these phases are below the
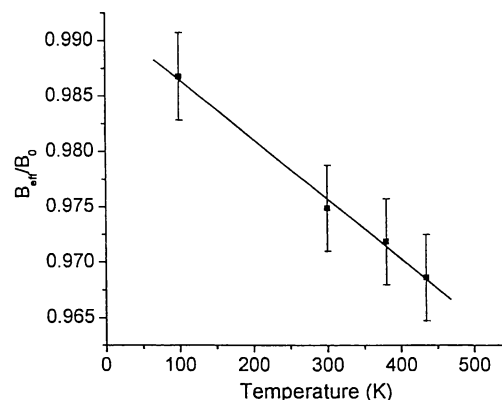
detection limit of Mössbauer spectroscopy (<1%). This implies that the high-temperature phases like spinel ferrites, which form in reducing environment could survive only in the spherules and the surrounding material mostly contains hematite, which forms in oxidizing conditions.

Montanari (1991) have made extensive studies of spheroids from the K-T boundary at Italian sites and have reported a large number of glauconite particles (dioctahedral mica group), as the characteristic paramagnetic iron-containing mineral at the K-T boundary sections. These particles are formed in reducing environment, as a result of potassium enhancement in newly formed mica. The silicate mineral found in our samples is very different from this and has almost all the iron in oxidized Fe^{3+} state. The magnetically ordered minerals also reflect this contrast in the spherules and the surrounding clay. The spherules observed at the K-T boundary contain minerals like spinel ferrite or magnetite, which form in low oxygen fugacity. On the other hand, the surrounding sample contains hematite, which is characteristic of an oxidizing environment. One possibility is that while the part of the impact ejecta that contained relatively larger particles formed the spherules and was transported following ballistic kinematics, those with very fine particle size (nanophase) reached the upper atmosphere and remained suspended for quite a long time. The large amount of this fine solid mass, circulating in the atmosphere for a long period could have caused major changes in the biogenic activity, for example, by considerably blocking sunlight. When this material finally settled on the Earth the reducing conditions were replaced by oxidizing conditions and it converted the fine particles into oxidized minerals. The fact that the nanophase minerals at the K-T boundary show a nearly uniform behavior all over the world is consistent with a long period of suspension of this fine material in the atmosphere.

CONCLUSIONS

Mössbauer studies of the K-T boundary section from the Gubbio show sharp variations in iron mineralogy with

stratigraphy. Magnetically ordered iron phase, mainly hematite, is present at the boundary, which is absent in the samples away from the layer. The particle size of this phase is in the range of 16 to 27 nm, as revealed by Mössbauer spectroscopy and TEM. Together with hematite, a paramagnetic silicate phase has been detected in the boundary layer, which shows a unique thermal decomposition behavior suggesting an oxidized 2:1 layer silicate, in fine particle form of a few tens of nanometers. It is suggested that the nanosized particles formed due to impact processes, remained suspended in the atmosphere for a long time before settling down on the Earth, when by then an oxidizing environment had been restored.

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