NANO-SIZED IRON PHASES AT THE K/T AND P/T BOUNDARIES REVEALED BY MÖSSBAUER SPECTROSCOPY, H.C. Verma[1], C. Upadhyay[1], R.P. Tripathi[2], A. Tripathi[2], A.D. Shukla[3] and N.Bhandari[3] [1]Indian Institute of Technology, Kanpur 208016; [2]Department of Physics, Jai Narain Vyas University, Jodhpur 342001; [3]Physical Research Laboratory, Navrangpura, Ahmedabad 380009, India, email: bhandari@prl.ernet.in

Abstract: The iron mineralogy of the Cretaceous-Tertiary boundary (KTB) and Permian-Triassic boundary (PTB) clays from several sites has been determined using Mössbauer spectroscopy. At all the sites, boundary samples show the presence of oxide and/or oxyhydroxide phases of iron, often in the form of particles of a few nanometers exhibiting quenching of magnetic moment due to superparamagnetic relaxation. Across the KTB, the abundance of these iron phases correlates fairly well with the impact marker iridium content, indicating their genetic relation with the impact ejecta fall out. The PTB samples also show characteristics which are in some respects similar to KTB samples.

Introduction: The mass extinction boundaries are generally marked by an event horizon. This event horizon is sometimes sharply defined as e.g. at KTB, but more frequently, at other geological boundaries, it is diffused and prolonged over considerable period of time such as at E/O or P/T boundaries. Furthermore, all the boundaries have some chemical, isotopic, mineralogical, climatological or lithological markers. For example, at K/T boundary a thin ferruginous clay layer, rich in iridium, is globally present indicating impact of an extraterrestrial body [1]. Extensive work has been carried out on chemical and mineral anomalies present in KTB clays but how the bulk of this clay material was formed is not well understood. In comparison, the P/T boundary is usually not defined by such a lithological or chemical marker but in the Spiti valley, a thin ferruginous layer has been found to occur between Permian black shales and Triassic limestones [2]. Realizing that a study of the chemical state of iron is useful in characterizing the geochemical and environmental conditions prevalent at the time of deposition, we have carried out ^{57}Fe Mössbauer spectroscopy of several K/T and P/T boundary clays. This technique is well suited for such a study because each type of iron complex gives rise to characteristic signatures in Mössbauer spectrum. A paramagnetic iron complex, e.g. gives rise to a quadrupole doublet and hyperfine magnetic field (HMF) existing in magnetically ordered materials causes a six line pattern with characteristic splitting [3]. However the direction of magnetization in nanosize single domain particles fluctuates rapidly among the easy axes of magnetization giving zero average HMF during the time of measurement (superparamagnetic relaxation). This causes a temperature dependent collapse of the usual six-line Mössbauer spectrum in magnetic systems to a doublet or a singlet [4]. At low temperatures, the superparamagnetic effects are reduced and the characteristic six line pattern reappears. The objective of the present analyses is to study the gross iron mineralogy across the KTB and PTB. A preliminary report of the first Mössbauer studies of some K/T boundary clays was reported by us at the Vienna conference [5]. Here we extend our studies on the KTB samples (Anjar, Gubbio, Meghalaya and Turkmenia described in [6]) and present the first Mössbauer studies of PTB (Attargoo, Spiti valley, India) samples. The spectra were recorded using a conventional constant acceleration Mössbauer spectrometer with ^{57}Co in Rh matrix as the Mössbauer source. Discrete doublets and sextets with Lorentzian peaks were fitted to the spectra using a least squares code. In the second approach a near continuous variation of HMF was assumed and probability of each HMF was calculated using Window's approach [7].

Results: The Mössbauer spectra of some of the KTB and PTB samples studied here are shown in Fig. 1. We see a clear sextet in the Gubbio spectrum and a weak sextet at similar locations of the peaks in the Attargoo spectrum. All the spectra contain a strong doublet. In Anjar, Meghalaya and Turkmenia, the doublets mainly correspond to superparamagnetic iron oxides/ oxyhydroxides like hematite and goethite.

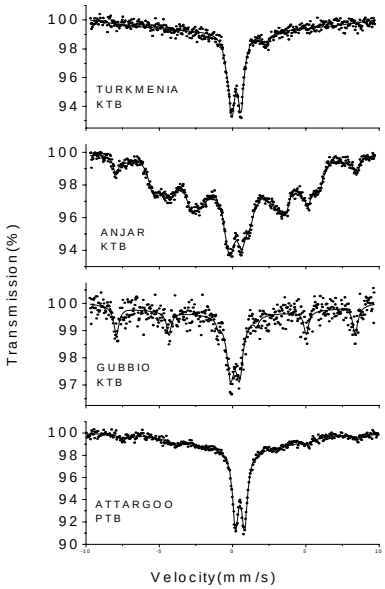

Fig.1: Mossbauer spectra of KTB and PTB samples at 295 K

NANO-SIZED IRON PHASES AT K/T AND P/T BOUNDARIES by H.C. Verma et al..

This is revealed by their low temperature spectra. From these temperature dependent studies we estimate the average particle size for the iron phases to be a few nanometers whereas in Gubbio, it is few tens of nanometers. The doublet in Gubbio comes from a complex paramagnetic phase having iron in Fe^{3+} state. The thermal decomposition behaviour of this phase studied by heating the sample for 15-20 hours at 400, 600, 800 and 1000 ^{0}C show phase changes in a manner which is not observed in paramagnetic iron phases commonly present in terrestrial sediments.

The intensity of the magnetically ordered part in the KTB samples in all the sections correlates with the iridium concentration indicative of their common origin with the impact ejecta fall out [6].

Implications of oxide/hydroxide phases in KTB layers

A significant result of the Mössbauer investigations of the KTB layers from four different basins, located far away from each other, is the common presence of hematite/goethite/limonite, irrespective of the local lithology, and that too as the major iron bearing minerals. Magnetic microspherules containing magnesioferrite and magnetite are known to occur in KTB clays [8]. Each of these two minerals shows two sextets with characteristic Mössbauer parameters, not found in our KTB samples even at low temperatures, implying that they occur only as minor constituents. Our study therefore suggests that hematite/goethite are the main iron-bearing magnetic material in the KTB samples and any other phases occur in relatively small quantity.

Although these oxides are commonly found in terrestrial sediments and are generally formed due to weathering of iron minerals, their association with iridium and global occurrence within the KTB layer irrespective of the local depositional environment (marine or continental) suggest that these were formed from the iron present in the impact vapour plume due to extreme pressure-temperature and climatic conditions (e.g. acid rains) created by the impact.

P/T Boundary layer: The P/T boundary throughout Spiti valley has been marked by a ferruginous band in which a high positive Eu anomaly was observed [2,9]. Discrete Mössbauer parameters fit to the sextet of small amplitude (Fig.1) yields an HMF of 498 kOe and isomer shift 0.44 mm/s. Interestingly, similar Mössbauer parameters were estimated in the iridium- rich layer at Gubbio at room temperature. This implies that the same phase as formed in the impact-chain processes and deposited at Gubbio KTB was formed at the PTB, though in small amount albeit the near absence of iridium. Fig. 2 shows the Mössbauer spectrum of two samples from Attargoo (at and 4cm below PTB) at 100 K. The off-boundary sample does not show any magnetic splitting indicating presence of only paramagnetic iron phases, whereas the boundary sample yields a distribution of HMF. The superparamagnetic doublet at room temperature (Fig. 1) has thus been split into sextets due to slower thermal fluctuation in the magnetic moments. The p-H distribution of the spectrum (Fig.2c) shows a separate peak around 520 kOe indicating hematite. Besides, there is a continuous distribution with maximum contribution coming from HMF around 400 kOe. The superparamagnetic effects, though considerably reduced at 100 K, are not completely quenched and spectra at still lower temperatures are needed to identify the phases quantitatively. Minor hematite phase with HMF 510 kOe was also seen at the Anjar KTB [6]. Since hematite is the end product of many different decomposition and transformation sequence of iron-bearing minerals, these similarities can not be taken as an evidence for impact at PTB till confirmed by further studies.

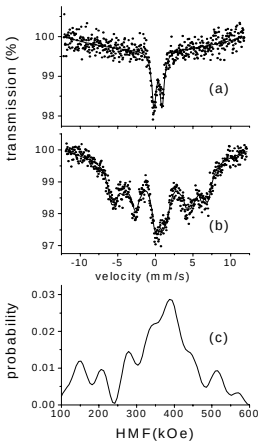

Fig.2: Mossbauer spectra of PTB samples at 100K (a) sample 4 cm below the boundary, (b) sample from the boundary and (c) p-H distribution of spectrum (b)

REFERENCES[1]Alvarez L.W. et al. (1980), *Science 208*, 1095-1108.[2] Bhandari N. et al. (1992) *Geophys. Res. Lett. 19*, 1531-1534. [3] Gütlich, P(1975) *Mössbauer Spectroscopy*, (Ed. U. Gonser), Springer-Verlag [4] Haneda, K.(1987*) J. Phys. 65*, 1233-1243.[5] Bhandari N. et al. (2000) *In Catastrophic Events and Mass Extinctions:Impacts and Beyond*, LPI Cont. 1053, 12, LPI Houston.[6] Bhandari N. et al. (2000) *In Catastrophic Events and Mass Extinctions:Impacts and Beyond; in Proc. Geol. Soc. Am.* (submitted) [7] Window, B.(1971) *J. Phy. E. Sci. Inst.4*, 401-402. [8] Kyte et al. (1996) *Geol. Soc.Am. spl paper 307*, 389-401. [9] Shukla A.D. et al. (2000) *In Catastrophic Events and Mass Extinctions:Impacts and Beyond*, LPI Cont. 1053., 195, LPI Houston.