MÖSSBAUER SPECTROSCOPY OF K/T BOUNDARY CLAYS: CHARACTERISTICS OF IRON BEARING MINERALS. N. Bhandari[1], H.C. Verma[2], Amita Tripathi[3], C. Upadhyay[2] and R.P. Tripathi[3]
[1]Physical Research Laboratory, Navrangpura, Ahmedabad 380009, India (bhandari@prl.ernet.in), [2]Department of Physics, Indian Institute of Technology, Kanpur 208 016, India, [3]Department of Physics, Jai Narain Vyas University, Jodhpur 342011, India.

Introduction: The K/T boundary in the marine sediments is generally characterized by a thin band of limonitic clay. Geochemical anomalies in KTB clays have been attributed to impact of a large bolide on Earth, 65 M.Y. ago [1]. Several studies have been made to determine the nature of the impactor, climatic conditions arising from the impact and their biological effects. On the basis of the isotopic composition of chromium ($^{53}Cr/^{52}Cr$) the impactor appears to belong to the carbonaceous chondrite group of meteorites [2]. These meteorites have high concentration of iron (~20%) in form of silicates, magnetite and other iron bearing minerals. Normally limonitic layers in terrestrial sediments are formed by subaerial exposure and represents a hiatus, but the limonitic layer at the KTB has been formed in a different process. A possible scenario can be described as follows. A large fraction of the impactor material and some target material would have vaporized and ejected into the atmosphere at high velocities during the impact. Because of its high abundance in the bolide as well as the large volume of the terrestrial material involved in crater formation, iron is expected to be a major component of the vapor cloud. The temperature of the vapor is likely to be high enough to dissociate many of the minerals. While the coarse ejecta would deposit in and around the foreground of the site of impact, the fine particulate material formed during the high temperature reactions in the vapor cloud followed by fast quenching is expected to disperse throughout the globe. The micron size nickel rich spinels [3] and the iridium nuggets[4] found to be associated with iridium in the limonitic layers were probably formed in such processes [5]. However, little is known about the nature of submicron particles, formed in such processes. They would be transported across the globe by atmospheric migration, followed by scavenging and deposition on land and oceans, and under the action of acid rain accompanying the large impact at KTB, resulted in formation of the limonitic layer. The variation in iron mineralogy across KTB can provide information about the chemical processes occurring in the atmosphere and the chemical environment prevailing at the deposition sites following the impact. We have therefore studied the limonitic layers from a few KTB sites, using ^{57}Fe Mössbauer spectroscopy, which is ideally suited for understanding the physico-chemical processes responsible for their formation.

Sample details: Mössbauer analysis was carried out on iridium rich (KTB) layers from Gubbio, Meghalaya, Anjar and Turkmenia and some samples from above and below the KTB layers. Gubbio (Bottaccione) section in Italy is a deep marine section where the Ir anomaly was first discovered [1] in the mass-extinction horizon and several other impact markers (Ni rich spinels, shocked quartz , soot, etc.) have been found. Meghalaya is a near coastal marine section in the eastern India [6] whereas Anjar (Kutch) is a continental lake section in the Deccan volcano-sedimentary sequence in western India [7]. Both these sites were located outside the fallout zone according to the demarcations made by Alvarez [8] for various ballistic velocities. The Meghalaya section has anomalously high Ir and Ni-rich spinels [9] at KTB whereas three well separated layers with high iridium have been observed in the Anjar section [7]. Turkmenia shows iridium anomaly and characteristic excursions of C and O isotopes.

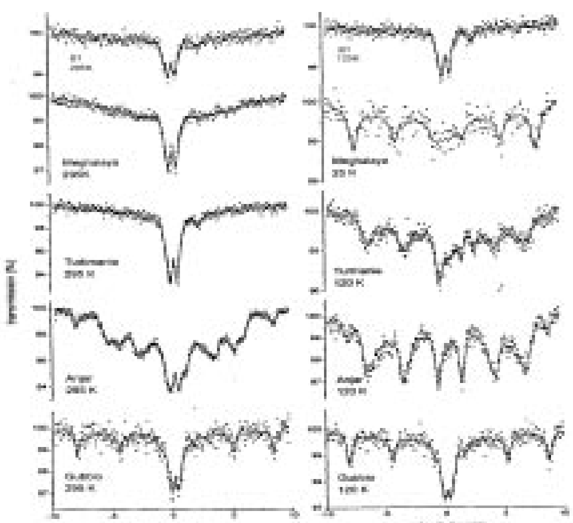

Fig.1 Mössbauer transmission at 295K (left) and at 120K (right) for various KTB clays. Mössbauer spectra of sample B1 away from KTB is given for comparison.

Experimental method: The Mössbauer spectroscopy was carried out using a conventional constant acceleration Mössbauer spectrometer at IIT, Kanpur. The absorbers for Mössbauer spectroscopy were prepared from the powdered samples. ^{57}Co in Rh matrix was used as the Mössbauer source. A liquid nitrogen cryostat was used for cooling, except for temperatures below 80K where a close-cycle helium cryostat system from APD Cryogenics was used. X-ray diffraction patterns were recorded using a Seifert Iso-Debyflex 2002 diffractometer using Cu K_α radiation.

Results: Fig.1 shows the Mössbauer spectra of KTB samples studied at 295K (RT) and at 120K (LT). The Mössbauer parameters show that all the KTB samples have magnetic phases of iron together with Fe^{3+} in clay minerals (largely illite). At RT, Gubbio shows a well developed six line pattern whereas Anjar shows partially relaxed spectrum. The RT spectra of Meghalaya and Turkmenia do not show magnetic splitting at RT but both of these are superparamagnetic (SPM) as confirmed by their low temperature spectra. Considering that the particle size of iron component is related to the blocking temperature at which the sextet collapses to a doublet, we find that particle size in the Gubbio KTB sample is well above 10 nm, whereas the particle size of the magnetic iron phases is smaller in Anjar and still smaller in Meghalaya and Turkmenia KTB samples. Such fine size is also inferred from the broadness of the XRD peaks. The particle size shows a decreasing trend with distance from the Chicxulub crater. Gubbio shows hyperfine magnetic field (HMF) of 522 kOe, indicating the presence of hematite (α Fe_2O_3) as the main magnetic phase. Anjar also has a small component of hematite but the major part is with HMF of 415 kOe or lower showing the presence of göthite, and possibly maghemite (γ Fe_2O_3). The HMFs of Meghalaya and Turkmenia spectra correspond to goethite. These observations are supported by the X-ray diffraction patterns. The Mössbauer parameters for the central doublet in Gubbio, Meghalaya and Turkmenia correspond to Fe^{3+} in illite, which is a common clay mineral. Thus we find that the oxide phases of iron appear at all sites irrespective of the lithology of the local sediments, indicating a global nature of the chemical environment at KTB.

Fig. 2 shows the Mössbauer spectra of the Anjar samples at 100 K collected at various stratigraphic distances above and below the limonitic layer. The sharp variation in the iron phases at KTB is quite clear. Magnetic oxides appear suddenly at KTB and disappear above and below it. The off-KTB samples are devoid of magnetic phases as well as iridium. The amount of magnetic phases of iron correlates with iridium content, indicating that they probably have a common origin. Similar correlation is found for the Meghalaya and other sites.

Discussion: The presence of oxide and hydroxide phases of iron at all the KTB layers irrespective of the local lithology is indicative of the climatic excursion at KTB. It is possible that these oxide and oxyhydroxide iron phases are formed by leaching of iron by the accompanying acid rains. The presence of hematite indicates severe environmental conditions (arid and warm) whereas göthite forms under milder conditions of temperature and aridity. Such information may be used to infer about the climatic conditions in various parts of the Earth at the K/T boundary. The decreasing size of SPM particles from impact to deposition site is consistent with atmospheric migration as discussed above. Based on these limited studies we suggest that sudden appearance of iron based oxide particles with a size distribution dominated by nanometer range at a geological boundary may be indicative of large-

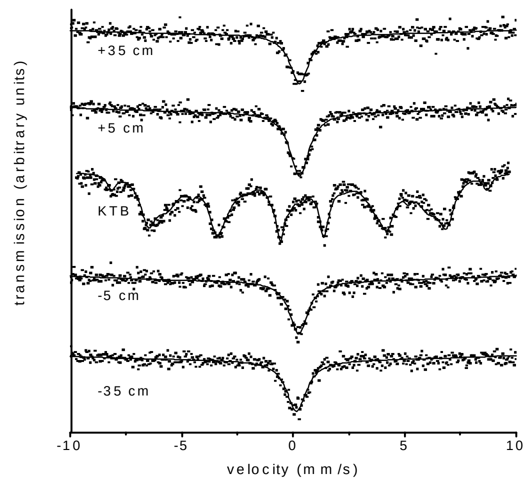

Fig. 2. Mössbauer spectra of samples at different stratigraphic distance from the KTB in Anjar section.

bolide impact. Work is in progress to confirm the magnetic phases present at other boundaries, such as at P/T boundary.

References : [1] Alvarez, L.W. et al. (1980) *Science*, 208, 1095-1109. [2] Shukolyukov A. and Lugmair G.W. (1998) *Science*, 282, 927-929. [3] Robin, E.et al. (1992), *Earth Planet. Sci. Lett.*, 108, 181-190. [4] Schuraytz B.C. et al. (1996), *Science*, 271, 1573-1576 [5] Kyte F.T., et al. (1996) *Geol. Soc. Am. Spec. Pap.*,307, 389-401.[6] Bhandari N. et al. (1994) *Chem. Geol*., 113, 45-60. [7] Bhandari, N. et al (1995). *Geophys. Res. Letts*., 22, 433-436. [8] Alvarez W. (1996) *Geol. Soc. Am. Spec. Pap.*, 307, 141-150. [9] Bhandari N. (1998) *Proc. Ind. Acad. Sci.*, 107, 251-263.