Prominent occurrence of iron oxides at KTB mass extinction: a review

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Abstract

Out of the five major mass extinction, which have taken place in the history of life, Cretaceous–Tertiary boundary (KTB) mass extinction was the 2nd most disastrous, the most severe being that at Permian–Triassic boundary (PTB). On the basis of iridium anomaly at a number of KTB sites it has been established that the cause of extinction was impact with an extraterrestrial bolide. The iron oxide/oxyhydroxide and iron minerals such as illite, phyllosilicate, jarosite etc. present in the rock samples from KTB form a major part. One can study different phases of iron oxide/oxyhydroxide present in the KTB samples with the help of Mössbauer spectroscopy. The Mössbauer studies showed that at KTB sites nanophas e goethite and/or hematite are present without coexistence of their counterpart bulk size iron oxide/oxyhydroxide minerals. The amount of nanophase iron oxides well correlate with iridium concentration showing that the nanophase iron minerals are genetically related to the events at KTB. Thus these nanophase iron compounds were formed in the geochemical conditions created by the impact, and not by slow weathering. The iron mineralogy at some other extinction sites is found to be very similar to that at KTB although there is no iridium anomaly. This raises an interesting suggestion that iron mineralogy i.e. presence of nano-sized oxide and oxhydroxide particles alone without the existence of bulk iron-oxide in sedimentary layers can be used as impact markers. Studies carried out on some off-KTB rock samples also showed iron mineral composition similar to that at KTB without having iridium anomaly. This opens up the new questions whether these layers are also result of some large meteoritic impact?

Keywords: Mössbauer spectroscopy, KT boundary, nanophase iron, iron mineralogy.

1. Introduction

The end of Cretaceous period was very tragic and disastrous. It occurred about 65 million years (My) ago when around 60% of the lives on the earth including the mighty dinosaurs were extinct over a small time interval on geological scale. The transition period is known as Cretaceous-Tertiary Boundary (KTB). The cause of this extinction has been widely studied and debated (Alvarez et al., 1980; Alvarez et al., 1982; Smith and Hertogen, 1980; Hsü, 1980; Kyte et al., 1980; Wolbach et al., 1985; Rampino and Reynolds, 1983; Officer and Drake, 1983; Officer and Drake, 1985; Officer et al., 1987; Snee 1991). Impact by a large extraterrestrial bolide (Alvarez et al., 1980; Alvarez et al., 1982; Smith and Hertogen, 1980; Hsü, 1980; Kyte et al., 1980; Izett et al., 1991; Marin et al., 1992; Swisher et al., 1992) and widespread Deccan volcanoes eruption in western India during the same geological slot (Rampino and Reynolds, 1983; Officer and Drake, 1983; Officer and Drake, 1985; Officer et al., 1987; Hoffman et al., 2000), are two major possibilities on which scientists have focused their studies. Each of these two was capable to create conditions for large scale extinction of living species and hence supplementary evidences from the sedimentary rocks; both geochemical and paleontological are important to distinguish between the two possibilities.

Typically 1-2 cm thick sedimentary rock layer corresponding to KTB usually distinguishes itself from the surrounding layers by its limonitic colour. This layer shows a sudden enhancement of siderophile and platinum group elements over the background value of the underlying and overlying layers. The pioneer work of Alvarez et al. showed that the concentration of iridium in the limonitic KTB layers in all the 50 sections studied, (Alvarez et al., 1980; Alvarez et al., 1982) was much higher (20–160 times) than that in the background. This finding made the extraterrestrial origin of KT extinction a great favourite. The study gained much more momentum by finding of ~200 km wide crater at Chicxulub (Sharpton et al., 1992), shocked quartz (Bohor et al., 1984; Alvarez et al., 1995), nickel rich spinel (Bohor et al., 1986; Robin et al., 1992) and abrupt change in the isotopic ratios such as δ 13C and δ 18O in the KTB layers.
However, the actual mass extinction is believed to be due to the geothermal and geochemical conditions created in the atmosphere and on the earth’s surface (Sutherland, 1994; Bhandari, 1998) as a result of the impact. The billions of tons of ejecta must have gone up as vapour plume and chemical reactions at the high temperature must have changed the redox conditions. While a part of the ejecta fell back on the earth following ballistic trajectory kinematics, the portion having lighter particles went into the upper atmosphere and dispersed all over the globe. It is stipulated that the plume and the soot (Wolbach et al., 1985) released from wide spread fire blocked sunlight for an extended period, may be in kilo years, bringing out a sharp drop in the temperature. Such extreme climatic changes are assumed to be responsible for the mass extinction. Though the impact represents an instantaneous event, the after effect on the climate such as blocking of sunlight etc., and the resulting geochemistry (for example, oxygen fugacity) could have lasted for much longer time.

The sedimentation during the KTB witnessed all the climatic changes and hence the mineral composition in the sedimentary rocks has signatures of these conditions. Iron being the most active and abundant element can provide a lot of evidences of the sequence of the events during the Cretaceous-Tertiary transition.

Though iron phases are so abundantly present at KTB layers, not much Mössbauer study have been undertaken. The journal reports on Mössbauer studies of KTB starting appearing in and after 1998 (Armendarez et al. 1998; Wdowiak’s et al., 2001; Bhandari et al., 2002; Verma et al., 2002a). In this review further insight that has been gained due to these Mössbauer studies of presence of iron oxides at the boundary layers has been presented.

2. Mössbauer studies of KTB Samples

2.1. Nanophase iron at KTB

The Mössbauer studies of four KTB sites, namely Meghalaya, Anjar (India), Turkmenia and Gubbio (Italy) by Bhandari et al. (2002), reproduced in Figure 1, show sharp variation in iron mineralogy across the boundary layers. Superparamagnetic and magnetic iron phases are found to occur in the boundary layer. In the Meghalaya site, Fe$^{3+}$ minerals and also the iridium are present across 17.5 cm vertical section. Figure 2, reproduced from Bhandari et al., (2002), shows that the total iron content goes as iridium profile with other siderophile elements in this layer. From the study it has been concluded that the marine sediment was already receiving these minerals before the peak of the impact got deposited, and this fact was in good agreement with the iridium concentration. In the beginning of the KTB study through Mössbauer spectroscopy the global occurrence of magnetic and superparamagnetic iron phases are in KTB clay well correlated with the iridium anomaly. And it becomes an important tool to study impact related environments.

The study of KTB samples from two different continents of our globe e.g. American and European sites by Wdowiak et al. (2001) brought some interesting features. The Mössbauer spectra from representative American and European sites are reproduced in Figure 3 from Wdowiak et al., (2001) with permission. From the low temperature Mössbauer data and by matching it with standard literature values the work concluded that at the entire KT boundary vis Europe and America nanophase iron minerals were present. To have a better insight of the iron mineral at different locations we consider these one by one. From Figure 3a, it is clear that the iron is in the form of ferric at the American site KTB samples. The relative area of the sextet increased with decreasing the temperature, this is clear evidence of a nanophase iron mineral, with particle size less than few tens of nanometer (nm). On the basis of Mössbauer spectral parameters this mineral is identified as nanophase goethite ($\alpha$-FeOOH). The powder X-ray diffraction spectra show only quartz and goethite which is also consistent with the Mössbauer result. The estimated particle size of goethite ranges from 15 nm to 25 nm. It would be worth to quote from Wdowiak et al. (2001) that “without Mössbauer spectroscopy, it would not be possible to arrive at a conclusion solely from XRD data about the presence of nanophase iron-bearing mineralogy in the American samples”. In one sentence one can say that at KTB samples of American sites, nanophase goethite is present.

On the other hand, in most of the European samples (Figure 3b), the behaviour of doublet and sextet at decreasing temperature gives signature of strong superparamagnetism. The situation of samples from Italian sites is somewhat different (Figure 3c), they do include a weak contribution from nanophase goethite but major sextet component come from hematite ($\alpha$-Fe$_2$O$_3$) without existence of Morin transition, that is because as temperature is lowered the quadrupole splitting remains negative. This confirms that at the European site nanophase iron is present in the form of hematite. One can see from Figure 3c, that there is a prominent major contribution from the iron containing phyllosilicate clay and illite in all the spectra which may be considered as local contribution of Gubbio region. Thus over all European sites KTB nanophase hematite is present.

While all the American and Asian KTB samples showed superparamagnetically relaxed Mössbauer spectra, the European samples including those from the Gubbio formation showed spectra representing collective magnetic excitations Bhandari et al. (2002). KTB samples from Bottaccione, of Gubbio formation were studied by Verma et al. (2002a). In this report the Mössbauer spectra were recorded not only below room temperature but also at higher than room temperatures. Also, the samples were independently heated at much higher temperature and data were recorded at room and low temperatures. Verma et al. (2002a) dissolved the samples in different acids (as HNO$_3$, HCl) for different time durations and with the help of Mössbauer spectroscopy it was concluded that the iron minerals like sulphide, sulphate or hydroxide minerals are not present in significant amounts. But
when the samples were dissolved in HF, it drastically changed the composition of the sample. Hence the Mössbauer absorption reduced, indicating that the paramagnetic complex has reacted with HF to form soluble compounds.

**Figure 1.** Mössbauer spectra of four KTB sites reproduced from Bhandari *et al.* (2002)

**Figure 2.** The vertical profiles of (a) iridium content, (b) magnetic fraction and (c) iron content in different samples of the Meghalaya section as a function of stratigraphic distance from the most iridium-rich (KTB) layer. The magnetic fraction has been obtained from the area under the sextets compared to the total absorption area at 100 K. All values are normalized relative to the corresponding value at the most iridium-rich layer, reproduced from Bhandari *et al.* (2002)
This indicates that the paramagnetic component in the Mössbauer spectra of Gubbio KTB samples is due to silicate minerals. From the temperature variation of hyperfine magnetic field ($B_{hf}$) corresponding to the hematite, the particle size of the hematite was estimated in the range of 16–27 nm.

Mössbauer studies, rule out the school of thoughts that favours the deposition of KTB by Deccan volcanism, can also be discussed. Firstly, one can mention that Mössbauer spectra of sample studied from all KTB sites including Anjar, lying in volcanic province, did not reveal presence of any volcanic mineral or volcanic glass like obsidian and secondly in volcanic originated samples presence of full grown magnetite in spectra is mandatory, but absence of magnetite in KTB samples is itself the evidence that KTB was not a consequence of volcanism. One can also discuss that precursors like pyrite etc. are absent in samples this means nanophase iron oxide was not the result of weathering and similar weathering cannot occur globally as the regional sedimentation is different. The Mössbauer spectroscopy studies suggest that the finding of nanophase iron minerals without co-presence of corresponding coarse size iron minerals over a wide geographic range may be taken as an apparent geochemical marker of the KTB.

2.2. Mössbauer studies of PTB (Permian Triassic Boundary)

It has also been established (Becker et al., 2001; Basu et al., 2003) that the Permian period ended because of the most severe mass extinction occurred about 250 million years (My) ago in which about 90% of the marine species and about 70% of the terrestrial vertebrates has been estimated to have gotten extinct. After tragic end of Permian period Triassic period started and the time boundary is known as the Permian Triassic boundary (PTB). The first Mössbauer report on the PTB appeared as late as in year 2002 (Verma et al., 2002b). They have presented the first Mössbauer study on the samples collected near the villages Attargoo, Lalung and Guling in Spiti valley, India. In this article they reported that the Mössbauer spectra of all the three samples show a strong doublet superimposed on a weak magnetically split component. The doublet intensity gradually diminished as the temperature is lowered and in its place magnetic splitting with a distribution of hyperfine magnetic field appears. It implies that each sample contains fine particles of iron minerals and the doublet at the room temperature is due to the superparamagnetic
fluctuation of the magnetic moment of the single domain particles. This component was assigned as goethite with particle size in nanometer range.

The Mössbauer spectra of PTB samples may be compared with those of KTB samples from Gubbio (Italy), Anjar (Deccan, India) and Meghalaya (India). Gubbio Mössbauer spectrum at RT shows presence of hematite and the Mössbauer parameter of sample from Attargoo sextet has the same average value. Goethite in nanometer range dominates in the Asian KTB site with smaller amount of hematite. In fact in all American and Asian KTB sites goethite has been found as the dominant component, and we also see the same trend in the Asian PTB site.

We have seen that in these two major mass extinctions the iron mineralogy as revealed by Mössbauer spectroscopy emerges as new tool to identify the impact related geological changes in the history of earth.

2.3. Mössbauer Study of two off-KTB samples

We have recently studied some of the off-KTB samples (Pandey et al., 2005). In that study we have reported the Mössbauer result of two limonitic layers in the exposed section at Petriccio (in Gubbio formation) which are much below the recognized most iridium rich KTB layer. One of the layers is 128 cm below the well known KTB and the other is 149 cm below it. Correspondingly, the two samples are named P128 and P149. The boundary sample itself is named P0. The two layers P128 and P149 do not show any iridium enhancement but they are still special because several of the siderophile elements have high concentration in these layers.

2.3.1. Composition of elements

Table 1 gives the composition of some of the siderophile elements in P0, P128 and P149 samples as reported by Bhandari et al. (1993). P0 contains enormous iridium (5.2 ppb) over a non detectable background. P128 and P149 layers are iridium deficient but have other elements in much larger concentration than the background, almost the same as that at KTB. Thus chromium has maximum concentration of 103.4 ppm at P0 against a background of 50-60 ppm. At P128 and P149 this concentration is 94.3 ppm and 90.0 ppm respectively. Ni concentration peaks at 1240 ppm at P128 against 778 ppm at P0. Similar is the case for Co, Ba or Na. Iron too has highest concentration at P128 (3.92% as against 3.51% in P0). The first question that arises is whether these layers P128 and P149 which are widely separated from the accepted KTB Layer P0 are genetically related to it. To look into this question, the samples were studied using Mössbauer spectroscopy.

Table 1. Composition1 of different elements in P0, P128 and P149 samples, data taken from Bhandari et al. (1993)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ir (ppb)</th>
<th>Cr (%)</th>
<th>Ni (%)</th>
<th>Co (%)</th>
<th>Ba (%)</th>
<th>Na (%)</th>
<th>Fe (%)</th>
<th>Ca (%)</th>
<th>K (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>5.2</td>
<td>103.4</td>
<td>778</td>
<td>46.1</td>
<td>322</td>
<td>2294</td>
<td>3.51</td>
<td>7.6</td>
<td>2.53</td>
</tr>
<tr>
<td>P128</td>
<td>-</td>
<td>94.3</td>
<td>1240</td>
<td>44.8</td>
<td>661</td>
<td>3396</td>
<td>3.92</td>
<td>5.4</td>
<td>2.73</td>
</tr>
<tr>
<td>P149</td>
<td>-</td>
<td>90.0</td>
<td>1053</td>
<td>46.7</td>
<td>863</td>
<td>3558</td>
<td>3.16</td>
<td>6.0</td>
<td>2.05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>La</th>
<th>Ce</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
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<tr>
<td>P0</td>
<td>29.9</td>
<td>36.9</td>
<td>27.1</td>
<td>6.5</td>
<td>1.47</td>
<td>2294</td>
<td>5.5</td>
<td>1.65</td>
<td>0.23</td>
</tr>
<tr>
<td>P128</td>
<td>32.8</td>
<td>46.5</td>
<td>34.6</td>
<td>7.36</td>
<td>1.66</td>
<td>3396</td>
<td>5.7</td>
<td>2.44</td>
<td>0.33</td>
</tr>
<tr>
<td>P149</td>
<td>28.0</td>
<td>46.2</td>
<td>31.5</td>
<td>6.27</td>
<td>1.66</td>
<td>3558</td>
<td>6.7</td>
<td>2.10</td>
<td>0.31</td>
</tr>
</tbody>
</table>

1 All values are in ppm except when mentioned otherwise.

2.3.2. Mössbauer findings

Mössbauer spectra of samples from (a) the most iridium rich KTB layer in Petriccio, P0 (b) P128 and (c) P149 layers are shown in Figure 4. The spectra for P0 are reproduced from Wdowiak et al. (2001) with permission. All three samples in Figure 4 give the spectra corresponding to the same iron phases, a six-line pattern corresponding to nanosize hematite, and two doublets, the major one corresponding to Fe$^{3+}$, most likely phyllosilicate, and the minor one corresponding to Fe$^{2+}$. In all the three, the ferric doublet is the strongest and the hematite is well split. Table 2 gives the Mössbauer parameters fitted to the spectra. We have included the parameters of KTB spectrum from Bottaccione section in the table. Bottaccione is also a well studied KTB section in the same Gubbio formation as the Petriccio and the Mössbauer spectra of the two are almost identical (Verma et al., 2002b). From Table 2 we see that all the three limonitic layers not only have the same iron phases, the relative areas corresponding to different components are also the same within experimental uncertainties.
Figure 4. Mössbauer spectra of (a) P0 (reproduced from Wdowiak et al. (2001) with permission) (b) P128 and (c) P149 samples.

Table 2. Mössbauer parameter of B0, P128 and P149 Layer

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (K)</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>B hf (T)</th>
<th>Area (%)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottaccione (KTB)</td>
<td>RT*</td>
<td>0.34</td>
<td>0.60</td>
<td></td>
<td>53</td>
<td>Ferric doublet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.13</td>
<td>2.78</td>
<td></td>
<td>6</td>
<td>Ferrous doublet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.37</td>
<td>-0.22</td>
<td>49.9</td>
<td>41</td>
<td>Hematite</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>0.38</td>
<td>0.55</td>
<td></td>
<td>45</td>
<td>Ferric doublet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.18</td>
<td>2.86</td>
<td></td>
<td>6</td>
<td>Ferrous doublet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.48</td>
<td>-0.08</td>
<td>52.1</td>
<td>49</td>
<td>Hematite</td>
</tr>
<tr>
<td>P128</td>
<td>RT</td>
<td>0.30</td>
<td>0.65</td>
<td></td>
<td>61</td>
<td>Ferric doublet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.28</td>
<td>2.26</td>
<td></td>
<td>11</td>
<td>Ferrous doublet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.37</td>
<td>-0.08</td>
<td>49.5</td>
<td>28</td>
<td>Hematite</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>0.36</td>
<td>0.63</td>
<td></td>
<td>42</td>
<td>Ferric doublet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.48</td>
<td>2.43</td>
<td></td>
<td>9</td>
<td>Ferrous doublet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.43</td>
<td>-0.10</td>
<td>51.0</td>
<td>49</td>
<td>Hematite</td>
</tr>
<tr>
<td>P149</td>
<td>RT</td>
<td>0.29</td>
<td>0.64</td>
<td></td>
<td>64</td>
<td>Ferric doublet</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>2.25</td>
<td></td>
<td>12</td>
<td>Ferrous doublet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.40</td>
<td>-0.10</td>
<td>49.5</td>
<td>24</td>
<td>Hematite</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>0.36</td>
<td>0.66</td>
<td></td>
<td>42</td>
<td>Ferric doublet</td>
</tr>
<tr>
<td></td>
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<td>-0.09</td>
<td>51.0</td>
<td>49</td>
<td>Hematite</td>
</tr>
</tbody>
</table>

* Verma et al.2002a, Meteoritics and Planetary Science 37, 901-909
At room temperature the hematite shows $B_{hf}$ somewhat smaller than the known values of 52.0 T in all the three cases. This is supposed to be due to small size of hematite particles (Verma et al., 2002b). As the temperature is decreased, the value of $B_{hf}$ and also the relative absorption area of the hematite component increase to some extent. This may be due to difference in the change of the recoil-free fraction of the phyllosilicate and hematite component as the temperature is changed. The important point is that all the three samples show very similar temperature dependence in the Mössbauer parameters, too.

The appearance of the same iron phases in P128 and P149 as in the KTB layer prompts us to think that these two limonitic layers are genetically related to the KTB layer P0. This is also supported by the enhanced concentration of the siderophile elements like Cr, Ni, Co, Ba, Na, Fe, etc., whose values are close to what we observe at KTB, i.e., in P0 sample. But then there is no iridium. If we assume that the P128 and P149 layers have originated from the KTB layer P0 due to some geological activity, the question arise what separated iridium from the sediment so selectively. As the Mössbauer parameters of the iron phases are characteristic of the extinction sites, most likely originating from impacts, and there is no explicit evidence of any hiatus, the another possibility is an impact other than that at KTB occurring prior to it. If so, these impacts were able to create the same geochemical climatic conditions as the KTB impact. This would also mean that the so called KTB mass extinction started much earlier, several hundred thousand years ago. Indeed there are palentological evidences for extinction taking place over a long time.

3. Conclusion

In this review an effort has been made to summarize the contribution of Mössbauer spectroscopy to identify impact related events on the basis of nanophase iron mineralogy. The same type of iron bearing minerals were formed in the impact related event in the air and then these deposited in the form of sedimentary rock such that they contain similar iron phases like nanophase hematite and nanophase goethite. Mössbauer spectroscopy has potential to give meaningful information about impact related events in the geological time frame.

References


**Biographical notes**

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