X-ray Diffraction and Trace Element Analyses of K/Pg Boundary Samples Collected from Agost and Caravaca, Spain

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Abstract: The boundary between Cretaceous and Paleogene (K/Pg) plays an important role in deciphering the Earth’s history and biological evolution from Mesozoic to Cenozoic. As such, the delineation and characterization of the boundary layer has attracted significant attention. In this study, X-ray diffraction (XRD) and elemental analyses were conducted to characterize the samples of boundary layer and the layers around Agost and Caravaca, Spain. The XRD results showed that the layers immediately above and below the boundary layer are made of limestone, while in the boundary layer, a significant increase in the clay minerals smectite, kaolinite, and illite was observed. The major element analyses revealed an increase in Si and Al contents, confirming the presence of clay minerals. The trace element analyses showed elevated concentrations of V, Cr, Ni, Zn, Pb, and Th, but not for Rb, Cu, and U. The rare Earth element (REE) analyses showed elevated La, Ce, and Nd concentrations in the boundary layer. Correlation analyses between selected trace elements and REE showed good agreements, with \( R^2 \) values of about 0.9. The results agreed well with the finding in the area, except the lower contents of Rb, Cu, and U; thus, they may promote further studies to make detailed comparisons.

Keywords: clay minerals; trace elements; K/Pg boundary; impact layer; anomaly

1. Introduction

An impact about 66 million years ago near Chicxulub, Yucatan Peninsula, Mexico, resulted in catastrophic mass extinction at the Cretaceous–Paleogene (K/Pg) boundary.

As such, the rock formations at the outcrops may provide a detailed record of environments during this critical geological time [1]. The locations of the boundary layer are distributed all over the world, including as north as Denmark, as south as New Zealand, as well as India and Japan. However, most of the sites were located near the Gulf of Mexico where the Chicxulub impact was located. Just in North America, about 20 localities were found in the Western Interior, the Gulf and Atlantic Coastal Plains of the US, and the eastern Mexican Coastal Plain [2].

The K/Pg boundary at different locations around world showed remarkable consistency in terms of catastrophic events. A drastic decrease in CaCO\(_3\) and \( \delta^{13}\)C, a measure of the ratio of the two stable isotopes of carbon \(^{13}\)C and \(^{12}\)C in samples against standards reported in parts per thousand (‰), and increases in clay contents, elements Ir and Ni, and total organic carbon (TOC) were reported [3]. The clay layer is characterized by higher iridium (Ir) and other platinum group element (PGE) contents and the presence of spherules [4]. Relatively high concentrations of Co and Zn in the boundary layer at Stevns Klint, Denmark, were reported [5,6]. In El Kef, northwestern Tunisia, the K/Pg boundary is characterized by a classic Ir-rich layer [7]. In Wasserfallgraben, Germany, the geochemical proxy analyses
showed a sharp positive Ir peak (2.3 ppb) at the K/Pg boundary [8]. As the boundary layer had significantly high clay contents and TOC values in comparison to the layers above and below the boundary [9–11], the study of the clay minerals in the boundary layer also attracted great attention. Although most of the clay minerals in the boundary layer were identified as smectite [8,12], corrensite (regularly interstratified chlorite/smectite) was the dominant clay mineral in the K/Pg Tanjero and Kolosh formations around Sulaimani City, Iraq [13]. In a recent study, clay minerals showed positive correlation of the adsorption of fullerenes and iridium in the K/Pg Anjar intertrappean beds, Kachchh district, Gujarat, India [8].

However, questions still remain about the nature and timing of the depositional processes that affected the region at the time of impact and mass extinction [1]. In addition, there are discrepancies for the types of elements that are above normal levels at the boundary layer. For example, the K/Pg fully marine stratigraphic section in the El Kef region, Tunisia, showed elevated concentrations in Cu, Pb, Zn, Zr, Cr, and U in the non-fossil zone [14]. On the other hand, at the Loma Cerca and El Peñon sites near the Gulf of Mexico, the Zn and Zr concentrations were nearly constant, as were the concentration variations in Cr, Ni, and V [15].

To obtain better answers to these questions, more data are needed, such as the mineral components, major, minor, trace, and rare Earth elements (REE), on or near the boundary layer, as they play a critical role in delineating the boundary layer. As such, a broad study was intended to conduct further analyses for the samples collected in different geographic locations around the boundary layer. In this specific study, samples were collected in two locations in South Spain, and mineral and chemical analyses were performed on these samples. It was anticipated that the results would add more information to the database to offer a more comprehensive explanation of the cause of the anomaly in mineralogy and geochemistry in the K/Pg boundary layer. Furthermore, could new anomalies in trace elements and REE be identified? If so, correlations between the elevated elements could be assessed and used in future studies.

2. Location and Stratigraphy

The Agost section is located in Alicante province, Southeastern Spain, and the sample locations are about 2 km north of the village of Agost (Figure 1). Below the boundary is the upper Cretaceous Maastrichtian formation, with sediments made of gray pelagic, massive marls, interbedded with marly limestones, and above the boundary layer is the Danian formation of Paleocene, which is made of about a 10 cm thick layer of clays followed by marly limestones, with a decimeter-thick intercalated layer of marls [9].

The Caravaca section is located near the town Caravaca de la Cruz, and the sample site is 2 km southwest of Caravaca (Figure 1). The sample site is located on the NW side of road C-336. Similar to the stratigraphic section of Agost, the lithology is made of light marls in the upper part of the Maastrichtian formation, followed by 7–10 cm of a lower Danian (lowermost Paleogene) blackish-gray clay layer, with a 2–3 mm thick reddish brown layer at the base (the boundary layer) [10]. The carbonate content gradually increased in the lower Danian layer [9]. Both sections are among the best-preserved sections in the world for the study of K/Pg boundary and catastrophic effects [10], which is why these sites were selected first for the study. Their brief boundary stratigraphy is illustrated in Figure 1.

As the boundary layer is marked with a black color that contains high amounts of clay minerals and TOC, samples were collected on and below the black clay layers. They were named AG-1, AG-2, AG-3, and AG-4 for samples from Agost, and CA-5, CA-6, CA-7, and CA-8 for samples from Caravaca, Spain. The exact locations of the sample sites are indicated in Figure 1.
Figure 1. Sample locations in Spain. Samples AG-1, AG-2, AG-3, and AG-4 are collected about 2 km north of Agost (right), while samples CA-5, CA-6, CA-7, and CA-8 collected 2 km southwest of Caravaca (left). Samples AG-1 and AG-2 were below the dark layer and AG-3 and AG-4 were collected in the dark layer. Samples CA-5 to CA-7 were collected below the dark layer, while CA-8 was collected in the dark layer.

3. Methods of Analyses

The purpose of X-ray diffraction analyses was intended to identify all possible minerals in the layers and to compare their relative contents. Thus, only the raw samples were analyzed after being ground. No clay separation nor purification was made. The instrument used was a Panalytical X’Pert PRO diffractometer with CuKα radiation at 40 kV and 30 mA. Scans were made from 3 to 65° 2θ at a speed of 2°/min. Samples were ground to less than 200 mesh (<0.064 μm) for XRD analyses, and randomly non-oriented samples were made for the analyses. For the powder samples, the major elements were analyzed via X-ray fluorescence (XRF) multi-element chemical composition analyzer Axios FAST (Panalytical Ltd., Malvern, UK) following the method GB/T14506.28-2010. The minor, trace, and rare Earth elements (REEs) were analyzed using inductively coupled plasma mass spectrometry X Series 2 (ICP-MS, ThermoFisher, Waltham, MA, USA) using the method GB/T 14506.30-2010 [16]. These are standard national standards in China, thus upholding precision and accuracy.

4. Results

4.1. XRD Analyses

Representative XRD patterns for samples collected below and at the boundary layer are plotted in Figure 2. The XRD patterns of the remaining samples can be seen in Figure S1 in the Supplementary Materials. The mineral composition below the boundary layer showed almost 100% calcite (Figure 2a). Previous results showed that the layer is marly limestone, indicating the presence of clay minerals in the limestone [11]. However, no XRD work was performed in that study. Although the XRD results from this study were not intended for the quantitative analyses of mineral contents, the XRD patterns for samples collected below the boundary layer showed essentially no clay minerals (Figure 2a).

In this study, the boundary layer is made of calcite, with a significant enrichment of clay minerals, including montmorillonite, illite, and kaolinite, although minute amounts of quartz and dolomite peaks were also observed (Figure 2b). This is so-called marly limestone in many studies [11,17]. Previous results showed that the mineralogy of the...
samples collected from the Agost boundary layer consisted mainly of calcite, phyllosilicates, and quartz, with their proportions varying between 67% and 77% for calcite, 20% and 28% for phyllosilicates, and less than 5% for quartz, while a sharp (49%) decrease in carbonate content and a 37% increase in phyllosilicates were noticed in the layer of the K/Pg boundary [18]. In another study among the extracted clay fractions from the Agost and Caravaca samples, illite contents were about 10% in the boundary layer, in comparison to 30% above and below the boundary layer. Additionally, in the clay fraction of the boundary layer, smectite and kaolinite make 80% and 10%, while they were 30–40% in the layers above and below the boundary layer [9]. A sharp decrease in carbonate content and a subsequent increase in the proportion of clays were also reported for the K/Pg boundary layer at Agost [19]. Overall, the results from this study agreed well with previous discoveries.

Figure 2. XRD patterns of sample AG-1 (a) and AG-4 (b). The XRD patterns of AG-2, CA-5, CA-6, and CA-7 are almost identical to the XRD pattern of AG-1, and the XRD patterns of CA-8 and AG-3 are almost identical to the XRD pattern of AG-4. Please note that for Figure 2a, sample is under the boundary layer, while for Figure 2b sample is right on the boundary layer. The letters C, I, K, Q, and S represent calcite, illite, kaolinite, quartz, and smectite.

In the K/Pg in the El Kef region, Tunisia, the fine-grained fractions are indicative of airborne components within the late Cretaceous through Paleogene sedimentary series, and the illite-smectite mixed-layers were considered as the first-order marker minerals resulting
from the alteration of a volcanic ash precursor of basic to intermediate composition [14]. For the K/Pg boundary layer in Stevns, Denmark, illite–smectite (I-S) was made of two phases, a high-smectitic phase (70%) having 95% smectite and 5% illite (leucophyllite) layers, and a low-smectitic phase (30%) having 50% smectite and 50% illite layers [12]. The smectite in the impact layer had a volcanic origin, enriched with Cr, Mn, Co, Ir, and Ni, while the kaolinite considered as being from a secondary origin in a Jordon K/Pg impact layer [20]. Again, the XRD results from this study agreed well with the phyllosilicate components and percentages, confirming that samples AG-3, AG-4, and CA-8 are the impact layer samples.

4.2. Major Elements

The contents of major elements are listed in Table 1. It can be seen that samples AG-1, AG-2, CA-5, CA-6, and CA-7 were dominated by calcite, the MgO contents were low, and the SiO$_2$ contents were in single or low-teen values. For the boundary layer samples AG-3, AG-4, and CA-8, significant amounts of SiO$_2$ suggested the presence of quartz and higher amounts of Al and K in these samples, an indication of the presence of clay minerals. These values confirmed the XRD results in Figure 2. Further, significant amounts of Fe were present in these samples, indicating that these are samples right at the boundary layer. The slightly elevated Mg contents confirmed the presence of minute amounts of dolomite in the boundary layer. The loss-on-ignition (LOI) values were high. A similar LOI value (ranging from 3–46%) was found for samples collected from four locations along the Mexico–Belize border where Chicxulub impact ejecta were exposed [21].

Table 1. Major elements of the samples in oxide format.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>AG-1</th>
<th>AG-2</th>
<th>AG-3</th>
<th>AG-4</th>
<th>CA-5</th>
<th>CA-6</th>
<th>CA-7</th>
<th>CA-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>7.55</td>
<td>8.93</td>
<td>39.43</td>
<td>37.75</td>
<td>13.01</td>
<td>6.55</td>
<td>13.49</td>
<td>30.44</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2.08</td>
<td>2.00</td>
<td>15.10</td>
<td>14.11</td>
<td>3.56</td>
<td>1.13</td>
<td>4.49</td>
<td>11.78</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.11</td>
<td>0.12</td>
<td>0.71</td>
<td>0.65</td>
<td>0.20</td>
<td>0.08</td>
<td>0.22</td>
<td>0.49</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.64</td>
<td>0.46</td>
<td>4.62</td>
<td>4.28</td>
<td>1.18</td>
<td>0.47</td>
<td>1.93</td>
<td>3.89</td>
</tr>
<tr>
<td>FeO</td>
<td>0.32</td>
<td>0.41</td>
<td>0.35</td>
<td>0.35</td>
<td>0.38</td>
<td>0.20</td>
<td>0.32</td>
<td>0.29</td>
</tr>
<tr>
<td>CaO</td>
<td>48.91</td>
<td>46.76</td>
<td>15.55</td>
<td>17.42</td>
<td>43.64</td>
<td>50.08</td>
<td>42.14</td>
<td>23.84</td>
</tr>
<tr>
<td>MgO</td>
<td>0.49</td>
<td>0.60</td>
<td>2.32</td>
<td>2.39</td>
<td>0.79</td>
<td>0.81</td>
<td>0.89</td>
<td>1.84</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.36</td>
<td>0.41</td>
<td>1.77</td>
<td>1.77</td>
<td>0.68</td>
<td>0.19</td>
<td>0.60</td>
<td>1.23</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.15</td>
<td>0.13</td>
<td>0.21</td>
<td>0.20</td>
<td>0.18</td>
<td>0.15</td>
<td>0.17</td>
<td>0.20</td>
</tr>
<tr>
<td>MnO</td>
<td>0.093</td>
<td>0.059</td>
<td>0.034</td>
<td>0.033</td>
<td>0.074</td>
<td>0.076</td>
<td>0.071</td>
<td>0.054</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.11</td>
<td>0.065</td>
<td>0.17</td>
<td>0.19</td>
<td>0.082</td>
<td>0.17</td>
<td>0.11</td>
<td>0.24</td>
</tr>
<tr>
<td>LOI</td>
<td>39.08</td>
<td>39.96</td>
<td>19.55</td>
<td>20.68</td>
<td>36.12</td>
<td>40.00</td>
<td>35.29</td>
<td>25.58</td>
</tr>
</tbody>
</table>

4.3. Trace and REE Elements

The contents of trace and REE elements of the samples are plotted in Figure 3. As can be seen, the following elements showed elevated concentrations right at the impact layer: La, Ce, Nd, Pb, Th, Li, V, Cr, Ni, Zn, and Zr. For the purpose of comparison, the upper Maastrichtian and lower Danian sediments in the Ocean Drilling Program (ODP) Hole 738C showed enrichment of Fe, Sc, Cr, Ni, Zn, Co, As, and Sb [22]. Additionally, these results mostly agreed with a previous study for samples collected in Caravaca, Spain, where the Ni, Co, Cr, Zn, Cu, and Sb concentrations increased relative to the underlying Maastrichtian layer [23].

The K-T boundary at Caravaca is made of a very thin layer of ochre clays that contain up to 70 ppb Ir [8]. Unfortunately, due to the experimental conditions, Ir could not be analyzed in this study. In a previous study, in the boundary layer of the marl bed of the Barranco del Gredero section, Caravaca, Spain, the REE depletion was observed and was attributed to the low REE concentration in common meteorites [24]. In this study, the concentrations of La, Ce, and Nb were higher in the impact layer in comparison to the formations below it (Figure 3).
The K-T boundary at Caravaca is made of a very thin layer of ochre clays that contain up to 70 ppb Ir. Unfortunately, due to the experimental conditions, Ir could not be analyzed in this study. In a previous study, in the boundary layer of the marl bed of the Barranco del Gredero section, Caravaca, Spain, the REE depletion was observed and was attributed to the low REE concentration in common meteorites [24]. In this study, the concentrations of La, Ce, and Nb were higher in the impact layer in comparison to the formations below it (Figure 3).

Figure 3. Element analyses by ICP-MS for the samples collected from Agost and Caravaca, Spain.

High authigenic uranium concentrations and positive Eu anomalies indicate very strong reducing conditions in Agost [25]. However, the presence of Fe and the red color of the boundary layer suggested less likelihood of reducing conditions. Further, it was noticed in a study that Cu/Al and Ti/Al ratios increased at the boundary layer in Agost [26]. In this study, Eu, U, and Cu anomalies were not observed or not significant at all (Figure 3). No abnormal Cu was found for the impact layer in Jordan [20]. In addition, no Cu anomaly was found for the impact layers near the Mexico–Belize border [21]. Thus, the results from this study present a new challenge regarding whether Cu should be an indicative element or not for the boundary layer.

Previous results showed that the Chicxulub impact resulted in a worldwide deposition of impact materials at distal sites, such as Agost and Caravaca in Spain; a major contribution of extraterrestrial material was indicated by platinum group elements and other siderophile elements that are typical of extraterrestrial components [27].

Great anomalies in Ni, Co, and Zn were found in the Fish clay collected from Stevns Klint, Denmark, and were predominantly present in the smectite [28]. Later, an elevated Pb concentration was also noticed in the samples, and the high concentration of Zn and Pb was suspected to be derived from the humics [29]. In this study, the Zn, Pb, and Ni concentrations were elevated for the boundary layer but not for Co. Again, further sample analyses may be needed to either negate or support the Co anomaly.

The correlation between selected elements and REEs was determined. As there are a total of 40 minor and trace elements and REEs, it is impossible to plot them all. Figure 4
shows correlation between Li and selected elements, Zn, Ce, La, Nb, and Th; between V and Zn, Ce, La, Nb, and Th; between Cr and Zn, Ce, La, Nb, and Th; and between La and Zn, Ce, Zr, Nb, and Th. They all had good correlation. These results suggest that the co-presence of these elements is critical in determining the boundary layer.

Figure 4. Correlation of selected elements of high anomaly for the samples collected from Agost and Caravaca, Spain.

5. Discussion

Previous research suggested that the geochemical composition of the boundary layer at Agost and Caravaca supported the impact scenario at the end of the Cretaceous, as the typical extra-terrestrial elements, such as Ir, Ni, Co, Cr, and Fe, were enriched in the boundary sediments [25]. On the other hand, trace-element concentrations may have been severely modified and, therefore, may not reflect the original extraterrestrial contamination accurately [25]. Additionally, the Os, Cr, and W concentrations in K-Pg boundary sediments may result from a mixing of local sediments and extraterrestrial matter [11]. In Agost, the ratios of Zn/Al, Cu/Al, Cr/Al, Ni/Al, Rb/Al, and U/Al at the ejection layer were all shown to be abnormal [30]. However, in this study, the ratios were mostly lower, as at the boundary layer, the clay contents were much higher. Thus, the denominator Al value is 7–8-times higher than the layers below it (Table 1), while the Zn, Cr, and Ni concentrations were only 2–3-times higher (Figure 3). Moreover, V, U, Ni, Cu, and Cr anomalies were found in the Caravaca impact layer [10]. In this study, the anomaly was high for V, Cr, Ni, Zn, Pb, and Th but not for Rb, Cu, and U (Figure 3). Most importantly, the anomaly of Ce and Nd in the impact layer was first noticed in this study in both locations (Figure 3). These findings warrant further studies on the elemental analyses to be organized by a team of experts from different regions of the world for an integrated study, including evaluating REE results of the same samples analyzed by different labs.

As for the minerals that are on the boundary layer or above and below the boundary layer, this finding from this study is in agreement with previous studies in general. In a recent study, the increase in clay minerals was attributed to highly variable source terrains and a lack of sediment mixing during transport during the impact period, but their XRD patterns revealed Illite > Illite/Smectite > kaolinite > Chlorite > Montmorillonite assemblages in the Langpar formation, Meghalaya, India [31]. On the other hand, the smectite and illite and the percentage ratio of phyllosilicate clay minerals to quartz in clay fractions from the latest Cretaceous through the earliest Paleogene in the Songliao Basin are generally higher during warming intervals than during cooling intervals, attributing the different clay minerals to different climatic conditions [32]. In another study, the distribution
of kaolinite and smectite in marine sediments of Tunisia on the K/Pg boundary layer may be partly related to the distance from the shoreline, as well as to sea level changes [33]. Most importantly, in a comprehensive report, different origins of clay minerals at the boundary layer were elaborated [34]. However, in combination with the anomaly of trace elements and REEs in this study, it is speculated that, for the association with the catastrophic impact event and the distribution of the clay deposits around the world, the likelihood of the clay minerals is, indeed, from the deposits of the dusts created by the events, while the different types and percentages of clay minerals on different locations of the boundary layer may reflect the location climatic and depositional environment.

6. Conclusions

The XRD results showed that the dominant mineral is calcite, with increased clay minerals smectite and kaolinite in the impact layer, while the elemental analyses showed anomalies in Ni, Zn, Cr, V, Zr, Pb, Th, Nb, Ce, and La. Overall, the anomaly is about 150–200% of the values in comparison to the samples collected below the boundary later. The anomaly could be as high as 7-fold for Cr and V. These data supported previous observations published extensively in the literature. In addition, these data provided new insights into the close correlations between the anomaly elements, as determined by simple linear correlation analyses. Considering the close association between the elevated trace elements and REE concentrations and the enrichment of clay minerals in the boundary layer, both should be closely associated with the catastrophic event. Most importantly, as the topic on K/Pg is extremely important in geology, biology, as well as astronomy, and a large dataset can provide better analyses more comprehensively and thoroughly, the results from this study would add more practical data, information, and analyses to the overall topic of catastrophic events at K/Pg to enhance future research and discussion, which is the main purpose of this study.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst13040670/s1, Figure S1: X-ray diffraction patterns of samples collected in Agost and Caravaca, Spain.

Author Contributions: Conceptualization, Z.L. and H.H. (Hongping He); methodology, H.H. (Hanlie Hong); formal analysis, H.H. (Hanlie Hong); investigation, Z.L. and L.L.; resources, Z.L. and H.H. (Hanlie Hong); data curation, H.H. (Hanlie Hong) and Z.L.; writing—original draft preparation, Z.L.; writing—review and editing, H.H. (Hongping He), H.H. (Hongping He) and L.L.; visualization, Z.L.; supervision, Z.L., H.H. (Hanlie Hong), L.L. and H.H. (Hongping He); project administration, Z.L.; funding acquisition, Z.L. All authors have read and agreed to the published version of the manuscript.

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