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Compositional studies on organic matter from iridium enriched Anjar intertrappean sediments: Deccan volcanism and palaeoenvironmental implications during the Cretaceous / Tertiary boundary

Composición de la materia orgánica de sedimentos intertrapeanos ricos en iridio de Anjar: Volcanismo en el Deccan e implicaciones paleoambientales durante el límite Cretático / Terciario

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Abstract

Various fractions of the soluble organic compounds were isolated from iridium rich sediments using combination of extraction techniques and different proportions of benzene, chloroform and methanol with petroleum ether. Analysis of these compounds showed the presence of α, β - unsaturated ester (C=C-COO-) and aliphatic long chain alkyl groups (-C-C-C-C-) in the iridium enriched Cretaceous-Tertiary (K-T) boundary sediments. The two proton peaks of δ 7.20 and 7.26 ppm of the ^{1}H NMR spectra, indicate that the molecule may be of glyceride with aliphatic long chain alkyl groups. Similarly, peaks in the region of δ 3.90-4.32 ppm show the presence of a double bond (-C=C-) structure attached to an ester group. Peaks found in the region of 7.5-7.7 ppm showed the presence of aromatic hydrocarbons. The peaks at δ 128 and 130 ppm in the ^{13}C NMR spectrum also support the presence of a double bond (-C=C-) structure attached to an ester group. Two peaks at δ 68 and 70 ppm are assigned to two alkyl groups attached to an ester group (-CH_2-CH_2-OOC-). The spectrum of clay-intercalated geopolymer of the Ir enriched layer is comparable to lignin having chemical shifts of aromatic C (160 to 110 ppm), O alkyl C (100 to 60 ppm) and (45 to 0 ppm) alkyl C structures. The solid-state ^{13}C NMR spectrum of lignin reveals a pattern comparable to those obtained in other studies of angiosperm woods. These simple predominantly long chain aliphatic organic compounds are derivatives of complex organic molecules, formed by sudden increase in temperature, but at low-pressure conditions. It is possible that hydrothermal fluids associated with Deccan volcanism supplied heat at the time of these transformations. These observations draw support from the presence of sepiolite-palygorskite-smectite complexes in the Anjar volcano-sedimentary sequences, indicating high basicity under arid conditions induced and influenced by the Deccan volcanism.

Keywords: Deccan Traps, volcanism, Iridium, K-T boundary, Anjar, Organic compounds.

Resumen

Se han aislado varias fracciones de compuestos orgánicos solubles a partir de sedimentos ricos en iridio. Se ha usado una combinación de técnicas de extracción con diferentes proporciones de benceno, cloroformo y metanol con éter de petróleo. Los análisis muestran la presencia de α, β - ésteres insaturados (C=C-COO-) y grupos alifáticos alquilo de larga cadena (-C-C-C-C-) en los sedimentos del límite Cretácico/Terciario (K/T) ricos en iridio. Los dos picos protónicos a δ 7,20 y 7,23 ppm del espectro ^{1}H NMR, indican que las moléculas pueden ser glicéridos con grupos alifáticos alquilo de larga cadena. Igualmente, los picos en la región de δ 3,90-4,32 ppm muestran la presencia de un doble enlace (-C=C-) asociado a un grupo éster. Los picos encontrados en la región de

7,5-7,7 ppm mostraron la presencia de hidrocarburos aromáticos. El pico a δ 128 y 130 ppm del espectro ^{13}C NMR también apoya la presencia del doble enlace antes mencionado. Se han asignado dos picos, a δ 68 y 70 ppm, a dos grupos alquílicos asociados a un grupo éster (-CH_2-CH_2-OOC-). El espectro de geopolímeros ocluidos en las arcillas, del lecho rico en iridio, es comparable a la lignina con desplazamientos químicos de C aromático (160 a 110 ppm), O alquílico C (100 a 60 ppm) y C alquílico (45 a 0 ppm). El espectro ^{13}C NMR en estado sólido de la lignina revela un modelo comparable a los obtenidos en los estudios de la madera de angiospermas. Estos compuestos orgánicos alifáticos de larga cadena derivaron de moléculas orgánicas complejas y se formaron por un incremento brusco de la temperatura, pero en condiciones de baja presión. Es posible que los flúidos hidrotermales asociados al volcanismo del Deccan fueran el foco de calor contemporáneo de esas transformaciones. Estas observaciones vienen avaladas por la presencia de sepiolita-palygorskita-esmectita en la secuencia volcanosedimentaria de Anjar, que indica una alta basicidad en condiciones áridas inducidas e influenciadas por el volcanismo del Deccan.

Palabras clave: Deccan Traps, volcanismo, Iridio, límite K-T, Anjar, compuestos orgánicos

1. Introduction

The absolute age and duration of Deccan volcanism and its genetic link with the Cretaceous-Tertiary (K-T) boundary events still remain inconclusive. Of late a rapid eruption model at the K-T boundary was proposed for Deccan volcanism on a combined consideration of available palaeomagnetic, geochronological and palaeontological data (Duncan and Pyle, 1988; Courtillot *et al*., 1988; Courtillot, 1990; Vandamme *et al*., 1991). The volcanism of high magnitude at the K-T boundary contested the extra-terrestrial impact theory (Alvarez *et al.*, 1980; Alvarez and Asaro, 1990), and indicated a cause intrinsic to this planet (Officer and Drake, 1985) for the cataclysmic K-T boundary events. The study of dinosaur fossil-bearing Maastrichtian sediments, intimately associated with the Deccan Traps, assumes significance in the interpretation of the initiation, intensity and duration of volcanism, as it would help in unveiling many issues shrouded in the K-T transition, such as, mass extinction, volcanism and the asteroid impact.

There has been intensive search in recent years, for any possible iridium rich layer within the Deccan volcano-sedimentary sequence (Rochia *et al.*, 1988). One such study by Bhandari *et al.* (1995) indicated presence of three levels of chocolate brown coloured clay layers, less than 1 cm thick and separated from each other by 25 – 30 cm, heavily enriched with Ir, Os and other siderophiles together with chalcophiles (Se, Sb, Ag, As and Zn) and depleted in lithophiles (Sc, Hf and Al) within the intertrappean bed of Anjar, in the western periphery of the Deccan volcanic province (Fig.1). These layers are unique in their anomalous exotic Ir and Os concentrations. The ^{40}Ar-^{39}Ar dates (63-67 Ma) of Venkatesan *et al.* (1993) indicated that the peak Deccan volcanic activity pre-dates the K-T boundary by about 2 Ma. But, Feraud and Courtillot (1994) disagree with this observation. Venkatesan e*t al.* (1996) have determined ^{40}Ar-^{39}Ar ages for seven basalt flows (Fig. 1). Three of them, Flow I (68.7 ± 0.8Ma), Flow II (66.6±0.6Ma) and Flow III (65.3±0.6Ma) yield good plateau ages. Flows IV, V and VI do not yield good age plateaus but give integrated ages of 65.1 ±1.5, 65.9±1.6 and 65.0±1.2 million years which are consistent with their isochron ages. Flow VII gives an age of 61±1.6 Ma. Hofmann *et al.*'s (1997) results also gave similar ages. Ignoring the age data for Flows I and VII then the remaining five flows were rapidly laid down between 65 Ma and 67 Ma, an interval of only two million years or less. A finer time resolution is not possible because of uncertainties due to errors (Shukla *et al.,* 1997). The deposition of Ir-rich layers above the dinosaurian fossil-bearing second and third intertrappean beds, suggests that dinosaurs survived the first phase of volcanism and still existed just before the deposition of these layers. Biota from the infra and inter-trappean beds of the eastern and southern parts of the Deccan volcanic province indicate that the dinosaurs survived the initial phases of volcanic activity (Prasad and Khajuria, 1995). Therefore, the extinction of dinosaurs can not be solely due to the initiation of Deccan volcanism. Micropalaeontological studies (Bajpai and Prasad, 2000) revealed abundance of theropod eggshell fragments in the beds overlying the Ir enriched layers but, absence of Palaeocene taxa in the levels above the Ir-rich layers, indicating that the extinction of dinosaurs occurred in the Indian sub-continent after the deposition of Ir layers in the Anjar area (Fig. 2). Sutherland (1994, 1996) reviewed the causal factors – asteroidal and cometary impact, volcanism only and coincidental impact and volcanism – responsible for the phenomenal spikes in Ir and Os concentrations and mass extinction at the K-T boundary. Although, the Ir anomalies can readily be explained through extraterrestrial chemical and mineralogical criteria, yet some explosive volcanism might result in significant Ir anomalies (Schmiz and Asaro, 1996). The enrichment of chalcophiles at the K-T boundary has been attributed to the effects of weathering of surface sediments (Schmitz, 1992), volcanism or has been considered to be the result

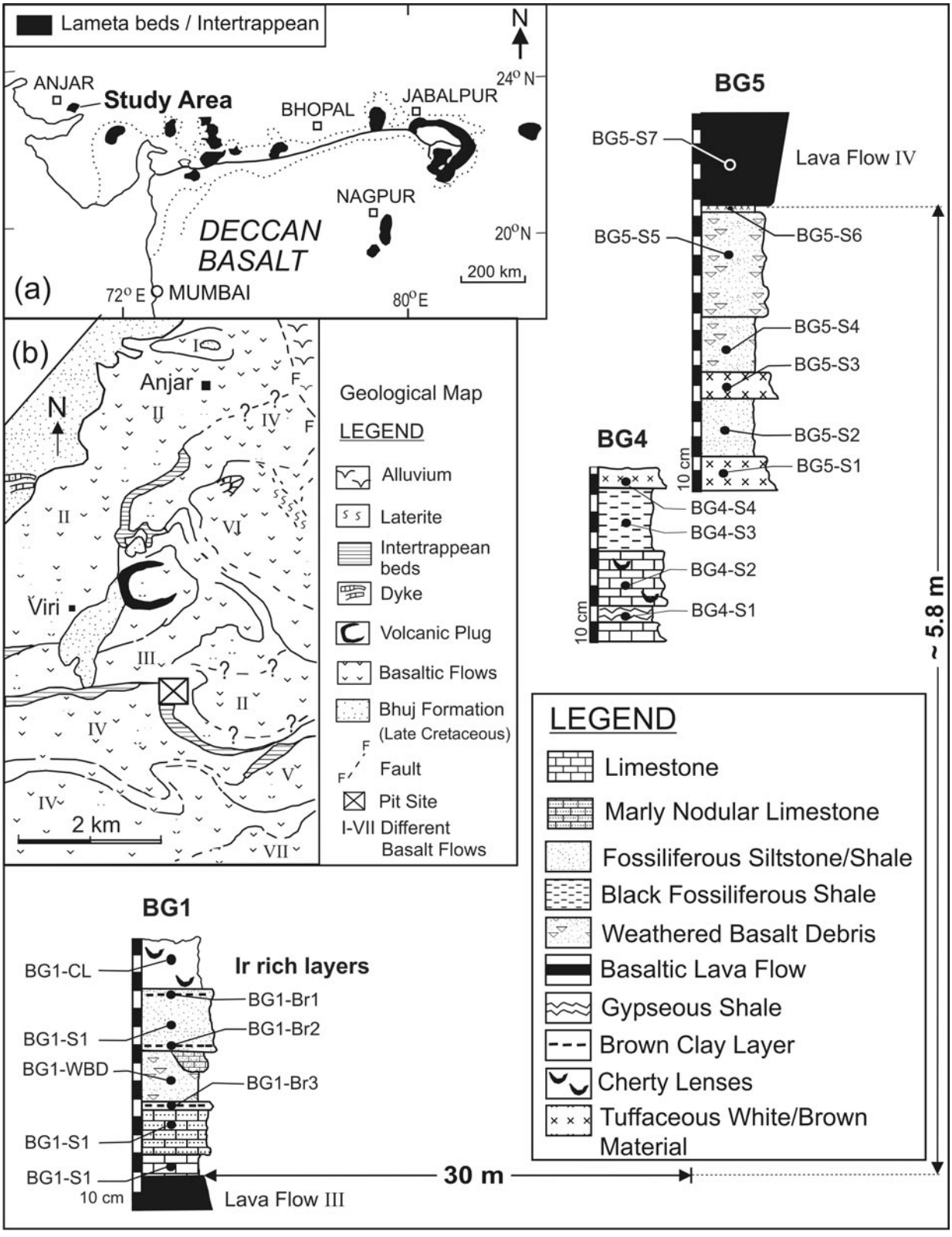

Fig. 1.- Lithostratigraphic logs (modified after Shukla *et al*., 1997) and sample location of the Iridium bearing intertrappean bed (~5.8m thick) in three pits BG1, BG4 and BG5 at the Anjar KTB section. Insets: a) location of the study area and other infra-/inter- trappean beds, b) geology of the area and the pit site.

Fig. 1.- Columna litoestratigráfica (modificada de Shukla *et al*., 1997) y situación de las muestras del lecho intertrappeano con iridio (~5,8m de potencia) en tres pozos BG1, BG4 y BG5 en la sección del límite K/T en Anjar. Recuadros insertados: a) localización del área de estudio y de las capas infra- e intratrappeanas, b) geología del área y situación de los pozos.

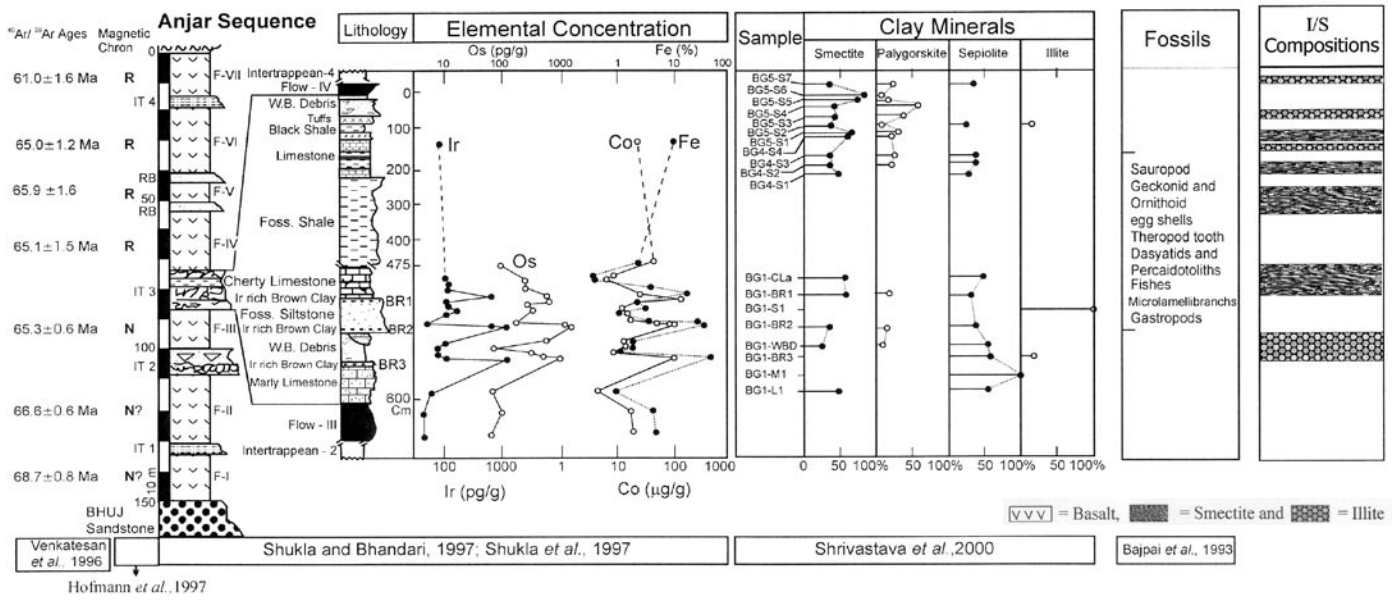

Fig. 2.- Synoptic view of sequential changes in clay mineral assemblages and concentration of important elements within the intertrappean KTB at Anjar (N=Normal, R=Reversed, RB=Red bole, IT 1=Intertrappean 1, F-I=Flow I).

Fig. 2.- Vista sinóptica de los cambios secuenciales en los conjuntos de minerales de la arcilla y concentraciones de elementos principales en el límite K/T intertrappeano en Anjar (N=Normal, R=Inverso, RB=Lecho intercalado rojo, IT 1=Intertrappeano 1, F-I=Colada I).

of acid rains produced following the impact (Bhandari e*t al.*, 1994). In the case of the Anjar intertrappean, the pertinent question arises as to whether the Ir enrichment occurred due to an extraterrestrial impact or from the fall out of the Deccan volcanism.

The intertrappean succession at Anjar (Fig. 2) shows considerable facies variations both laterally and vertically, encompasses the K-T boundary layer (Bhandari e*t al.*, 1994) and consists of interlayered peloidal cherty limestones and shales. The biotic extinction does not correspond to the Ir-rich layers at Anjar (Bajpai and Prasad, 2000) therefore the proposed connection of these layers with the K-T boundary remains suspect unless their chemostratigraphic implications are well understood. The clay mineral attributes of the K-T Boundary section at Anjar (Shrivastava e*t al.,* 2000) show dominance of smectite, sepiolite, palygorskite and subordinate amounts of montmorillonite, illite and calcite (Fig. 2). The BR2 layer characterized by spikes in Ir and Os concentrations contains sepiolite and subordinate amounts of palygorskite and smectite. Presence of these common clay minerals of volcanogenic derivation under local sedimentation conditions supports the volcanic theory of K-T boundary events (Fig. 2) and does not provide any evidence of asteroidal impact during the K-T transition.

Association of Ir anomalies with the basal coal layer at the K-T boundary site of Raton in Colorado (Tschudy *et al.,* 1984), soot layers at widely separated geographical boundary sites (Wolbach *et al.,* 1985, 1988, 1990a and 1990b and Heymann *et. al.,* 1998) and spikes in polycyclic aromatic hydrocarbons at the K-T boundary at Caravaca, Spain (Arinobu e*t al.,* 1999), provide evidence of global fires during the K-T transistion. Venkatesan and Dahl (1989) reported pyrosynthetic polycyclic aromatic hydrocarbons mainly of nonalkylated species, from the K-T boundary clays at Woodside Creek (New Zealand), Gubbio (Italy), and Stevns Klint (Denmark). The biostratigraphically well defined K-T boundary at Arroyo el Mimbral, Tamaulipas, Mexico is marked by the presence of fluoranthene, pyrene, chrysene, benzoanthracene, and several penta-aromatic compounds (Kruge *et al.,* (1994). In the present work, compositional studies on organic matter of the Ir enriched clay layer were undertaken to investigate the nature and type of organic macromolecules plausibly associated with sepiolite-palygorskite-smectite complexes, their derivation from the original source organic material would unveil palaeoenvironmental constraints about the origin and restricted enrichment of iridium in the Anjar intertrappean.

2. Materials and Methods

Excavation at three site pits (BG1, BG4 and BG5 shown in Fig. 1b) revealed 5.8 m of intertrappean sediments, stratigraphically above the third lava flow (Fig. 2). Samples (approximately 1kg weight) were collected from these three pits. The sample location sites are shown over the lithologs (Fig. 1b). Organic matter was isolated from

finely powdered (-200 mesh size) sediments by Soxhlet extraction, solvent extraction and elution extraction, using combinations of different proportions of benzene, chloroform and methanol with petroleum ether (Table 1). The solvent was concentrated to 25 ml on a rotary evaporator under reduced pressure. The concentrate was made into slurry with silica gel and it was purified by silica gel column chromatography (60-120 mesh, 2.5 x 45 cm). The column was eluted with benzene (0-100%) and petroleum ether (0-100%) and similar fractions (after thin liquid chromatographic analysis, chloroform 100%, $R_f = 0.5$) were combined and the solvent was evaporated to dryness to give a semi solid compound (Fraction I). Further elution of the column with chloroform (0-100%) and methanol (0-100%) gave fractions II and III with R_f values of 0.41 and 0. 29, respectively.

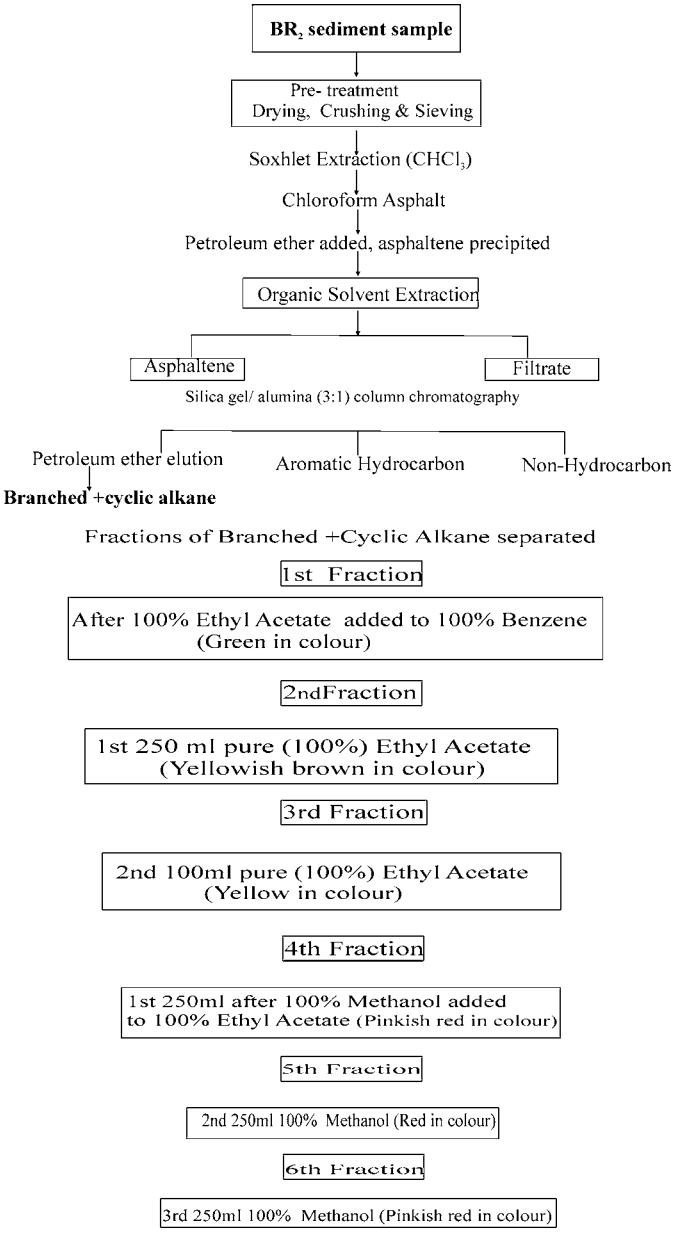

Table 1.- Sequence of steps followed for the isolation of organic matter from sediments by Soxhlet extraction, solvent extraction and elution extraction techniques.

Tabla 1.- Pasos seguidos en el aislamiento de la materia orgánica de los sedimentos mediante técnicas de extracción en continuo por un Soxhlet, por disolvente y por elución.

The purity of these compounds after column chromatography was examined by high pressure liquid chromatography (Waters, Model 991 photodiode array μ-Bondapak C_{18} reverse phase column, 3.9 x 300 mm) using 100% methanol as the elutent at a flow rate of 1 ml/ min, monitored at 235 nm and found to be 99.5% pure. The characterization of these compounds was made using infra-red (IR) and nuclear magnetic resonance (NMR) spectroscopic techniques. Electronic spectra were recorded on Shimadzu UV 260 spectrophotometer. IR spectra were recorded on Perkin-Elmer 1710 FTIR spectrophotometer (ν_{max} in cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on Bruker 300 MHz spectrophotometer. Electron induced mass spectra (EIMS) were recorded on Jeol SX 102/DA-6000 (6 kv, 10 mA) spectrophotometer.

3. Results and Discussion

Six separated fractions were analysed using high pressure liquid chromatography (HPLC), infra red (IR) spectroscopic, ^{13}C neutron magnetic resonance, ^1H neutron magnetic resonance, and gas chromatography – mass spectroscopic techniques. The HPLC spectrum showed high purity of the compounds (Fig. 3). The peak at 1729 cm^{-1} in the IR spectrum (Fig. 4) of faction I indicated the presence of α, β - unsaturated ester (C=C-COO-) and aliphatic long chain alkyl groups (-C-C-C-C-). The appearance of various peaks in the region of δ 14 - 35 ppm in the ^{13}C NMR spectrum (Fig. 5) of fraction I shows presence of aliphatic long chain alkyl groups (-C-C-C-C-). The ^1H NMR spectrum (Fig. 6) of fraction I contains two proton peaks of δ 7.20 and 7.26 ppm, which indicate that the molecule may be an unsaturated, or glyceride, with aliphatic long chain alkyl groups (Ludemann and Nimz, 1974; Wilson, 1987; Knicker, 1993). Similarly the presence of various peaks in region δ 3.90-4.32 ppm show presence of double bond (-C=C-) attached to an ester group. However, an ambiguity of the presence of aromatic protons was eliminated as the IR spectrum shows an absence of peaks in the region of 750-850 cm^{-1} (Fig. 4). The presence of double bond in the molecule is also supported by the ^{13}C NMR spectrum, which has two peaks at δ 128 and 130 ppm (Fig. 5). Further fraction I shows positive bromine test for unsaturation. The two peaks at δ 68 and 70 ppm in the ^{13}C NMR spectrum

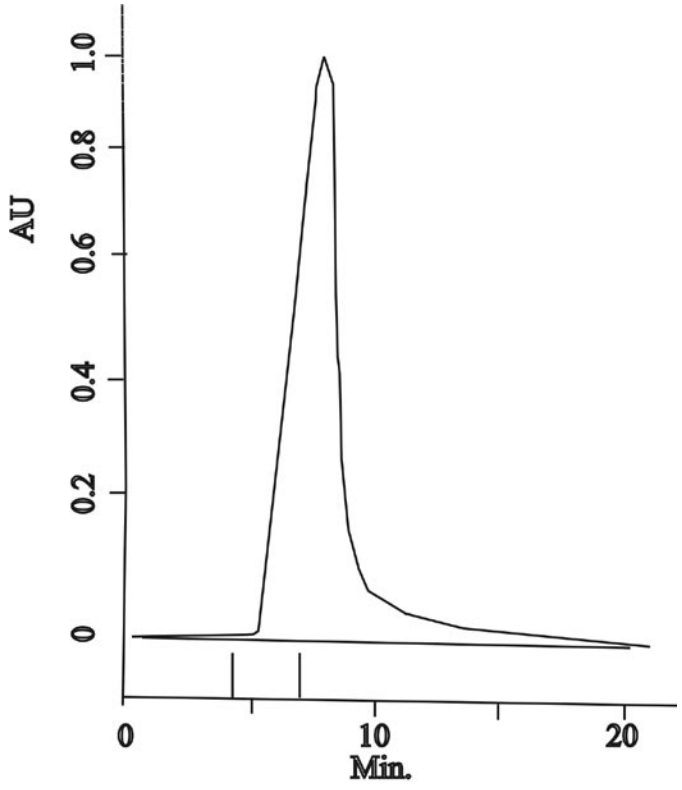

Fig. 3.- High pressure liquid chromatography (HPLC) spectrum showing purity of organic compounds of fraction-I.

Fig. 3.- Espectro de cromatografía líquida de alta presión (HPLC) mostrando la pureza de los compuestos orgánicos de la fracción-I.

(Fig. 5) may be attributed to alkyl groups attached to ester groups (-CH_2-CH_2-OOC-). Similar characterization work for the other fractions (II, III, IV, V and VI) has not been undertaken. These observations are distinctive from the earlier reported high resolution profiles of Arinobu *et al.* (1999) that show spikes of the pyrosynthetic polycyclic aromatic hydrocarbons (coronene, benzo-perylene and benzo-pyrene) and sudden decrease in δ^{13} C values of *n*-C_{29} alkane. In Anjar, simple long chain aliphatic organic macromolecules were found associated with yellowish-brown iridium rich sediments. The presence of considerable amounts of pericondensed pyrosynthetic polycyclic aromatic hydrocarbons just above the K-T boundary at Caravaca, Spain is indicative of massive global fires, as evidenced by the soot (polymer of polybenzenoid radicals). Highly pericondensed pyrosynthetic polycyclic aromatic hydrocarbons are the products of early termination of polymerization (Venkatesan and Dhal, 1989). The absence of aromatic hydrocarbons in the Anjar intertrappean sediments rules out the possibility of global fires or wild fires. Stratigraphic variation studies of Arinobu *et al.* (1999) across the K-T boundary at Caravaca, Spain show an abrupt decrease in δ^{13} C values of *n*-C_{29} alkane that coincides with the increase in the polycyclic aromatic hydrocarbons. The iridium enriched Anjar sediments show α, β - unsaturated ester and aliphatic long chain alkyl groups. The high value of carbon preference index for some of the Caravaca K-T boundary samples prompted Arinobu *et al.* (1999) to speculate that the input of unburned higher plant material can account for the long-chain *n*-alkanes. At Anjar it is also possible that the unburned higher plants served as a main source of biomass.

Recent studies of Kahle *et al.* (2004) demonstrated retention of dissolved organic matter by phyllosilicates and clay fractions, and identified their sorption sites in the reactive hydroxyl groups as well as siloxane surfaces of the phyllosilicate clay minerals. In the present study also the spectrum of clay-intercalated geopolymers of the Ir enriched layers at Anjar is comparable to lignin having chemical shifts of aromatic C (160 to 110 ppm), O alkyl C (100 to 60 ppm) and (45 to 0 ppm) alkyl C (Michael *et al.,* 1997). The solid-state ^{13}C NMR spectrum of lignin reveals a pattern comparable to those obtained in other studies of angiosperm woods (Bartuska *et al.,* 1980; Hatfield *et al.,* 1987). It is possible that the aliphatic organic compounds present in the clay interlayers had most likely been transported there by pulveric acid or other humic materials within which they were captured and that acted as vehicles for the transport of hydrophobic compounds within the sediments. Hence, these terrestrially derived sediments containing organic matter were transported by streams / rivers and deposited in the shallow water basins or marshy land and provided the main flux for these simple, long chain, aliphatic, organic compounds which are associated with yellowish-brown iridium-rich sediments. These are derivatives of complex organic molecules, formed due to a sudden increase in temperature but at low-pressures. Possibly the hydrothermal fluids associated with the Deccan volcanism acted as a catalyst at the time of these transformations.

4. Palaeo-environmental Implications during K-T boundary

Simple long chain organic compounds are formed by a sudden increase in the temperature, but at low-pressure conditions. The plants and organisms deposited under shallow, lacustrine and peri-marine environmental conditions at the time of Deccan volcanism (Shrivastava *et al.,* 2000) during the K-T boundary transition have possibly undergone such changes. Hydrothermal fluids associated with Deccan volcanism served as a main source of heat at the time of these transformations. These observations draw support from the presence of sepiolite-palygorskite-smectite complexes (Fig. 2) present in the Anjar

volcano-sedimentary sequences, indicating high basicity under arid conditions induced and influenced by Deccan volcanism (Shrivastava *et al.,* 2000). The clay minerals of the Anjar intertrappean sequence show dominance of smectite, sepiolite, and palygorskite with subordinate amount of montmorillonite, illite and calcite. The K-T boundry layer (BR2) is characterised by spikes in Ir and Os concentrations. It contains sepiolite and subordinate amounts of palygorskite and smectite considered to be the carrier phase of the Ir (Shrivastava *et al.,* 2000). The sequence at Anjar contains common clay minerals of volcanic derivation that are explained by local sedimentation conditions and support the volcanic theory on K-T boundary events. The boundary clay layer is not homogeneous, differs in mineralogy in different sections studied at the Cretaceous-Tertiary transition and does not contain minerals derived from the asteroid. The bulk of trace metals (Co, Ni, Cr and Ir) are in the clay fractions of the K-T boundary smectitic marls (Elliot, 1993). The basal part of the boundary clay exhibits no signature that indicates a mixture of meteoritic and terrestrial ejecta.

The origin of the Ir-rich K-T boundary layer and associated mass extinction events is a topic of considerable controversy and recent papers have reviewed the intricacies of the different hypotheses (Sutherland, 1994, 1996; Rampino, 1995; Shukla and Bhandari, 1997). Available data on K-T boundary layers do not conclusively decide that the mass extinction resulted, only by bolide impact (McLaren and Goodfellow, 1990; Rampino and Haggerty, 1994) or only by volcanism (Courtillot *et al.,* 1986; McLean, 1985), but suggest that a multiple-causal theory (Raup, 1995) appears to be more relevant. Mantle material rich in Ir can emanate during volcanic episodes resulting in an Ir-rich layer at the K-T boundary (Courtillot *et al.,* 1986). Combined with the Deccan, Coral Sea and Cameroon eruptions at least 22 significant southern hotspots were contributing to mantle-derived K-T activity (Sutherland, 1994). The Ir anomalies in airborne particles emanating from Hawaiian (Olmez *et al.,* 1986) and Kam Chatka (Felitzyn and Vaganov, 1988)

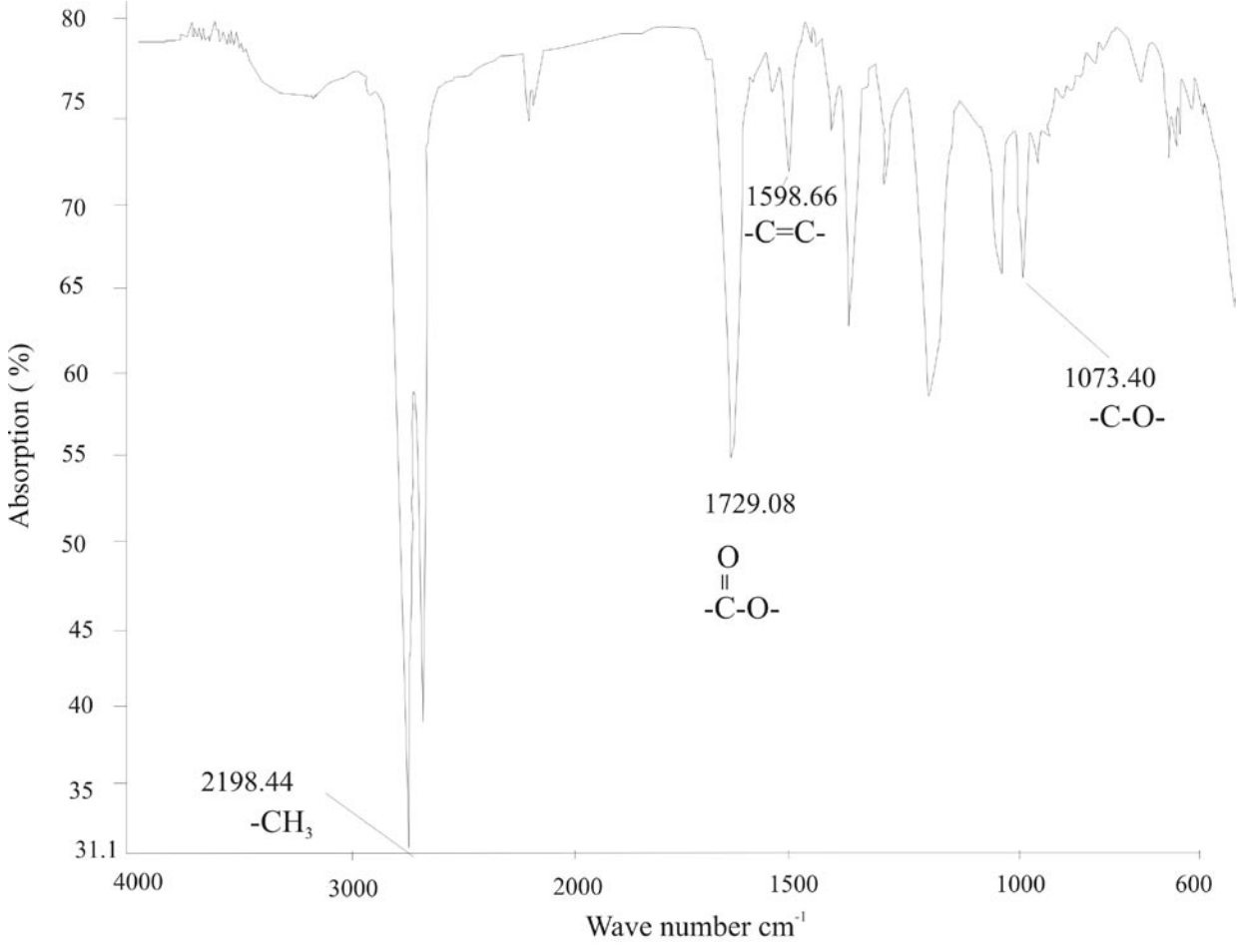

Fig. 4.- IR spectrum of fraction - I showing presence of $-CH_3$, O=-C-O- and -C-O- functional groups.
Fig. 4.- Espectro IR de la fracción - I mostrando la presencia de grupos funcionales $-CH_3$, O=-C-O- y -C-O-.

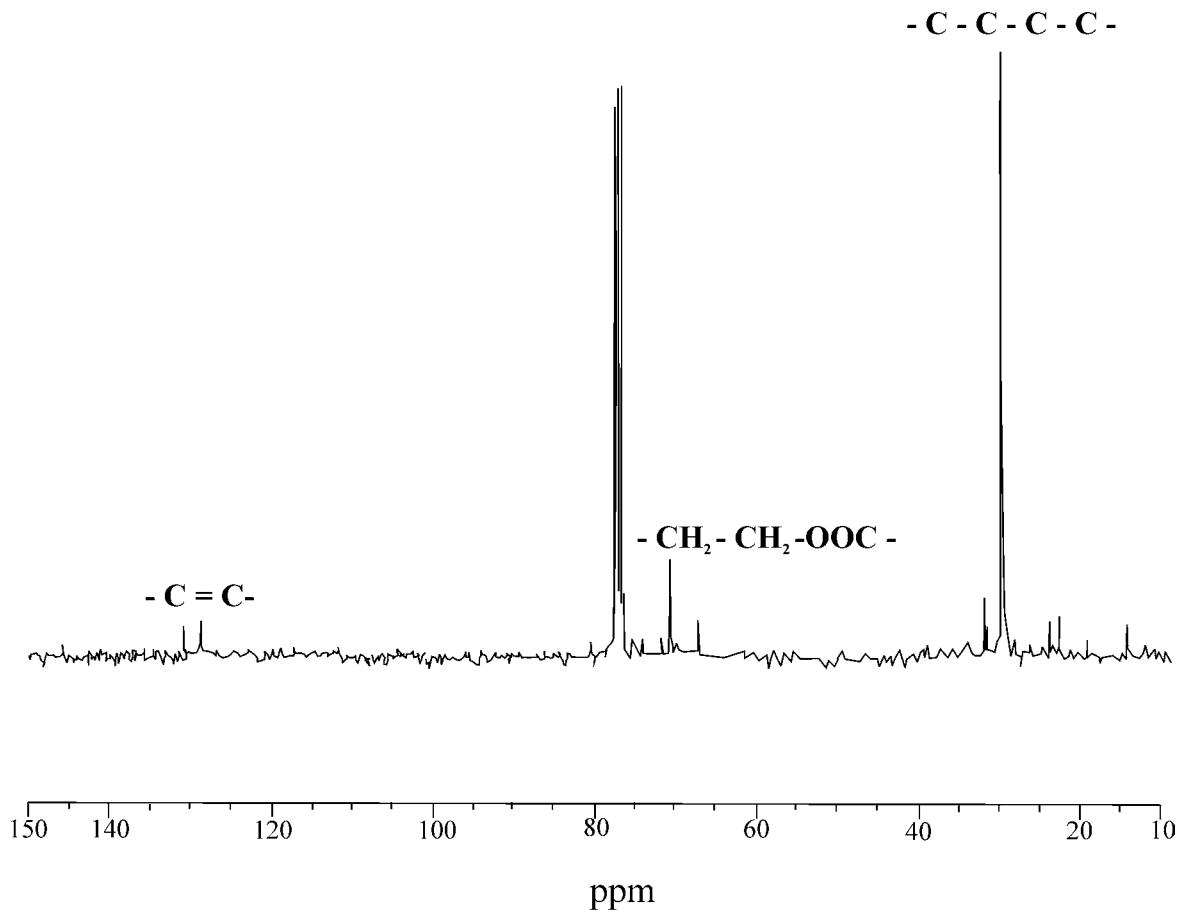

Fig. 5.- ^{13}C NMR spectrum of fraction - I showing presence of -C-C-C-C-, -CH_2-CH_2-OOC- and -C=C- functional groups.
Fig. 5.- Espectro ^{13}C NMR de la fracción - I mostrando la presencia de grupos funcionales -C-C-C-C-, -CH_2-CH_2-OOC- y -C=C-.

volcanoes preserved within the southern ice sheet being contributed by volcanism along Ross Sea (Koeberl, 1989), is evidence to support the volcanic theory. Iridium and other trace metals are enriched in some andesitic volcanic ashes, possibly in the heavy minerals (Goldsmidt, 1954). The eruptives from MgO-rich (~16%) parental picritic magma (Krishnamurthy and Cox, 1977) would yield higher platinum group element (PGE) concentrations than typical Deccan basalts and their Cr/Ni ratios are closer to those in the Spanish Caravaca K-T layer than to chondritic ratios (Vannucci *et al.,* 1990; Sutherland, 1994). However, the present exposures of picrites in the Deccan province are limited and their PGE contributions seem quite insufficient to approach the magnitude of the K-T Ir anolmaly (Sutherland, 1994).

Several intertrappean samples from the Deccan Traps, other than from Anjar (Bhandari *et al.,* 1993a and 1993b) showed low Ir levels (8 - 120 pg / g), compared to the concentrations at various K-T boundary horizons (5 - 187 ng / g in marine K-T sequences) of the world. The intertrappean samples do not show enhanced levels of Se, As and Sb as observed in Hawaiian volcanic particulates. If Deccan volcanism was contributing Ir and other elements similar to Hawaiian volcanic emissions, then these elements ought to be enriched in many intertrappean sediments. This does not support the volcanic source hypothesis.

The Chicxulub crater and Deccan province lie in a first order antipodal relationship, but neither the positions nor the timing appear exact (Sutherland, 1994). It seems very unlikely that the impact would have triggered flood basalt volcanism in the Deccan (White and McKenzie, 1989), but the large volumes of basaltic melt could have been produced by decompression melting of anomalously warm mantle (McKenzie and Bickle, 1988). Moreover, the volcanism might have been induced by lithospheric fracturing at the antipodes of the large impact site (Rampino and Caldeira, 1992). Other than the Chixulub crater, several large impacts occurred on the Earth, more recently and do not coincide with extinctions. The unusual bolide impact that coincided with the K-T boundary plausibly was responsible for the elimination of a fraction of the species however the extinction event was already under way due to Deccan volcanism (Courtillot, 1994).

Recently from the geometry of impact (angle, velocity, palaeogeographic locations) Alvarez (1996) modeled the fall out ejecta debris and concluded that impact ejecta did not reach India, which was located in the "forbidden zone" for 50° elevation angle. The fireball ejecta containing Ir can probably be launched at velocities approaching escape velocity and at an elevation angle lower than 45°, and thus could have reached the area forbidden to ejecta-curtain material (Alvarez, 1996).

5. Conclusions

It is concluded that α, β - unsaturated ester (C=C-COO-) and aliphatic long chain alkyl groups (-C-C-C-C-) are present in the iridium enriched K-T boundary sediments at Anjar. It is observed that glyceride groups are also present in these sediments and associated with aliphatic long chain alkyl groups. The peaks at δ 128 and 130 ppm in the ^{13}C NMR spectrum indicate the presence of a double bond (-C=C-) structure attached to an ester group. The two peaks at δ 68 and 70 ppm in ^{13}C NMR spectrum are attributed to alkyl groups attached to ester groups ($-CH_2-CH_2-OOC-$). The spectrum of clay-intercalated geopolymer of the Ir enriched layer of Anjar is comparable to lignin having chemical shift of aromatic C (160 to 110 ppm), O alkyl C (100 to 60 ppm) and (45 to 0 ppm) alkyl C (Michael *et al.,* 1997). The solid-state ^{13}C NMR spectrum of lignin reveals a pattern comparable to those obtained in other studies of angiosperm woods (Bartuska *et al.,* 1980; Hatfield *et al.,* 1987). The aliphatic organic compounds present in the clay interlayer had most likely been transported there by pulveric acid or other humic materials within which they were captured and that acted as vehicles for the transport of hydrophobic compounds within the sediments. These simple predominantly long chain aliphatic organic compounds, derived from complex organic molecules, formed due to sudden increase in the temperature but at low pressures. Possibly the hydrothermal fluids associated with the Deccan volcanism acted as a catalyst at the time of these transformations. These observations draw support from the presence of sepiolite-polygorskite-smectite complexes in the Anjar volcano-sedimentary sequences, indicating high basicity under arid conditions induced and influenced by Deccan volcanism.

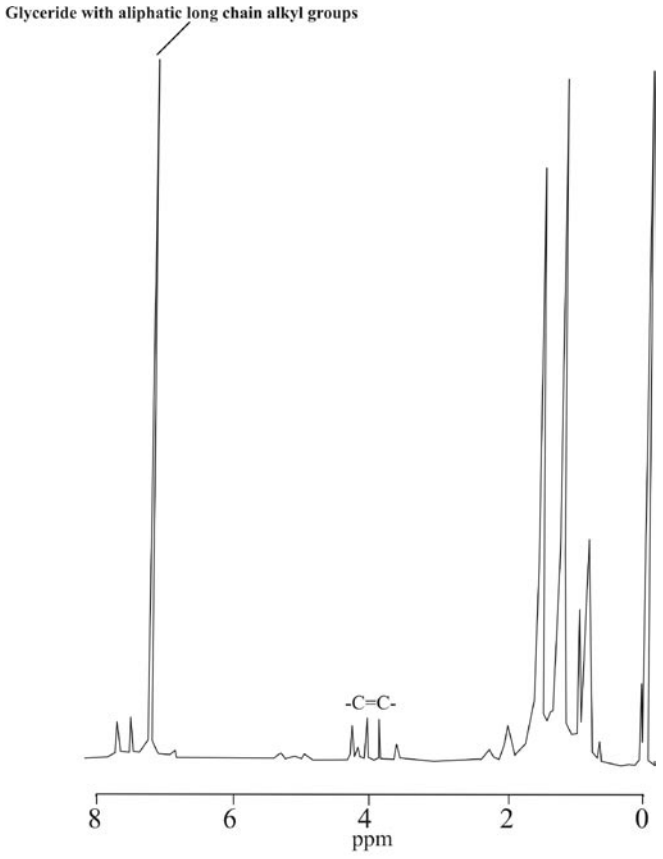

Fig. 6.- ^{1}H NMR spectrum of fraction - I showing presence of glyceride with aliphatic long chain alkyl group and double bond -C=C- group attached to ester group between 3.5-4.5 ppm.

Fig. 6.- Espectro ^{1}H NMR de la fracción - I mostrando la presencia de un glicérido con grupo alifático alquilo de larga cadena y grupo de dobre enlace -C=C- asociado a un grupo éster entre 3,5-4,5 ppm.

The present study on organic matter supports the "volcanic theory" but does not provide evidence to negate the "impact theory". The results from different geochronological studies (Duncan and Pyle, 1988; Venkatesan *et al.,* 1993; Baksi, 1994) on Deccan lavas are incoherent with no interaction of the uncertainties for what must be coeval flows based on field relationships (Courtillot, 1994) and the palaeomagnetism of the exposed sequence in most parts of the Deccan is also not well understood. Furthermore, most of the Deccan flows / sequences are eroded (Watts and Cox, 1989). These are facts which reduce the validity of the volcanic theory of extinction in the Deccan province. In this scenario the impact (s) and volcanism and their precise controls over extinctions need to be evaluated further in the light of detailed data from Anjar and other K-T boundary sections. Moreover, the palaeontological extinction does not correspond to the Iridium rich - layers at Anjar, therefore the proposed connection of these layers with the K-T boundary remains suspect unless their chemostratigraphic implications are well understood.

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