

ORIGIN OF THE Mg-SMECTITE AT THE CRETACEOUS/TERTIARY (K/T) BOUNDARY AT STEVNS KLINT, DENMARK

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Abstract—The clay mineralogy and major element geochemistry of four distinct layers within the Cretaceous/Tertiary (K/T) boundary marl (i.e., II, IIIa, IIIb, and IV) at Stevns Klint, Denmark, including “impact layer” (layer IIIa), were examined, and there was not a marked change in the clay mineralogy throughout this K/T boundary marl. A magnesium smectite (i.e., Mg-smectite) was the predominant clay mineral at the K/T boundary not only at Stevns Klint and at Nye Kløv; it was also found to be the predominant clay mineral in the K/T boundary at Karlstrup Quarry. In addition, Mg-smectite was found in a smectitic marl 32 meters below the K/T boundary at the Limhamn Quarry (near Malmö, Sweden), and it did not have anomalous concentrations of iridium or other siderophile trace elements. Given its occurrence in a Maastrichtian marl, it is therefore argued that the Mg-smectite is not derived from meteorite impact.

The rare earth element (REE) signatures of the Mg-smectites ranged from being comparable to the North American Shale Standard (NASC) to being one-half an order of magnitude depleted relative to NASC. One Mg-smectite collected from layer IIIb, immediately above the “impact/red layer,” was depleted in REE by one order of magnitude relative to NASC, and these levels of REE are comparable to those of smectite and illite/smectite (I/S) formed authigenically in bentonites and K-bentonites, respectively. Thus, the REE data suggest this Mg-smectite in all likelihood was formed authigenically from a glassy precursor. The presence of the low levels of REE of the Mg-smectite in the layer IIIb has no particular significance other than to suggest that this Mg-smectite separate was the least contaminated with illite or apatite having higher REE levels. With better separation, the other Mg-smectites would be expected to have comparably low levels of REE. Given the presence of the Mg-smectite throughout the K/T boundary and in Maastrichtian and Danian marls, the Mg-smectite is thought to be of volcanic origin. However, is not certain whether the Mg-smectite formed from volcanic glass deposited at the K/T boundary or whether it was formed from volcanic glass as young as late Cretaceous.

Key Words—K/Ar dating, K/T boundary, Rare earth elements, Smectite.

INTRODUCTION

Since the original discovery of anomalous amounts of Ir at the Cretaceous/Tertiary boundary (K/T) by Alvarez *et al.* (1980), impact-derived minerals (e.g., shock metamorphosed quartz, tektites, spinels, soot) and the Ir anomaly have been identified at the K/T boundary worldwide, and these data have greatly supported K/T boundary meteorite impact hypothesis (e.g., Alvarez *et al.*, 1982; Bohor *et al.*, 1984, 1987a, 1987b; Smit and Kyte, 1984; Kyte and Smit, 1986; Wolbach *et al.*, 1987; Izett *et al.*, 1990, 1991; Izett, 1991; Kring and Boynton, 1991; Sigurdsson *et al.*, 1991; Smit *et al.*, 1992; Robin *et al.*, 1992a, 1992b). The discoveries of these impact-derived minerals and the Ir anomalies are striking. Yet, impact phases typically comprise a small fraction of a given K/T boundary clay far from the purported K/T boundary impact crater(s) at Chicxulub, Yucatán Peninsula (Penfield and Camargo, 1981; Hildebrand *et al.*, 1981; Pope *et al.*, 1991), and/or at Manson, Iowa (French, 1984; Izett, 1987; Kunk *et al.*, 1989). The provenance of the more abundant, non impact-derived minerals (e.g., clay minerals) seen at the K/T boundary worldwide must be determined to understand the geologic events taken place in addition to meteorite impact during the K/T boundary

transition (Robert and Chamley, 1990). Ultimately, knowledge of these geologic events, including meteorite impact, is necessary to test hypotheses for the cause of the mass extinction at the K/T boundary (Hallam, 1987).

One of the highest K/T boundary Ir anomalies was found at Stevns Klint, Denmark (Ganapathy, 1980; Schmitz, 1988). Consequently, this K/T boundary marl, informally called the Fish Clay (Christensen *et al.*, 1973), was thought to contain a high fraction of “extraterrestrial components” (Kyte *et al.*, 1980). The clay mineralogy of the K/T boundary there has been studied in detail at least three times to determine its origin(s). Rampino and Reynolds (1983) suggest the smectite, the predominant clay mineral, was volcanic in origin because it had virtually no interlayers of illite in it. Kastner *et al.* (1984) later argued that the smectite was formed from meteorite impact glass, citing that its major element chemistry is similar to microtektite-like spheres seen in the Fish Clay (Varekamp and Thomas, 1982) and that the enriched $^{18}\text{O}/^{16}\text{O}$ ratio indicated that these smectites formed from these microtektite-like spheres in a low water/rock regime. In addition, they found the smectite had an unusually high MgO content (~7 wt. %) possibly attesting to an input of

chondritic debris from meteorite impact. Elliott *et al.* (1989) argued that this magnesium smectite (i.e., Mg-smectite) was not derived from impact glass because the Mg-smectite was identified in a marl without anomalous levels of iridium ~8 meters above the K/T boundary at the Limhamn Quarry in southwest Sweden. Thus, it is likely that Ir and Mg-smectite are of different origins. Moreover, Schmitz (1988) noted the major element compositions of the insoluble residues of the Fish Clay were similar to the major elemental compositions of the insoluble residues in the adjacent chalks. However, Elliott *et al.* (1989) did not analyze the clay mineralogy of the "impact layer" in the Fish Clay as defined by B. F. Bohor and G. A. Izett (in Elliott *et al.*, 1989), and the presence of Mg-smectite in Cretaceous rocks is unknown. Of note, Schmitz (1990) found shocked quartz in small amounts throughout the Fish Clay.

In this study, the clay mineralogy and the concentrations of major, trace elements were determined for the four distinct layers of the Fish Clay including the "impact layer." In addition, marls and clayey chalks in Maastrichtian chalks at Limhamn Quarry near Malmö, Sweden were analyzed similarly for the presence of the Mg-smectite. The Mg-smectite is not believed to be derived from impact as it is found throughout the Fish Clay and in a Maastrichtian marl 32 meters below the K/T boundary. In addition, it was also found at the K/T boundary at the Karlstrup Quarry nearby Stevns Klint. Based on the stratigraphic distribution of the Mg-smectites in the late Cretaceous and in the early Tertiary, the Mg-smectites are believed to have formed authigenically from a volcanic precursor either as a result of repetitive volcanism before, during, and after the K/T boundary or the Mg-smectites are formed from volcanic glass no younger than late Cretaceous.

SAMPLES AND METHODS

The lithology of the K/T boundary marl at Stevns Klint has been described by Christensen *et al.* (1973). The authors noted four distinct layers within the K/T boundary marl, layers II–V. Of note, layer III, a black marl with pyrite concretions with a red-rust basal layer, was subdivided by Schmitz (1985) into a red-rust basal clay layer and the black marl layer. The basal red layer is referred herein as layer IIIa, and it is the "impact layer" noted by B. F. Bohor and G. A. Izett. Layer IIIb is a black marl containing minor amounts of pyrite. Bulk samples of layers II, IIIa, IIIb, and IV were collected from outcrop south of Hojerup Church. Layer V was not analyzed in this study. A bulk sample of the K/T boundary marl was collected from Karlstrup Quarry northwest of Stevns Klint (Gravesen, 1983).

Drill core of Maastrichtian and Danian chalks from the Limhamn Quarry were examined for marls that might contain Mg-smectite. The biostratigraphy of these

core were described by Malmgren (1982). Typically, both Maastrichtian and Danian chalks contained thin (1" thick) seams of chalk with clay laminae (i.e., clayey chalk). One marl was found at 30.5 meters in core D-103, 32 meters below the K/T boundary. However, the marl at 8 m above the K/T boundary on the north wall of the -60 meter level described by (Elliott *et al.*, 1989) was not seen in core. A Danian clayey chalk was collected from the Karlstrup Quarry approximately 5 m above the K/T boundary. Basaltic tuff and two shales were collected from core 30/2-1 through the Paleocene-Eocene Balder Formation in the North Sea (Malm *et al.*, 1984) for comparison with the K/T boundary in Denmark.

The marls, clayey chalks, shales, and basaltic tuff were treated chemically to remove carbonate minerals using a 1N sodium acetate-acetic acid buffer and ferric oxides using 1N sodium citrate-bicarbonate-dithionate buffer (CBD method) following the procedures outlined in Jackson (1979) at 50°C. Sands (>50 μm) and silts (>20 μm) were separated by screening and timed settling, respectively. The clay minerals were separated using centrifugation. The submicron clay mineral fractions were separated using a continuous flow Sharples centrifuge, and they were obtained to separate smectite from detrital illite in the coarser clay fractions (Elliott *et al.*, 1989). The submicron fractions were dialyzed in distilled water for 3 to 5 days to remove methanol and nitric acid used to flocculate the clays. Then they were dried at 50°C.

The clay minerals were identified using Norelco X-ray diffractometer with Ni-filtered CuK_α radiation and 1° divergence and receiving slits. Air-dried, ethylene glycol-solvated, and heated specimens were scanned at 1° 2 θ per minute. The percent expandable layers in illite/smectite (I/S) were determined by measuring the difference in the 2 θ positions of the (001)_{10Å}/(002)_{17Å} and (002)_{10Å}/(003)_{17Å} peaks is described by Moore and Reynolds (1989).

Major elements were determined on the <0.1 μm fractions and on USGS SCo-1 standard by Prof. Stanley A. Mertzman at Franklin and Marshall College using X-ray fluorescence. Four-tenths gram (0.4000) of unknown and 3.6000 grams of $\text{Li}_2\text{B}_4\text{O}_7$ were fused to a homogeneous disk in a 95% Pt-5% Au crucible and pan. Several drops of LiI were added to reduce the viscosity of the melt. USGS standard SCo-1 was prepared and analyzed as an unknown, and results were compared to accepted values in Govindaraju (1989). Trace and rare earth elements were analyzed by instrumental neutron activation (INA) by Activation Laboratories Ltd., Toronto, Canada. Interlaboratory standard rocks G-2 and MRG-1 were run as unknowns, and the results were compared to accepted values (Flanagan, 1969; Perrault *et al.*, 1984, as listed in Govindaraju, 1989). Also, the concentrations of REE were measured on whole rocks and illites from the

Table 1. Clay mineralogy and major element compositions of clay mineral fractions of marls, shale, and basaltic tuff.

Sample ID	Size fraction (microns)	Mineralogy*	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ **	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total	
FC (II)	2-20	I/S (25% I), I, Q, F	44.43	0.65	12.47	0.97	0.00	4.59	10.63	0.85	0.75	5.92	19.05	100.31	
	1-2	I/S (20% I), I, Q, F (tr.)													
	<0.1	Smectite													
FC pyrite (IIIa)	2-20	Smectite, J	51.31	0.57	14.07	5.49	0.00	5.68	0.09	2.58	0.18	0.38	19.81	100.16	
	1-2	Smectite													
	<0.1	Smectite													
FC pyrite-black clay (IIIb)	2-20	I/S (15% I), I, Q, J, F	54.15	0.54	14.68	4.43	0.00	5.64	0.10	2.38	0.16	0.51	17.99	100.58	
	1-2	Smectite													
	<0.1	Smectite													
FC (IV)	2-20	I/S (15% I), Q, I, F	50.09	0.72	13.67	3.82	0.00	5.20	3.59	0.36	0.68	0.70	21.18	99.80	
	1-2	Smectite													
	0.25-1.0	Smectite													
D 103 (-30.5 m)	<0.1	Smectite	53.24	0.26	16.36	1.70	0.00	4.38	0.52	1.93	1.21	0.07	19.70	99.37	
	Limhamn Quarry east wall (-60 m) upper marl	1-2													Smectite
		0.1-1													Smectite
lower marl	<0.1	I/S (27% I)	62.02	0.50	14.33	4.27	0.01	2.88	1.04	0.64	2.23	0.20	12.41	100.53	
	Karistrup Quarry (K/T boundary) Danian chalkstone	<0.1													Smectite
		0.25-1													Smectite
Balder Fm. (1955.9 m) shale tuff	<0.1	I/S (60% I), I	55.48	0.72	15.56	1.56	0.00	5.60	0.71	2.24	0.37	0.24	17.92	100.40	
	SCO-1	<0.1													Smectite
		<0.1													I/S (20% I), I Chlor./smectite
SCO-1 (accepted)	<0.1	I/S (20% I), I	62.12	0.62	13.32	5.53	0.06	2.65	2.63	1.02	2.79	0.19	9.34	100.32	
	<0.1	Chlor./smectite													

* I = illite, F = feldspar, Q = quartz, J = jarosite, I/S = mixed layer illite/smectite. Predominant clay minerals listed first.

** Fe as Fe₂O₃.

Table 2. Trace element contents of Mg-smectites from Cretaceous, Danian and K/T boundary marls.

	Ag	As	Au	Co	Cr	Ir	Ni	Sb	Sc	Se	Zn
FC Layer II	<2	<1	20	14	322	10	110	1.5	11	1.1	190
FC Layer IIIa	<2	72	44	86	304	22	880	7.8	12	6.8	820
FC Layer IIIb	<2	78	33	27	415	77	280	6.4	13	14	320
FC Layer IV	<2	25	92	65	320	54	540	3.1	13	7.4	710
Nye Klov (K/T)	<2	<1	5	29	232	1	340	0.6	10	<0.5	330
Karlstrup Quarry (K/T)	<2	<1	9	12	342	3	130	0.7	11	<0.5	140
Non-K/T Boundary											
D103 (–30.5 m), 32 m below K/T	<2	2	3	6.1	145	<1	<50	0.9	6.4	1.2	190
LQ, 8 m above K/T	<2	1	5	9.0	60.3	<1	<50	0.5	2.9	<0.5	92
KQ ~ 5 m above K/T*	<2	<1	9	12	342	3	150	2.0	11	1.2	430
Smectite-Bentonite**	<2	<1	5	5.4	14	<1	<50	0.6	7.2	<0.5	150
Illite-Ordovician K-bentonite**	<2	<1	6	2.4	22	<1	<50	0.2	8.5	<0.5	110

Notes: Concentration in ppb. LQ = Limhamn Quarry. KQ = Karlstrup Quarry.

* An illite/smectite (70% I) was analyzed.

** Smectite and illite from Cretaceous Skull Creek bentonite and from Ordovician K-bentonite described in text.

Devonian Cleveland and Chagrin Shales collected from the Cleveland, Ohio area.

K/Ar ages were measured on smectites from layers II–IV of the Fish Clay. Elliott *et al.* (1989) previously measured the K/Ar age of smectite from layer III, which would correspond to layer IIIb in this study. K was determined by flame photometry using a Li internal standard (Ingamells, 1970). Ar isotopic compositions were measured using an MS-10 mass spectrometer in the static mode on line to the CWRU Argon Extraction line. Since these smectite were low in K₂O, the Ar isotopic ratios were measured without an ³⁸Ar spike. The unspiked analyses were bracketed by spiked analyses.

RESULTS

The mineralogical composition of the clay fractions (<2 μm) of the marls, chalks, basaltic tuff, and shales and the major element chemistry of the smectites are summarized in Table 1. The concentrations of trace elements and the rare earth elements are summarized in Table 2 and 3 respectively. The K/Ar ages of the smectites are summarized in Table 4.

Clay mineralogy

Smectite with trace amounts of illite were found throughout the Fish Clay, including layer IIIa. Illite was seen only in the coarse clay fractions (1–2 μm). Smectite was the predominant clay mineral in the <0.1 μm fractions of layers II, IIIa, and IIIb and in the 0.25–1.0 μm fraction of layer IV (Figure 1). Smectite with trace amounts of illite were seen in the <0.1 μm fraction of the marl 32 meters below the K/T boundary at Limhamn Quarry (Figure 1). A trace amount of a previously unidentified non-phyllsilicate mineral was found in the 2–20 μm fraction in layers IIIa and IIIb of the Fish Clay using X-ray diffraction. It has a d-value of 3.59 Å without any larger rational d-values. It is soluble in Na-EDTA (pH = 9), and thus it is identified

tentatively as jarosite. Presumably, this phase is a weathering product of pyrite. Smectite was also the predominant clay mineral in the K/T boundary marl at Karlstrup Quarry.

The MgO contents of the smectites of the K/T boundary marls at Stevns Klint and from the Karlstrup Quarry ranged from 4.59 wt. % to 5.68 wt. %, and as such they are called Mg-smectites. Mg-smectite was also the predominant clay mineral in marls at the Limhamn Quarry located approximately 8 meters above the K/T boundary (i.e., the upper marl, Elliott *et al.*, 1989), and smectite with a relatively high amount of MgO (4.38 wt. %) was found at 30.5 meters in core D-103, approximately 32 m below the K/T boundary. Two marls of middle or upper Danian age were found on the east wall of the –60 m level of the Limhamn Quarry. Smectite was the predominant mineral of the upper marl, and the MgO content of the smectite was 3.97 wt. %. The lower marl contained I/S and illite. Of note, relatively high amounts of CaO and P₂O₅ were found in the <0.1 μm fraction of layer II of the Fish Clay, which is indicative of the presence of minor amounts of apatite. Schmitz (1988) also noted high CaO and P₂O₅ in an analysis of an insoluble residue of sample S4, which corresponds to the uppermost layer II of the Fish Clay in this study.

Mixed-layer illite/smectite (I/S) containing 60–70 percent expandable (smectite) layers and trace amounts of illite were the predominant clay minerals in Maastichtian clayey chalks collected at 7.84 m in core D-103 and at 131.2 m in core D-105 as well as in a Danian clayey chalk collected at 48.8 m in core D-105 of the Limhamn Quarry. I/S with a high percentage of illitic layers is evident in one Danian clayey chalk from the Karlstrup Quarry approximately 5 m above the K/T boundary.

I/S with a high percentage of smectite layers (60–80%) was the predominant clay mineral of one shale collected at 1955.9 meters from core 30/2-1 through

Table 3. Rare earth element analyses.

Sample	Size fraction or whole rock	Clay mineral	Concentration (ppm)									
			La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Yb	Lu
Fish Clay Layer II	<0.1 μm	smectite	22.8	21.0	19.0	3.9	0.9	3.6	0.6	3.6	0.87	0.13
Fish Clay Pyrite Layer (layer IIIa)	<0.1 μm 0.1–0.25 μm	smectite	10.4	13.0	12.0	2.7	0.64	—	0.3	—	0.75	0.13
Fish Clay Layer IIIb	<0.1 μm	smectite	15.7	18.0	16.0	3.6	0.87	3.6	0.5	3.0	0.97	0.16
Fish Clay Layer IV	<0.1 μm 0.1–0.25 μm	smectite	3.5	4.0	2.0	0.56	<0.05	0.5	0.1	0.7	0.25	0.04
Basalt Tuff (Balder Formation)	<0.1 μm	smectite	55.1	52.0	59.0	11.0	2.61	—	1.8	—	3.27	0.50
Nye Klov	<0.1 μm	smectite	187.0	170.0	186.0	38.0	8.02	—	5.6	—	11.0	1.49
Karlstrup Quarry	<0.1 μm	chlorite	14.1	37.0	16.0	3.5	1.00	3.2	0.8	4.6	2.32	0.41
Chagrin Shale	<0.1 μm (treated)	smectite	16.7	20.0	13.0	2.6	0.58	—	0.4	—	0.43	0.06
Chagrin Shale	<0.1 μm (untreated)	smectite	13.9	18.0	14.0	3.3	0.82	—	0.6	—	1.07	0.16
Chagrin Shale	whole rock	illite	51.3	91.0	32.0	3.8	0.69	—	1.2	—	2.39	0.37
Cleveland Shale (Forest Hill)	whole rock	illite	34.0	72.0	32.0	7.4	1.54	—	1.2	—	1.81	0.24
Cleveland Shale (Dunham Road)	whole rock	illite	45.5	94.0	49.0	10.0	2.06	—	1.4	—	3.60	0.56
Limhamn Quarry 32 m below K/T	<0.1 μm 0.1–1.0 μm	illite	40.3	80.0	38.0	6.8	1.33	—	1.0	—	3.75	0.50
8 m above K/T	<0.1 μm	illite	44.4	85.0	45.0	8.5	1.53	—	1.3	—	3.88	0.64
Mowry Bentonite	<0.1 μm	smectite	18.0	29.0	11.0	1.5	0.35	—	0.2	—	0.68	0.12
Ordovician K/bentonite	<0.1 μm	smectite	51.5	88.0	42.0	71.0	1.64	5.9	0.2	—	1.92	0.32
NASC (Gromet <i>et al.</i> , 1984)	—	smectite	5.5	11.0	5.0	1.0	0.28	0.9	0.1	0.6	0.33	0.04
MRG (ave., N = 4)	—	smectite	2.5	6.0	3.0	0.67	0.20	0.5	0.1	0.6	0.23	0.03
MRG (accepted)	—	illite/smec- tite	3.9	10.0	3.0	0.61	0.14	0.5	0.1	0.6	0.26	0.04
G-2 (ave., N = 2)	—	—	31.1	66.7	27.4	5.59	1.18	—	0.85	—	3.06	0.456
G-2 (accepted)	—	—	9.4	28.0	19.0	4.8	1.42	—	0.6	—	0.88	0.13
	—	—	9.8	26.0	19.2	4.8	1.39	—	0.6	—	0.6	0.12
	—	—	90.0	160.0	53.0	7.2	1.34	—	0.6	—	0.77	0.10
	—	—	112.0	166.0	—	8.3	1.50	—	0.52	—	1.0	0.13

Table 4. K/Ar ages of smectites.

Sample name	Size fraction	K ₂ O (wt. %)	⁴⁰ Ar _{rad} (%)	⁴⁰ Ar/gm (mole - 11/gm)	K-Ar (m.y.)
Limhamn Quarry					
32 m below K/T	<0.1 μm	1.936	64.1	11.020	141.0 ± 2
8 m above K/T	<0.1 μm	0.04 ¹	38.4	4.713*	80.0
Fish Clay (K/T boundary)					
Layer II	<0.1 μm	0.441	22.0	3.896*	60.0
Layer IIIa	0.1-0.25 μm	0.175	10.8	1.521*	59.0
Layer IIIb	<0.1 μm	0.16 ¹	13.1	1.344*	57.0
Layer IV	0.1-0.2 μm	1.394	53.1	17.030	83.0 ± 1

¹ = % K₂O from XRF analyses, Table 1.

* = unspiked determination.

the Paleocene Balder Formation, North Sea. The I/S of the <0.1 μm fractions contained more smectite layers (80-85%) than the coarser clay fractions. Mixed layer chlorite/smectite was the predominant clay mineral in a basaltic tuff adjacent to the shale at 1955.9 meters.

Trace and rare earth elements

As shown in Table 2, the <0.1 μm fractions of three K/T boundary smectites (Fish Clay, Nye Kløv, and Karlstrup Quarry) contained higher concentrations of siderophilic trace elements (Co, Cr, Ir, and Ni) relative to the trace elemental compositions of the smectites from the Maastrichtian and Danian marls collected from the Limhamn Quarry. Moreover, the concentrations of these metals are also higher with respect to smectite and I/S formed authigenically in bentonites. Generally, the trace elements in the smectite of the Fish Clay are lower than the concentrations of these trace elements in the insoluble residues of the corresponding samples analyzed by Schmitz (1988). However, Ir in the smectites of layers II and IV were higher than in the corresponding insoluble residues analyzed by Schmitz (1988).

Of note, the <0.1 μm fraction of the clayey chalk at the Karlstrup Quarry 5 m above the K/T boundary also contains rather high concentrations of iridium and other trace metals (Cr, Ni, and Zn), yet they did not contain shocked quartz or spherules (Birger Schmitz, personal communication, 1992).

The concentrations of the rare earth elements (REE) are summarized in Table 3. The REE concentrations of the Mg-smectites from Stevns Klint (except the smectite from layer IIIb), Nye Kløv and Karlstrup Quarry range from being slightly depleted in REE to near unity relative to the North American Average Shale Composite (NASC; Gromet *et al.*, 1984; Figure 2). Generally, the REE of the smectites are comparable to the whole rock values (less carbonate) measured by Tredoux *et al.* (1989), and this agreement suggests that the bulk of the REE is in the clay mineral dominant <0.1 μm fractions. This is consistent with the previous studies on the distributions of the REE in shales (Taylor

and McClennan, 1988; Condie, 1991). However, the smectite from layer IIIb of the Fish Clay is most depleted in REE relative to NASC (Figure 2), and the smectite from layer IV is the most enriched in REE relative to NASC of the Fish Clay Mg-smectites. In addition, the smectites from the Fish Clay all show Ce depletions, and the layer IIIb smectite shows an Eu depletion. Graup *et al.* (1992) also noted negative Ce anomalies throughout the Fish Clay. As listed in Table 3, the coarser submicron fractions (where measured) contain higher contents of REE compared to the <0.1 μm fractions. The REE contents of the chlorite/smectite from the Balder Formation tuff and an illite from the Devonian Chagrin Shale are also comparable to the contents of REE, with exception of layer IIIb, of the Mg-smectites from the Fish Clay (Figure 2).

The REE signatures of the Mg-smectites from the Limhamn Quarry (8 m above the K/T boundary and 32 m below the K/T boundary), a smectite from a

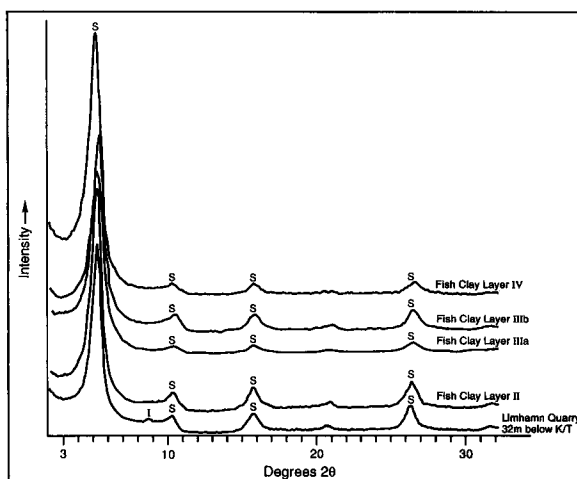


Figure 1. X-ray diffraction of glycol-solvated smectites from the Fish Clay and from the marl 32 m below the K/T boundary from the Limhamn Quarry. Note, the smectite from layer IV is the 0.25-1.0 μm size fraction. Otherwise, the <0.1 μm fractions are shown. S denotes smectite. I denotes illite.

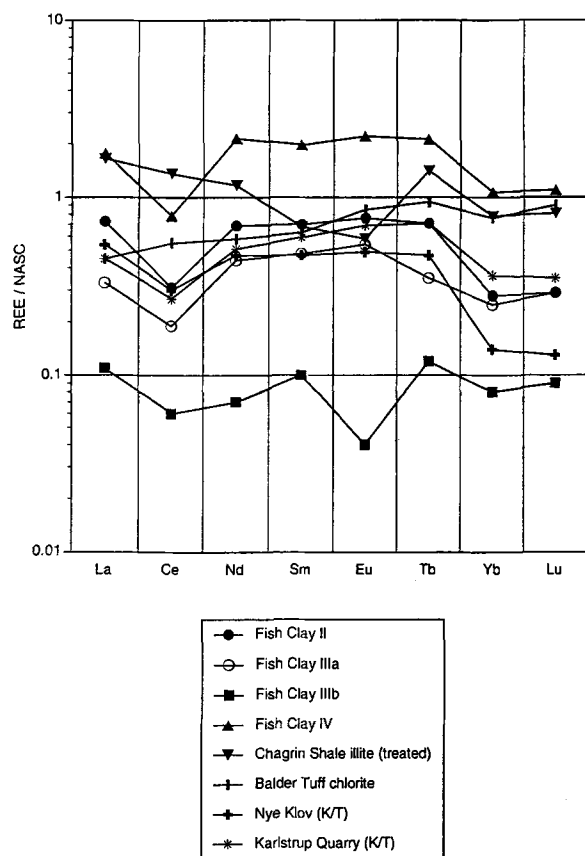


Figure 2. The REE concentrations of the Mg-smectites of the Fish Clay, Chagrin Shale illite, Balder Tuff chlorite, and the K/T boundaries at Nye Kløv and Karlstrup Quarry plotted relative to NASC.

Cretaceous bentonite from the Skull Creek Formation collected at Horsecreek, Wyoming (Elliott *et al.*, 1991), and an I/S (90% illite layers) from an Ordovician K-bentonite collected at Gadsden, Alabama (Elliott and Aronson, 1987), are shown in Figure 3. With exception of Eu, the REE signature of the Mg-smectite of layer IIIb is comparable to the REE signature of the Mg-smectite at +8 m above the K/T boundary. It is also comparable to the REE signatures of the I/S and smectite separated from the bentonite. The REE signature of the smectite 32 m below the K/T boundary is more similar to the REE signatures of the other Mg-smectites shown in Figure 2. Note, the smectite from 32 m below the K/T boundary at Limhamn Quarry has a trace amount of illite (Figure 1) which perhaps gives it a higher REE content.

K-Ar data

The K/Ar ages of the Mg-smectites from the Fish Clay and the marls from the Limhamn Quarry are summarized in Table 4. The K/Ar ages of the Mg-smectites of layers II, IIIa, and IIIb of the Fish Clay all range from 57–60 m.y. These ages are similar to

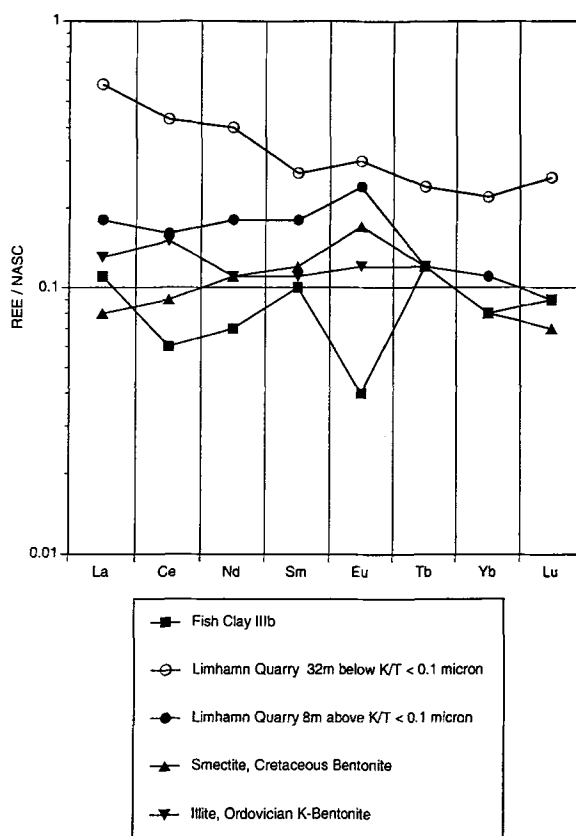


Figure 3. The REE concentrations of the Mg-smectites of layer IIIb of the Fish Clay, from the Limhamn Quarry, and smectites and illite from bentonites and K-bentonites, respectively, plotted relative to NASC.

the age measured without Ar spike from layer III by Elliott *et al.* (1989). The K/Ar age of the Mg-smectites from layer IV of the Fish Clay and from 8 m above the K/T boundary at Limhamn are both slightly older. Given its low K_2O , the K/Ar age of the Mg-smectite 8 m above the K/T boundary is imprecise. The Mg-smectite of layer IV is higher in K_2O , which might be attributed to the presence of trace amounts of potassic phases (i.e., illite) not seen in X-ray diffraction. The oldest age measured from the smectite-rich <0.1 μm fraction of the marl 32 m below the K/T boundary, and this <0.1 μm fraction does have trace amounts of illite (Figure 1).

INTERPRETATION

There is not a distinct difference in the clay mineralogy of the K/T boundary marl relative to the clay mineralogy seen in late Cretaceous and early Tertiary marls from the Limhamn Quarry. Moreover, Mg-smectite from neither of the Limhamn Quarry marls contained anomalous (i.e., >1 ppb Ir) levels of Ir. Thus, the Ir and the Mg-smectite are in all likelihood from separate origins. At best, the K/Ar ages of the Mg-

smectites indicate that they are not Caledonian-aged detrital minerals (see Elliott *et al.*, 1989). The K/Ar ages alone can not be used to discriminate between impact versus volcanic origin for the Mg-smectites.

The REE concentrations of the Mg-smectites in the Fish Clay ranged from being near unity relative to NASC to one order of magnitude depleted relative to NASC. The negative Ce anomalies in this study contrast with the lack of the pronounced Ce anomaly reported by Kastner *et al.* (1984). The negative Ce anomalies suggest the Mg-smectites were formed in the water/rock system higher than indicated by Kastner *et al.* (1984), and that they could have equilibrated with sea water. The range of REE of the various smectites from unity to one order of magnitude depleted relative to NASC might reflect the presence of trace amounts detrital illite possibly having enriched light REE and apatites definitely having very high contents of REE (Schmitz *et al.*, 1988). The concentrations of REE of layer IV and the marl 32 m below the K/T boundary from the Limhamn Quarry increase with increased grain size (Table 3). Thus, the low REE levels of Mg-smectite of Fish Clay layer IIIb is interpreted to be the purest (i.e., best-separated) smectite studied herein. This speculation is supported by the data of Schmitz *et al.* (1988) who found the REE levels of HCl-leached insoluble residues of layers III and IV of Fish Clay were also very depleted relative to NASC. Also, given the enrichment of the middle rare earth elements in apatite noted by Schmitz *et al.* (1988), middle REE being concentrated by apatite during early diagenesis forming the Eu anomaly in the layer IIIb smectite.

The low REE level of the Mg-smectite of layer IIIb is a significant result with regard to the origin of the Mg-smectite. Izett *et al.* (1990) noted that the smectite altered from tektites at the K/T boundary in Haiti (i.e., sample 90GISX, Table 1) were depleted in all REE (<0.13 ppm). In fact, they are more depleted in REE than the Mg-smectite of layer IIIb (Table 3). The extremely low values measured by Izett *et al.*, as they mention, might be a function of the analytical technique used, laser ablation inductively coupled mass spectrometry (LA-ICP-MS); and the authors add that this particular analysis is uncertain. Ultimately, they claim that the REE are present in that smectite are certainly less than 0.1 ppm. The depleted REE of the smectite clay encasing the glassy tektite host usurps previous dogma that the REE would be relatively immobile in glass-clay reactions (e.g., Zielinski, 1983). They showed, consequently, that there is a significant loss and mobility of REE associated with the genesis of this smectite. As shown in Figure 3 and Table 3, smectite and I/S formed authigenically in bentonites and K-bentonites, respectively, are also depleted in REE relative to NASC. Given REE data alone, the layer IIIb smectite is argued to have been formed authigenically from an impact or volcanic glass precursor.

The other Mg-smectites are thought to be formed from a glassy precursor because it would be highly unlikely for smectite of comparable chemistry and mineralogy within a single marl to have more than one origin.

Based on the stratigraphic distribution of the Mg-smectite, Ir analyses, REE data, and the K/Ar ages, the Mg-smectite is formed either from volcanic rocks as young as late Cretaceous, or it is formed *in situ* directly by chemical alteration of volcanic glass deposited during the K/T boundary transition.

DISCUSSION

The clay mineral data presented herein support earlier data indicating that the Mg-smectite is of volcanic origin. The presence of this Mg-smectite in both Maastrichtian and Danian marls and the depleted REE values of the layer IIIb smectite in the Fish Clay are critical data leading to this interpretation. The Mg-smectites studied herein collected from marls as opposed to clayey chinks. The clayey chinks typically contained higher amounts of illite and/or I/S. However, the smectitic marls can not be construed to be bentonites because zircon and other accessory pyroclastic minerals have not yet been found in these marls. The Mg-smectite containing marl at the K/T boundary is widespread, though diachronous (Hultburg, 1987), throughout the Danish basin (e.g., Hakanson and Hansen, 1979). Thus, the K/T boundary marl was probably deposited as a result of a basin wide regression.

The carrier phase of Ir in the K/T boundary is still not known with certainty. The bulk of trace metals (Co, Ni, Cr, and Ir) are in the <0.1 μm fractions of the K/T boundary smectitic marls. Premovic *et al.* (1993) claim the trace metals were incorporated into the smectite structure prior to being deposited at the K/T boundary. However, the Maastrichtian and Danian Mg-smectites at Limhamn Quarry typically are not as enriched in these metals relative to the K/T boundary. Considering that all these Mg-smectites are in all likelihood redeposited sediments, these metals could have been incorporated into these Mg-smectites as they were being deposited during the K/T boundary transition. Perhaps, these Mg-smectites were open to exchange with sea water that was enriched in these metals from meteorite impact (see also Schmitz *et al.*, 1988). Alternatively, these anomalously high metals present in the K/T boundary marls are present in trace, fine grained, phases undetected by X-ray diffraction, or in the organic carbon (Schmitz *et al.*, 1988).

It has been argued the iridium anomaly was the result of extensive volcanism taking place during the K/T boundary (e.g., Zoller *et al.*, 1983). Graup (1992) found clinopyroxene in the Fish Clay, and it is consistent with the discovery of pyroclastic labradorite in the Fish Clay as well. The results presented herein suggest different origins for the Mg-smectite and Ir. Moreover, even in the most fortuitous case of sizable pyroclastic basaltic

volcanism occurring during the opening of the North Atlantic and of comparable magnitude to the eruption of the Deccan Traps, this sizable pyroclastic basaltic volcanism did not form a K/T boundary-type Ir anomaly in a given basaltic tuff in the Balder Formation (Elliott *et al.*, 1992). Thus, a consistent picture is emerging with respect to the separate origins of the clay minerals, presence of volcanic minerals (Graup, 1992), and Ir anomaly at the K/T boundary in Denmark.

Lastly, the results presented herein are also relevant to study of mineral and chemical changes that take place during the smectite-to-illite transformation. It is very interesting to note that the I/S with 90% illite layers formed in the Ordovician K-bentonite were depleted in REE relative to NASC. If this I/S in this K-bentonite formed progressively from a pure smectite precursor (e.g., smectite from the Cretaceous Skull Creek bentonite at Horsecreek, Wyoming), and if it had as much access to the REE as the I/S in shales, then these results tentatively indicate that there is no significant increase or fractionation of REE with progressive smectite illitization in forming K-bentonites. However, Awwiller (1992), Awwiller and Mack (1991) and Ohr *et al.* (1991) have presented evidence for fractionation of REE, and increases in REE in the I/S during progressive illitization of Gulf Coast shales. At first approximation, the low REE of the I/S with 90% illite layers in the Ordovician K-bentonite suggest that I/S might have formed directly from volcanic glass bypassing smectite.

Also, given the depleted REE in authigenically formed smectite both in bentonites and at the K/T boundary in Haiti (Izett *et al.*, 1990) and the higher concentrations of REE in Paleozoic illites (Table 3), it is conceivable that the concentrations of REE, especially the light REE (e.g., lanthanum), could be a sensitive indicator for the presence of detrital illite in smectite-dominant clay mineral separates from shales at shallow burial temperatures. Thus, the analysis of light REE might be helpful in the interpretation of K/Ar ages of diagenetic I/S in shales containing detrital illite. For example, the smectite of layer IV of the Fish Clay has both the highest K/Ar age and the highest REE contents.

CONCLUSIONS

Based on the occurrence of Mg-smectite in a late Maastrichtian marl and the REE, trace element, and K/Ar data, the Mg-smectite seen at K/T boundary marl at Stevns Klint is believed to be volcanic in origin. The REE analyses of the layer IIIb smectite of the Fish Clay was a critical result prompting this conclusion. However, it is not certain whether the Mg-smectite was formed from volcanic glass deposited episodically during the late Maastrichtian through early Danian or whether the Mg-smectite was a detrital mineral of volcanic origin formed before the K/T boundary event

(i.e., late Cretaceous or older). The anomalous concentrations of siderophile elements in the Mg-smectite at the K/T boundary are thought to have been incorporated into the smectite structure by exchange with sea water enriched in these elements from meteorite impact, or they are present in trace fine grain minerals not detected using X-ray diffraction.

The REE data presented herein are useful in geochronologic studies of I/S in shales and possibly in understanding the smectite-to-illite transformation. The REE levels in smectite and I/S in bentonites were not markedly different and they were depleted relative to NASC. Illite from the Chagrin Shale contained much higher REE relative to smectite and I/S from K-bentonites. Thus, REE analyses might be useful to indirectly discern the presence of small amounts of detrital illite in clay mineral fractions of shales containing diagenetic I/S. The depleted REE in illitic I/S might indicate that it was formed directly from a glass bypassing smectite.

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