

## Physicochemical conditions of sedimentation of the Fish Clay from Stevns Klint, Denmark, and its detrital nature: Vanadium and other supportive evidence

PAVLE I. PREMLOVIĆ,<sup>1</sup> NEBOJŠA Z. PAVLOVIĆ,<sup>2</sup> MIRJANA S. PAVLOVIĆ,<sup>2</sup> and NIKOLA D. NIKOLIĆ<sup>1</sup>

Laboratory for Geochemistry and Cosmochemistry, Faculty of Science, University of Niš, 18 000 Niš, Yugoslavia

<sup>2</sup>Boris Kidrič Institute of Nuclear Sciences Vinča, Beograd 11 000 Beograd, Yugoslavia

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**Abstract**—Cretaceous-Tertiary (K/T) boundary samples of the Fish Clay in Denmark from three sites (Stevns Klint, Nye Kløv, and Dania) have been analyzed mineralogically and chemically. All samples contain major amounts of biogenic calcite and smectite. In some samples, minor amounts of authigenic pyrite and siderite (Stevns Klint), and lepidocrocite (Dania) are also present.

To obtain an indication of the chemical nature of the V present in the Danish boundaries, the samples were analysed for V and vanadyl ( $\text{VO}^{2+}$ ) at various stages of selective leaching. The results obtained indicate that the bulk of V is associated with the smectite fractions ( $\geq 47\%$  of total V); all  $\text{VO}^{2+}$  resides in the smectite portions.

From the chemistry of  $\text{VO}^{2+}$ , pyrite, and carbonates, it is deduced that the oxidation potential and pH of the interstitial seawater of the Stevns Klint boundary was approximately 0.0 to  $-0.2$  V and 6 to 7, respectively, during the accumulation of the lower black basal part, but rose during the accumulation of the upper grey part.

The geochemical data do support the hypothesis that the Danish boundary smectite represents weathered clay (along with some asteroid and local material) that was redeposited to the Danish boundary sites after the K/T event. Substantial proportions of the  $\text{VO}^{2+}$  contents of the Nye Kløv and Dania smectite were probably already contained in the detrital clay arriving at the site of boundary sedimentation, but at the Stevns Klint site they have been significantly augmented by uptake from the interfacial and interstitial seawaters through the humic substances involvement.

Abundances and major mineralogical residences have been determined for trace metals: Cr, Ni, Co, and Ga, and minor Fe. Much of these elements is located in the boundary smectite structure as the corresponding ionic forms ( $\text{CrOH}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ga}^{3+}$ , and  $\text{Fe}^{3+}$ ) and is strictly detrital in character, i.e., having been transported to the Danish boundary sites already contained in smectite. All these metals in the Danish boundary smectite are well above normal abundances in clays.

### INTRODUCTION

ALVAREZ ET AL. (1980) HAVE REPORTED anomalous high Ir concentration in the K/T boundary from Stevns Klint, Denmark (Fig. 1). This boundary is marked by a thin black marl: the Fish Clay. ALVAREZ et al. (1980) interpreted the high Ir content in terms of an asteroid impact that deposited a worldwide layer of Ir. The L.W.A. (L.W. Alvarez) asteroid-impact concept has been, however, vigorously challenged by OFFICER and DRAKE (1983, 1985). They suggested that the various geological signatures at K/T time including Ir and other elements (ALVAREZ et al., 1980) are attributable to a period of intense volcanism. Apart from Ir, the boundary is also enriched in other trace metals, such as V. In the Fish Clay at the Stevns Klint, the content of V ranges from 40 to 200 ppm (CHRISTENSEN et al., 1973) and is thus of the same order of magnitude as in other ancient shaly type sedimentary rocks of marine origin (TUREKIAN and WEDEPOHL, 1961).

Vanadium is found in the trivalent oxidation state in magmatic rocks but as such is too insoluble for transport except at pH values below those expected for natural waters ( $\text{pH} \leq 1$ ) (EVANS and GARRELS, 1958). During ordinary rock weathering with (neutral to mildly alkaline pH) natural waters,  $\text{V}^{3+}$  (mostly in low concentrations) is readily oxidized (by air oxygen) to  $\text{V}^{5+}$ , forming highly soluble and highly mobile vanadate ion,  $\text{VO}_4^{3-}$ . In normal (oxic) seawater, V is

predicted to occur in the +5 oxidation state, primarily as  $\text{HVO}_4^{2-}$ ,  $\text{H}_2\text{VO}_4^-$ , and as the complex  $\text{NaHVO}_4^-$  (TURNER et al., 1981). As a consequence, the V species involved in adsorption processes appear to be anionic, resulting in a relatively low affinity for the clay particles (WHITFIELD and TURNER, 1987). In reducing environments, the dominant V species is  $\text{VO}^{2+}$ . This ion has a strong tendency to interact with the surface of Al and other metal hydrous oxides and is thus capable of becoming specifically adsorbed to particulate materials such as the clay minerals (WEHRLI and STUMM, 1989).

Chemical conversion of V into  $\text{VO}^{2+}$  in the sedimentary water is strictly conditioned by the depositional environment. Both redox potential and acidity are key factors in the preservation of  $\text{VO}^{2+}$  in this environment (EVANS and GARRELS, 1958). Thus,  $\text{VO}^{2+}$  is an excellent geochemical indicator of physicochemical conditions of sedimentation and it may provide clues to the origin of sedimentary deposits of the past. Furthermore, one way to get an objective evaluation of the nature of seawater that has interacted chemically with the Fish Clay is to examine components that undoubtedly were introduced into the clay matrix during seawater/clay interaction: one such component is  $\text{VO}^{2+}$  ion. These facts led us to search for  $\text{VO}^{2+}$  in the Fish Clay (at Stevns Klint) and related Danish boundaries in Jylland: Nye Kløv and Dania. Then, using the thermodynamic properties, we at-

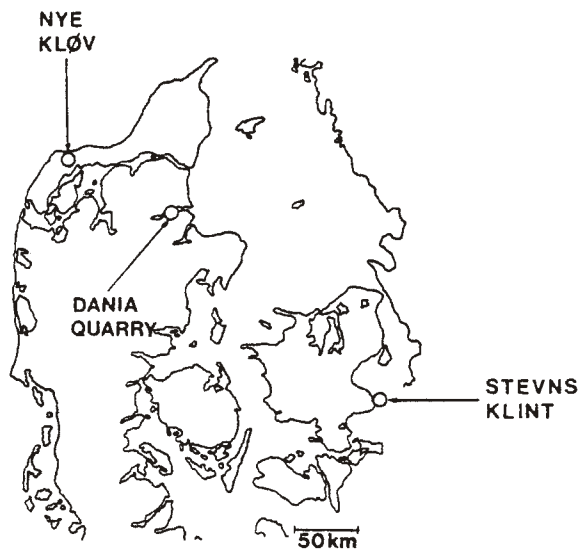


FIG. 1. Location of samples of the Danish boundaries.

tempt to evolve an equilibrium which shows the stabilities of  $\text{VO}^{2+}$  and pyrite (as minor authigenic mineral component) in aqueous solution. Besides V, we have analysed the samples of the basal part of the Fish Clay (at Stevns Klint) and related Jylland boundaries for meteoritic (Cr, Ni) and non-meteoritic metals (Co, Ga, and Fe). These metals were chosen primarily for two reasons: (a) their ease in analysis and (b) the relatively simple chemistry of these metals in seawater governed by their ions present.

#### GEOLOGY, SEDIMENTOLOGY, AND DEPOSITIONAL ENVIRONMENT

The most complete description of the Fish Clay (at Stevns Klint) is that given by CHRISTENSEN et al. (1973). They subdivided this section into four beds from the bottom bed II to the top bed V. Bed II is underlain by Maastrichtian chalk (bed I), and bed V is overlain by the Danian Cerithium limestone (bed VI). All beds contain anomalously high concentrations of Ir and other associated elements in beds III and IV. KYTE et al. (1980) suggested that only beds III and IV of the Fish Clay at Stevns Klint (hereinafter referred to as III and IV) could be used to estimate the primary asteroidal fallout, as the Ir in bed V may stem mainly from secondary lateral transport. It is suggested that the combination of black shales with pyrite and the undisturbed lamination implies that III was laid down in a shallow sea environment under strong reducing conditions with slow, prolonged, but stable deposition (SCHMITZ, 1985; SCHMITZ et al., 1988). The X-ray diffraction analyses of samples from the Stevns Klint boundary by RAMPINO and REYNOLDS (1983) indicate that the central part of the boundary (III and IV) is a pure smectite which is relatively abundant and of local derivation formed by diagenetic alteration of glassy volcanic ash. KASTNER et al. (1984) presented detailed mineralogical, chemical, and oxygen isotope analyses of the clay minerals from the K/T boundary region of Stevns Klint. In the central (black basal) part (III), precisely at the K/T boundary, the only clay mineral detected by X-ray diffraction was a pure smectite. No detrital clay minerals were observed in the clay size fraction. According to these authors, the mineralogical purity of the boundary smectite fraction and the oxygen isotope analyses indicate authigenic formation by alteration of glass in the marine environment. KASTNER et al. (1984) concluded that formation from asteroidal impact ejecta rather than from volcanic material is supported by the major element chemistry of the Stevns Klint boundary. Very recently, ELLIOT et al. (1989) pointed out that the Fish Clay at Stevns Klint is composed

predominantly of volcanic, detrital phases and lesser amounts of impact phases. According to these authors, the presence of subhedral labradorite in III indicates that pyroclastic basaltic volcanism was the predominant progenitor of this clay unit.

In contrast to the Fish Clay (at Stevns Klint), the precise stratigraphic horizon of Ir concentrations in the Jylland sequences has not been well documented. A small Ir anomaly, however, has been reported by some workers, and it ranges from 0.17 ppm (Nye Kløv; NAZAROV et al., 1988) to 4 ppm (Dania; GANAPATHY et al., 1981). EKDALE and BROMLEY (1984) have attributed the difference in the Ir content between the Stevns Klint and Jylland boundaries to a calcite (acid) dissolution pulse at the end to Maastrichtian. This affected the shallow and/or surface water (ca. 150 m at Stevns Klint) more than deeper, basinal waters (in Jylland) (EKDALE and BROMLEY, 1984).

Boundaries at both Nye Kløv and Dania are mineralogically smectite identical to that at Stevns Klint (RAMPINO and REYNOLDS, 1983). Microscopic analyses of the basal boundary layers at Nye Kløv and Dania imply that there is no pyrite or organic residue to indicate the possibility of anoxic conditions occurring at the boundary in Jylland (EKDALE and BROMLEY, 1984).

#### EXPERIMENTAL

##### Fourier Transform (FT) Infrared (IR) Spectrometry

Rock samples were powdered finely and dispersed evenly in anhydrous potassium bromide (KBr) pellets (1.5 mg/150 mg KBr). Spectra were taken at room temperature using a Perkin-Elmer 1600 FTIR spectrometer set to give underformed spectra.

##### Emission Spectrometry

A PGS-2 plane grating spectrograph (Carl Zeiss, Jena) was used with an attachment for photoelectric detection, an arc plasma excitation source, and a Bausch and Lomb diffraction grating as the monochromator (MARINKOVIĆ and VICKERS, 1971).

##### Atomic Absorption Spectrometry (AAS)

A Perkin-Elmer model 4000 atomic absorption spectrometer was used with a Perkin-Elmer platinum hollow-cathode lamp and a nitrous oxide/acetylene burner head.

##### Instrumental Neutron Activation Analyses (INAA)

The rock samples and corresponding standards of  $(\text{NH}_4)_2\text{VO}_4$  were irradiated simultaneously in the TRIGA MK II reactor at a neutron flux of  $4 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ . The  $\gamma$ -induced activity of  $^{52}\text{V}$  isotopes was measured on a germanium Ge(Li) detector connected to a 4000 channel analyser (Canberra).

##### Electron Spin Resonance (ESR)

ESR measurements were performed on the finely ground powders of rock samples which were transferred to an ESR quartz tube (4 mm o.d., 3 mm i.d.). Spectra were recorded on a Bruker ER 200 ESR spectrometer employing 100 kHz modulation and a nominal frequency of 9.5 GHz. The  $g$ -values and hyperfine coupling constants were determined relative to a solution of potassium nitrosodisulfonate (Fremy's salt) for which  $g = 2.0055 \pm 0.0001$  and the nitrogen hyperfine splitting  $a_N = 1.309 \pm 0.002 \text{ mT}$  (FABER and FRAENKEL, 1967).

Spin concentrations of  $\text{VO}^{2+}$  ions in the K/T rock samples were determined by the sample interchange method using powdered potassium tartarate doped with 0.01%  $\text{VO}^{2+}$  standard. Further details of the ESR concentration measurements and associated controls for precision and accuracy are given in NIKOLIĆ (1992).

##### X-Ray Analysis

X-ray analysis of the whole rocks and their carbonate-free and silicate fractions were performed by a Philips diffractometer (PW 1050/25) equipped with proportional counter and discriminator.

using Ni-filtered Cu radiation at 40 kV and 20 mA. The clay-size fractions were separated from the carbonate-free residues by conventional settling methods and analyzed by X-ray diffraction (as well as ESR) before and after treatment with ethylene glycol (KASTNER et al., 1984).

#### Electron Microprobe

All analyses were obtained with a Jeol JSM-35 electron microscope equipped with a Tracor TN-2000 energy dispersive X-ray spectrometer. Operating conditions for energy-dispersive analyses were at 25 keV accelerating voltage, 0.1  $\mu$ A beam current, and a beam spot diameter of approximately 3  $\mu$ m.

#### Analysis and Fractionation

The fractionation procedure was similar to that used by SAXBY (1976), PREMOVIĆ (1984), LYLE et al. (1984), and SCHMITZ et al. (1988). The flow chart in Fig. 2 outlines the major steps in preparing the four fractions. These are:

- 1) Powdered rock (10 g) was treated with cold hydrochloric acid (HCl, 6 M) or with acetic acid/sodium acetate (1 M) solution at pH 5.0 (LYLE et al., 1984) to remove most of the carbonates. The soluble material constitutes the cold-HCl or carbonate fraction. Carbonate removal was checked by FTIR and X-ray analyses. The acetate leach procedure is used to avoid slight solubility of smectite in cold (6 M) HCl (SCHMITZ et al., 1988) for determination of the Fe, Cr, Ni, Co, and Ga contents in the inorganic fractions of the Danish boundary samples.
- 2) The insoluble residue from (1) above was demineralized further by repeated treatment with boiling HCl (6 M). This acid solution removes smectite fraction (SCHMITZ et al., 1988). Smectite removal was checked by FTIR and X-ray analyses. Soluble part constitutes the boiling HCl-fraction.
- 3) The insoluble residue from (2) was demineralized with boiling hydrofluoric acid (HF)/HCl (22 M and 0.25 M, respectively).

This acid mixture removes silica ( $\text{SiO}_2$ ).  $\text{SiO}_2$  removal was checked by FTIR and X-ray analyses. The soluble part constitutes the HF fraction.

- 4) The final residue from (3) above is the organic fraction.

## RESULTS AND DISCUSSION

### Mineralogical Analysis

Mineralogical analyses samples from III and IV indicate that those rocks contain the major mineral constituent smectite and the minor constituents pyrite, siderite, quartz, anatase, feldspar, and silicate glass. Microscopic inspection of thin sections of III and IV indicates that these contain predominantly calcite ( $\text{CaCO}_3$ ) derived from calcareous algal plates (coccoliths  $\geq 95\%$ ). These observations are generally in accord with those of many other researchers (e.g., CHRISTENSEN et al., 1973). Electron microprobe distribution of major elements (Ca, O, Si, Al, and Fe) indicates that bulk composition remains essentially unchanged and the variations are largely isochemical (Fig. 3). This means essentially uniform sedimentation conditions.

### Siderite ( $\text{FeCO}_3$ )

The circumstances leading to the formation of authigenic  $\text{FeCO}_3$  are not fully understood. In general,  $\text{FeCO}_3$  forms by three basic mechanisms: (1) chemical reduction of a  $\text{Fe}^{3+}$  compound; (2) direct precipitation from solution; and (3) substitution of  $\text{Fe}^{2+}$  into another carbonate mineral (e.g.,  $\text{CaCO}_3$ ). All these mechanisms indicate a  $\text{FeCO}_3$ -forming environment under reducing conditions so that Fe would occur in the 2+ state rather than the 3+ state (BABCAN, 1970).

### Pyrite ( $\text{FeS}_2$ )

Experimental evidence suggests that primary sedimentary  $\text{FeS}_2$  forms in anoxic depositional environment with near neutral pH provided that organic matter, dissolved sulfate, S-reducing bacteria, and a source of  $\text{Fe}^{2+}$  occur in sufficient quantities (KRUMBEIN and GARRELS, 1952). Geochemical (CHRISTENSEN et al., 1973; SCHMITZ, 1985) and other (SURLYK and JOHANSON, 1984; EKDALE and BROMLEY, 1984) studies showed that the sedimentary environment of III contained all of these features. High content of polyaromatic paramagnetic structures (PPS) of the III organic matter ca.  $4 \times 10^{18}$  spins  $\text{g}^{-1}$  (determined by ESR) is consistent with strong anoxic sedimentation conditions (PREMOVIĆ, 1992). Thus, III would represent an organic rich ooze accumulating in nearly stagnant water by the settling of very fine-grained products. Such water would be of Eh < 0 and pH 6 to 9 (BAAS BECKING et al., 1960).

### Vanadium and Iridium

A characteristic geochemical feature of the Ir-enriched Danish boundary rocks is their high concentration of V (Table 1). To obtain an indication of the chemical nature of V present in the III and IV samples, they were analysed for V at various stages of demineralization (Table 1). It is obvious that V occurs in a variety of chemical forms: (1) cold-HCl soluble ( $\geq 49\%$ ), hydrated oxides or vanadates precipitated in carbonates or adsorbed on the smectite surface; or (2)

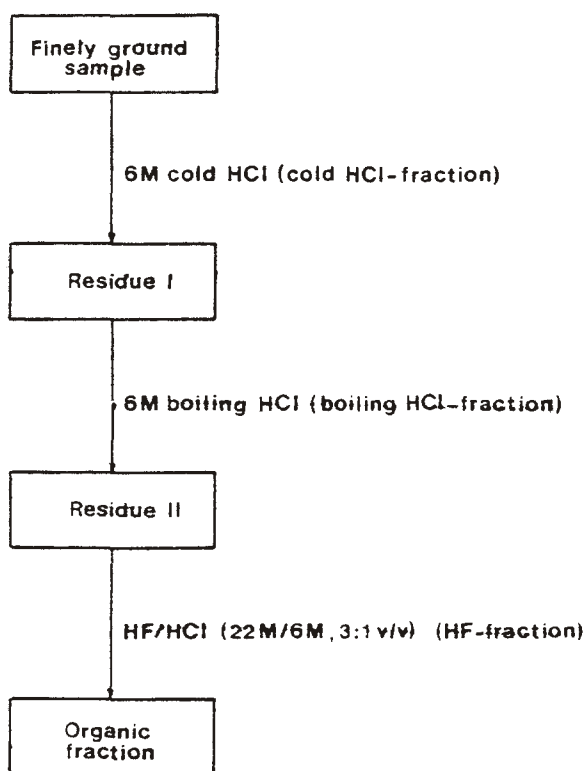


FIG. 2. Flow chart of fractionation procedure.

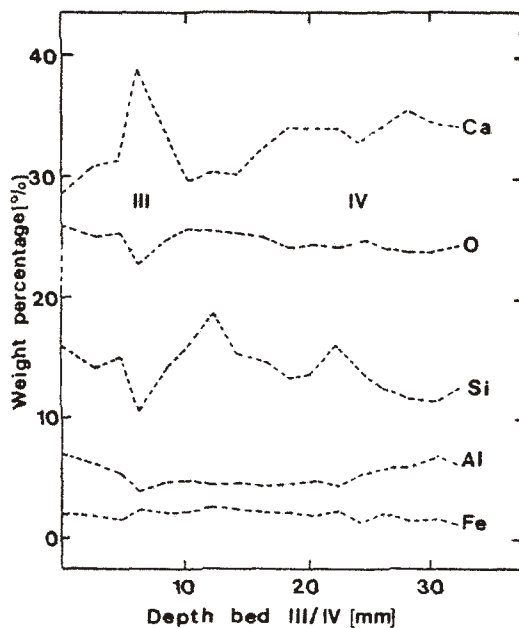


FIG. 3. Abundance profiles for five elements (Ca, O, Si, Al, and Fe) across the III/IV boundary. In general, there is a little difference between the base and top of the section.

boiling-HCl soluble ( $\geq 47\%$ ), incorporated within the smectite structure. The origin of V is of particular interest because anomalously high concentration of V coincides with Ir anomaly (SCHMITZ, 1985; SCHMITZ et al., 1988). This fact suggests some doubts on a terrestrial origin. We verified whether this notion is quantitatively reasonable for III. Though V is siderophile and enriched at the boundary, its high ratio to Ir (Table 2), however, is in accord with a terrestrial origin.

#### Vanadium and Fallout

If we eliminate allochthonous sources of the Fish Clay smectite from weathering of terrigenous or marine rocks, then this smectite was chemically produced in situ by either alteration of the volcanic or the asteroid impact fallout. In this case, it is probable that noncarbonate fractions of III and IV contain a large fraction of fallout and some minor amount of local material (GILMOUR and ANDERS, 1989). Large biogenic  $\text{CaCO}_3$  crystals of III and IV are pure, with only Ca (as major) and Sr (as minor) elements being detected (NIKOLIĆ, 1992). For this reason, we suggest that the bulk of V was already present in fallout settled into the Stevns Klint basin. Very recently, using the results from computer simulation of large (10 km diameter C1 like) asteroid impact into oceanic or continental sites, RODDY et al. (1991) made a set of preliminary comparisons of Fe/Ir ratios of the ejected vapor with recently measured ratios in K/T boundary strata on the Shatsky Rise, Holes 577, 577B (C. Pacific). According to these authors the target rocks contribution to global impact ejecta was less than 0.2% and all of asteroid (with total mass of  $1.2 \times 10^{18}$  g) was vaporized. If these results are correct then ca.  $0.24 \text{ g cm}^{-2}$  of global C1-like ejecta was distributed, as well as an average of ca.  $120 \text{ ng cm}^{-2}$  of globally distributed

Ir. Consequently, based on the average V of 57 ppm (ANDERS and GREVESSE, 1989) in a C1 chondritic-type asteroid, one would expect ca.  $14 \mu\text{g cm}^{-2}$  of V from a global dispersion. In this case, the asteroid contribution to total V (193 ppm, Table 2) of III (corrected for  $\text{CaCO}_3$ ) is less than 7% (NIKOLIĆ, 1992). Hence, rather than being related to the C1-like asteroid or C1-like equivalent fraction of a comet, the V abundance in III may be related largely to terrestrial source(s) which are crustal and mantle (volcanism, hydrothermalism).

In order to evaluate the overall (terrestrial) source of V, we calculated the V concentration in carbonate-free III sample and compared with those in normal seawater, black shale, volcanic ash, and crust (Table 2). Table 2 also gives the ratio of V in III relative to seawater (MIDDLEBURG et al., 1988), black shale (VINE and TOURTELOT, 1970), volcanic ash (LEVENTHAL et al., 1983), and crust (MASON, 1966). The V concentration of III (corrected for  $\text{CaCO}_3$ ) is similar to volcanic ash and crust. On the other hand, the degree of V enrichment in III similar to that reported by VINE and TOURTELOT (1970) for their average black shale. In general, there is still controversy over the source of V (and other metals) in black shales. Some of these shales seem to show V is syngenetic and extracted by organic matter from ordinary seawater (HOLLAND, 1979), but in others V is related to beds of volcanic pyroclastic materials on the land that were leached of their V (PREMOVIĆ et al., 1986). For the Danish K/T rocks, the method of HOLLAND (1979) does not seem to explain the V concentrations since, relative to present-day normal seawater, the V concentration factor ranges from  $0.3 \times 10^5$  to  $0.8 \times 10^5$  (NIKOLIĆ, 1992). In addition, the V concentrations in our Danish K/T samples are similar and are not related to their organic contents (Table 1).

#### ESR and $\text{VO}^{2+}$ Ion

The investigation of untreated III sample showed multiline ESR spectrum (Fig. 4a) similar to the spectrum of  $\text{CaCO}_3$  doped with  $\text{Mn}^{2+}$  reported by HURD (1954). After removal of carbonates of the boundary samples investigated by treating with cold HCl, the  $\text{Mn}^{2+}$  lines diminished. ESR spectra of boundary samples (after removal of carbonates) were identical to the spectrum of the III carbonate-free sample shown in Fig. 4b. Identical ESR spectra were recorded by PREMOVIĆ (1984) for  $\text{VO}^{2+}$  ions incorporated into the clay lattices of ancient shaly-type sedimentary rocks of marine origin. These ESR signals can be described by the spin-Hamiltonian valid for  $d^1$  metal ions in axial symmetry:

$$\mathcal{H} = \beta_0 [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y)],$$

where  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$ , and  $A_{\perp}$  are the parallel (z) and perpendicular (x, y) components of the g- and  $^{51}\text{V}$  hyperfine coupling tensors, respectively.  $H_i$ ,  $S_i$ , and  $I_i$  represent the vector components of the magnetic field, electron spin, and  $^{51}\text{V}$  nuclear spin along the  $i = (x, y, z)$  axes, respectively. These parameters for  $\text{VO}^{2+}$  in the Danish K/T smectite are given in Table 1.

The HCl demineralizing steps remove 72 (III) and 91% (IV) of the samples. This is a result of the total dissolution of  $\text{CaCO}_3$  (cold HCl: 58 and 82%, respectively) and the

Table 1. Geochemical distributions of V [ $\pm 10$  ppm] and VO<sup>2+</sup> [ppm]<sup>a</sup> from selective leaching experiments.

| Fraction                                     | Sediment<br>( $\pm 5$ wt%) | V <sup>d</sup>   | Total<br>V(wt%) | VO <sup>2+</sup> <sup>e</sup> | Fraction of V<br>as VO <sup>2+</sup> (wt%) |
|--|----------------------------|------------------|-----------------|-------------------------------|--|
| (a) III: 110 <sup>b</sup> ; 115 <sup>c</sup> |                            |                  |                 |                               |  |
| Cold-HCl                                     | 58                         | 100              | 51              | n.d.                          | —  |
| Boiling-HCl                                  | 14                         | 390              | 47              | 300                           | 58   |
| HF   | 25                         | 10               | 3               | n.d.                          | —  |
| Smectite                                     | 28                         | 195              | 47              | 150                           | 58   |
| Organic                                      | 3                          | n.d.*            | 0               | n.d.                          | —  |
| Sediment                                     | 100                        | 120 <sup>f</sup> | 100             | 40                            | 26   |
| (b) IV: 55; 65                               |                            |                  |                 |                               |  |
| Cold-HCl                                     | 82                         | 40               | 49              | n.d.                          | —  |
| Boiling-HCl                                  | 9                          | 370              | 52              | 170                           | 35   |
| HF   | 9                          | 1                | 0.02            | n.d.                          | —  |
| Smectite                                     | 18                         | 190              | 52              | 85                            | 35   |
| Organic                                      | 0.3                        | n.d.*            | 0               | n.d.                          | —  |
| Sediment                                     | 100                        | 65 <sup>f</sup>  | 100             | 15                            | 18   |
| (c) Nye Kløv: 55, 55                         |                            |                  |                 |                               |  |
| Cold-HCl                                     | 71                         | 25               | 37              | n.d.                          | —  |
| Boiling-HCl                                  | 8                          | 350              | 58              | 30                            | 7  |
| HF   | 21                         | 10               | 5               | n.d.                          | —  |
| Smectite                                     | 16                         | 180              | 58              | 15                            | 7  |
| Organic                                      | 0.1                        | n.d.*            | 0               | n.d.                          | —  |
| Sediment                                     | 100                        | 50 <sup>f</sup>  | 100             | 2                             | 3  |
| (d) Dania: 50; 45                            |                            |                  |                 |                               |  |
| Cold-HCl                                     | 75                         | 20               | 27              | n.d.                          | —  |
| Boiling-HCl                                  | 8                          | 400              | 68              | 70                            | 13   |
| HF   | 17                         | 10               | 4               | n.d.                          | —  |
| Smectite                                     | 16                         | 200              | 68              | 35                            | 13   |
| Organic                                      | 0.1                        | n.d.*            | 0               | n.d.                          | —  |
| Sediment                                     | 100                        | 50 <sup>f</sup>  | 100             | 6                             | 10   |

<sup>a</sup>The VO<sup>2+</sup> content determined by ESR.

<sup>b</sup>The V content determined by INAA.

<sup>c</sup>The V content determined by emission spectrometry.

<sup>d</sup>The V content determined by AAS.

<sup>e</sup>Its ESR parameters:  $g_{\parallel} = 1.924 \pm 0.003$ ;  $g_{\perp} = 1.979 \pm 0.010$ ;  $A_{\parallel} = 18.6 \pm 0.02$  mT; and,  $A_{\perp} = 6.2 \pm 0.4$  mT.

<sup>f</sup>The V content obtained by summation of fraction V concentrations, determined by AAS.

\*n.d. - not detected

Table 2. Comparison of the V contents and ratios.

| N | Geological material                   | V [ppm]              | Ratio V <sub>1</sub> /V <sub>N</sub> |
|---|---------------------------------------|----------------------|--------------------------------------|
| 1 | III(corrected for CaCO <sub>3</sub> ) | 193                  | 1                                    |
| 2 | Seawater                              | 1.6x10 <sup>-3</sup> | 1.2x10 <sup>5</sup>                  |
| 3 | Black shale                           | 93                   | 2.1                                  |
| 4 | Ash bed                               | 200                  | 1.0                                  |
| 5 | Crust                                 | 135                  | 1.5                                  |
| 6 | V/Ir (for III) <sup>a,b</sup>         | 3x10 <sup>3</sup>    | —                                    |

<sup>a</sup>Schmitz, 1985

<sup>b</sup>V/Ir (for C1 chondrite) = 118 Anders and Grevesse 1989).

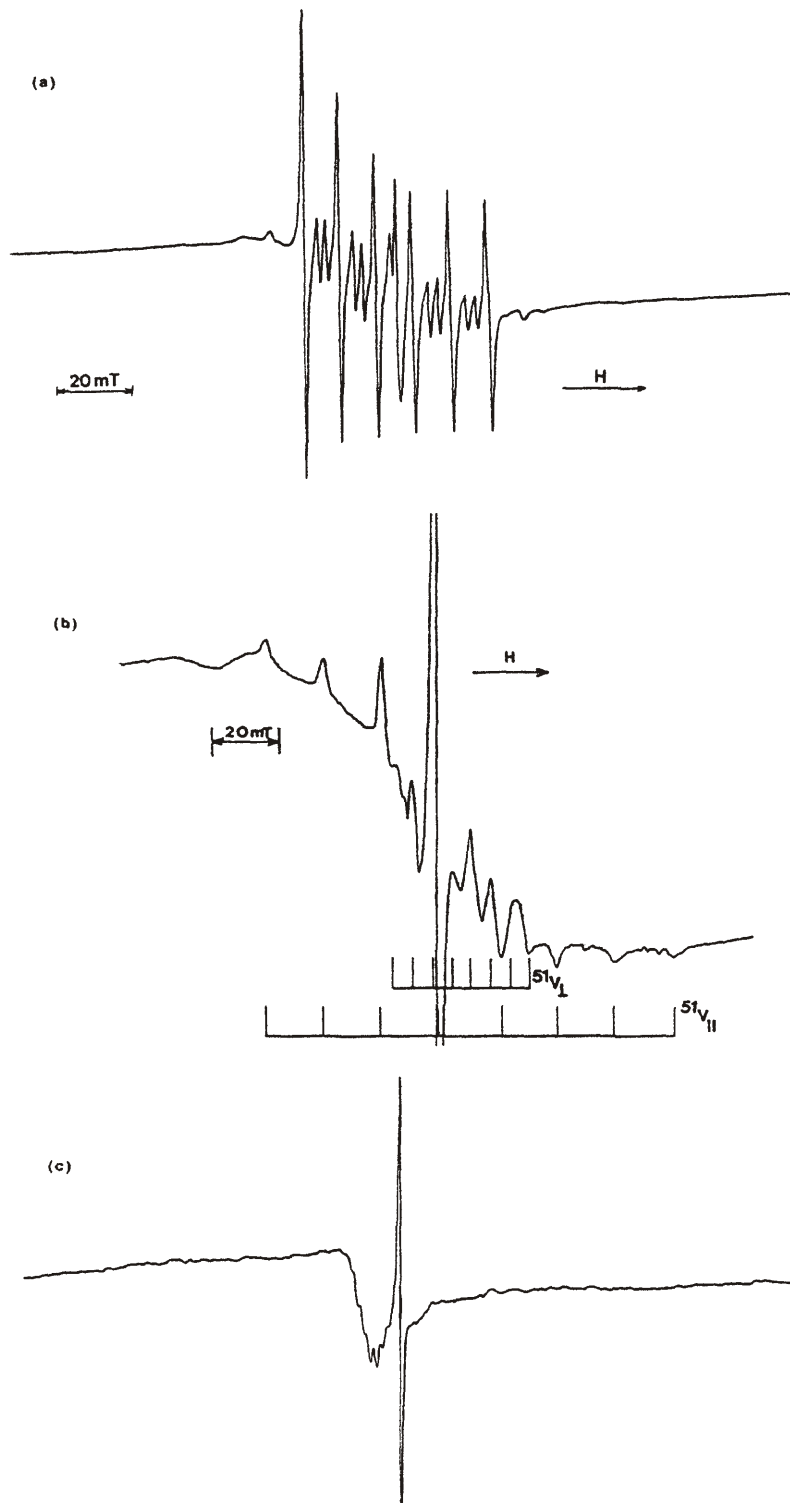


FIG. 4. ESR spectra of the III samples: (a) untreated; (b) cold-HCl (6 M); and (c) boiling-HCl (6 M).

destruction of smectite (boiling HCl: 14 and 9%, respectively; Table 1).  $\text{SiO}_2$ , a dominant constituent of the smectite lattice, seems relatively unaffected (III, ca. 25%; and IV, ca. 9%) by the boiling HCl demineralization. This indicates that protons ( $\text{H}^+$ ) substitute for Mg and Al in the smectite lattice (SCHMITZ et al., 1988). Much of  $\text{SiO}_2$ , however, also exists as HCl-insoluble quartz and silicate glass. Our geochemical analyses indicate that more than 99% of total V in III and IV is removed by the boiling HCl (6 M), Table 1. Moreover,  $\text{VO}^{2+}$  disappears completely during the boiling HCl step (6 M for 8 h) (Fig. 4a). It may be reasonable to assume therefore that  $\text{VO}^{2+}$  is incorporated into the smectite structure.

MCBRIDE (1979) demonstrated that at low levels of adsorption (5%  $\text{VO}^{2+}$ ) on exchange sites  $\text{VO}^{2+}$  ion was nucleated on the smectite particle surface as hydrolyzed species:  $\text{VO}(\text{OH})_2(\text{H}_2\text{O})_3$ . According to this author the hyperfine coupling constants for this species are:  $A_{\parallel} = 19.4 \text{ mT}$  and  $A_{\perp} = 7.1 \text{ mT}$ ; and for coprecipitated  $\text{VO}(\text{OH})_2$  in  $\text{Al}(\text{OH})_3$ :  $A_{\parallel} = 18.7 \text{ mT}$  and  $A_{\perp} = 6.7 \text{ mT}$ . The hyperfine coupling constants of  $\text{VO}^{2+}$  ions in the Danish K/T smectites are:  $A_{\parallel} = 18.6 \text{ mT}$  and  $A_{\perp} = 6.2 \text{ mT}$  (Table 1). It is evident that a species such as  $\text{VO}(\text{OH})_2$  is probably responsible for the  $\text{VO}^{2+}$  ESR spectra of the Danish boundary smectites. It seems probable that this species is derived from initially adsorbed  $\text{VO}(\text{OH})_2(\text{H}_2\text{O})_3$  through the compaction and dehydration processes during the smectite diagenesis.

#### $\text{VO}^{2+}$ and the Danish Boundary Smectites

The most intriguing result of this report is the relative abundances of  $\text{VO}^{2+}$  in the Danish boundary sediments, especially those incorporated into the III (150 ppm) and IV (85 ppm) smectite fractions (Table 1). In general, the incorporation of  $\text{VO}^{2+}$  into the smectite matrix is almost certainly a result of geochemical conversion of primary V. Smectite is virtually free from  $\text{VO}^{2+}$  when it deposits on the seafloor but absorbs this ion from seawater during early diagenesis. According to FOSTER (1959) V, in general, occurs as both V (III) and V (IV) in the smectite lattice. MCBRIDE (1979) has shown that  $\text{VO}^{2+}$  was taken up from aqueous solution by smectite. The authors concluded that coordinating sites were formed slowly during smectite genesis, and while the clay was dispersed in the aqueous solution these sites would be rapidly filled by  $\text{VO}^{2+}$ . Relatively high  $\text{VO}^{2+}$  contents of both the  $<2 \mu\text{m}$  and  $\leq 2 \mu\text{m}$  clay-size fractions of III strongly support this view (NIKOLIĆ, 1992).

The behaviour of V in natural acid solutions is largely governed by the fact that it occurs in three stable oxidation states as V (III), V (IV), and V (V). These ions may be obtained in natural waters through weathering of magmatic rock by acid waters. These weathering solutions are evidently sufficiently acid ( $\text{pH} \leq 1$ ) to carry out appreciable amounts of  $\text{VO}^{2+}$ , but this ion is quickly oxidized by air oxygen (V<sup>3+</sup> even in acid medium) if the pH is raised ( $\text{pH} \geq 6$ ), as then it passes through the carbonate-rich rock layer or reaches seawater with high content of carbonate ions such as the Danish K/T seawater.

The III sample contains the highest organic matter (3%) and  $\text{VO}^{2+}$  (200 ppm) in the smectite fraction (Table 1a), suggesting that organic matter played an important role in

concentrating  $\text{VO}^{2+}$  in the clay fraction.  $\text{VO}^{2+}$  is usually associated with humic substances (i.e., humic and fulvic acids) which form soluble complexes with  $\text{VO}^{2+}$ . Terrestrial and/or marine humic substances may have played a significant role in the  $\text{VO}^{2+}$  transport and fixation through the III smectite column. As noted above, under typical aquatic conditions, the most stable form of V is generally vanadate ion:  $\text{VO}_4^{3-}$  (i.e.,  $\text{H}_2\text{VO}_4^-$ ,  $\text{HVO}_4^{2-}$ , and  $\text{NaHVO}_4^{2-}$ ). However, several authors have observed that humic substances reduce  $\text{VO}_4^{3-}$  to  $\text{VO}^{2+}$  in acid media accompanied by chelation (WILSON and WEBER, 1979). The fact that more than 50% of total V in the smectite fraction of the III sample or more than 25% of total V in the sediment is present as  $\text{VO}^{2+}$  (Table 1) strongly supports this humic concept. The abundance of PPS in the III sample lends further support to the reducing humic concept (PREMOVIĆ, 1992). In contrast to  $\text{VO}^{2+}$ , complexation with organic matter is not a major factor in determining the aquatic behaviour of  $\text{VO}_4^{3-}$  species (VAN DER SLOOT, 1976).

To obtain information about the fate of  $\text{VO}^{2+}$  ions migrating through the III and IV column, the  $\text{VO}^{2+}$  content was measured throughout the III and IV samples. Figure 5 shows vertical distribution of the normalized concentrations of  $\text{VO}^{2+}$  across III and IV. This indicates that the  $\text{VO}^{2+}$  concentration is the highest in the basal few millimeters of III decaying sharply across the section. These results indicate that the K/T event caused an abrupt change in the chemical environment and the high amounts of  $\text{VO}^{2+}$  and that humic substances are clearly linked with the event. The sudden and sharp drop in  $\text{VO}^{2+}$  content from III to IV (Fig. 5) is associated with marked fall in the organic matter content. Tentatively, it is suggested that during the deposition of IV the input of humic substances, mainly terrigenous-type (HANSEN

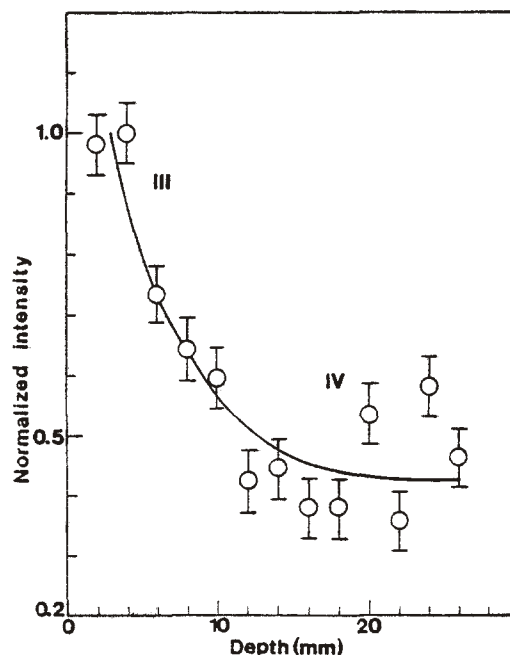


FIG. 5. The  $\text{VO}^{2+}$  profile across the III/IV boundary. Data are normalized to give depth 0 (mm) a value of 1.

et al., 1986, 1987), was considerably reduced or ceased to exist at all.

#### The $\text{VO}^{2+}$ Critical Boundary: $\text{VO}^{2+}$ Ion and $\text{FeS}_2$

Using published thermodynamic data (WAGMAN et al., 1982) the stability field of  $\text{VO}^{2+}$  ion, under atmospheric pressure and 300 K, can be plotted on a Eh (oxidation potential)-pH diagram. This field may be further restricted by superimposing the Eh-pH field for  $\text{FeS}_2$  (Fig. 6). Thermodynamic data used for the  $\text{FeS}_2$  field are also reported by WAGMAN et al. (1982). The total dissolved element concentrations in the construction of the  $\text{VO}^{2+}$  and  $\text{FeS}_2$  superimposition are those found in the average seawater as reported by GOLDBERG (1961) and later data, i.e., ( $\mu\text{g/L}$ ): V(1.6), Fe(0.04), and inorganic C (28000) and S ( $9.0 \times 10^4$ ).

The acidity of the seawater in which the III and IV sedimentation occurred and the interstitial seawaters in the sediments is unlikely to have varied outside the range pH 6 to 9 (buffering of carbonate ions  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ). Physicochemical conditions during the III accumulation are probably represented by the shaded area drawn on Fig. 6. Although this construction has been prepared for (arbitrarily) selected values for the total metal concentrations, the critical boundary is not significantly affected by modifying these values 10-fold in either direction. It is highly likely that relative concentrations of V and Fe in the III seawater at the K/T enrichment were at least one order of magnitude higher than their relative concentration in normal seawater of today. The shaded area of the diagram in Fig. 6 indicates the position of the critical  $\text{VO}^{2+}$  and  $\text{FeS}_2$  boundary for anoxic conditions. This boundary would be depressed to somewhat lower Eh and pH values with increase in the concentrations of these metals. Thus, the Eh and pH values for the coexistence of  $\text{VO}^{2+}$ ,  $\text{FeS}_2$ , and carbonate ions in the sedimentary realm in which accumulation of III occurred should be in the region of 0.0 V to -0.2 V and 6 to 7, respectively (Fig. 6). It must be recognized, however, that any predictions about the Eh-pH of sedimentation refer to conditions within the upper part of sediment

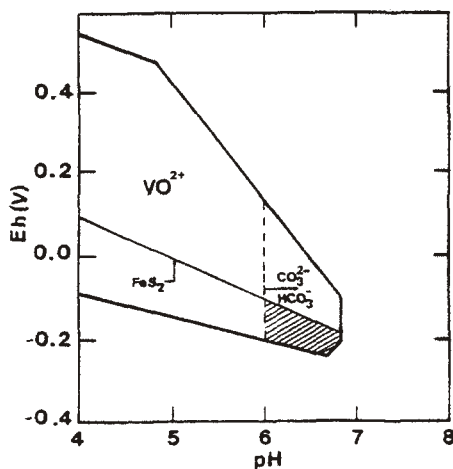


FIG. 6. Eh-pH stability fields for  $\text{VO}^{2+}$  and  $\text{FeS}_2$  at 300 K and 1 atm. Probable conditions in the sediment during the accumulation of III is represented by the shaded area.

accumulation. Many researchers demonstrated that the Eh values for interstitial waters in the upper part of sediment are below those at the seawater/sediment interface. On the other hand, the interstitial waters of sedimentation have a slightly higher pH than interfacial seawaters (GARRELS and CHRIST, 1965).

The results provide strong support for the view that physicochemical conditions during the III sedimentation were not materially different from those of common marine carbonaceous shales (SCHMITZ, 1985). This sediment was either deposited under anoxic conditions or soon after deposition the conditions became anoxic and hydrogen sulfide ( $\text{H}_2\text{S}$ ) was present within the sediment. The presence of  $\text{H}_2\text{S}$  in the overlying seawater itself could also be suggested. This reflects the sudden onset of strong anoxic conditions on the Stevns Klint seafloor after K/T event.

Chemical (Table 1a and b) and mineralogical analyses indicate that there are relatively small differences in chemical and mineral compositions between the III and IV samples, but there are some significant minor differences. The bed IV contains a notably lower content of  $\text{VO}^{2+}$ , organic matter (Table 1b),  $\text{FeS}_2$ ,  $\text{FeCO}_3$ , and PPS. This suggests that the physicochemical conditions of the IV sedimentation were probably less reducing and less acidic than those of III.  $\text{CaCO}_3$  is less abundant in III than IV (and in the Jylland boundary sequences; Table 1a and b).

#### Nye Kløv and Dania K/T Boundaries

X-ray analyses of deposits from the boundary sequences at Nye Kløv and Dania show that the boundary layers contain major mineral constituents: quartz, anatase, feldspar, and silicate glass. The Dania sediment also contains the minor authigenic mineral lepidocrocite ( $\gamma\text{-FeO}\cdot\text{OH}$ ). In contrast to the Fish Clay at Stevns Klint the Jylland boundary rocks show the absence of lamination, inferring extremely uniform sedimentation over a long period of time. The uniformity in thickness of the Danish boundaries over a distance of at least 300 km indicates that the deposited material came from a common source(s) at a considerable distance.

The absence of  $\text{FeS}_2$ ,  $\text{FeCO}_3$ , and PPS (NIKOLIĆ, 1992) in the Nye Kløv and Dania boundary samples and their low contents of organic matter (Table 1c and d) indicate oxidizing ( $\text{Eh} > 0$ ) and neutral to weak alkaline ( $7 \leq \text{pH} \leq 9$ ) physicochemical conditions of sedimentation. The presence of authigenic  $\gamma\text{-FeO}\cdot\text{OH}$  (as the Fe (III) mineral) in the Dania KT sample lends support to this conclusion. KRUMBEIN and GARRELS (1952) pointed out that this mineral occurs in sedimentary milieu under oxidizing conditions with Eh above +0.15 V.

The V concentrations in the Danish K/T smectite fractions are also given in Table 1. These values are much higher than those of average clays (130 ppm; TUREKIAN and WEDEPOHL, 1961) and suggest that either V in the source material of this smectite was greater than normal or its formation water was enriched by V. The V contents of the K/T smectite fractions from Danish localities show relatively small variation (Table 1). These materials were deposited in the same marine basin though separated by about 320 km (Stevns Klint-Nye Kløv), 220 km (Stevns Klint-Dania), and 100 km (Nye Kløv-



Dania). It seems that the smectite fractions of the Danish K/T sedimentary rocks, whatever their source, were derived from the alteration of similar material. Relatively small differences in the V contents between the Danish K/T smectite fractions suggest that perhaps local variables (such as physicochemical conditions of sedimentation, sedimentation rate, organic matter, depth, etc.) may not have played an important role in concentrating V. This also argues against (1) local source for the V enrichment, e.g., porewater leaching V from volcanic or terrigenous detrital material in the underlying Cretaceous limestone (SCHMITZ, 1985), and (2) the CaCO<sub>3</sub> (acid) dissolution pulse concept (EKDALE and BROMLEY, 1984).

#### Danish K/T Boundary Smectite and VO<sup>2+</sup>

Based on the SiO<sub>2</sub> analyses and chemical data in Table 1, we estimated that the noncarbonate fractions of the Danish K/T boundaries contain smectite: ca. 50% (III), 70% (IV), 40% (Nye Kløv), and 50% (Dania; Table 1). Of potential sources, we can immediately rule out the asteroid or comet itself, which, as was shown, is grossly inadequate in terms of global ejecta. This leaves only one possible source: detrital material. For this reason, we suggest that the bulk of Danish K/T boundary smectite is fine-grained products formed elsewhere (before K/T) and transported (during and after K/T) from their original sites to their K/T boundary sites. This is in harmony with the conclusion of various investigators (CHRISTENSEN et al., 1973; RAMPINO, 1982; SMIT and ROMEIN, 1985; WOLBACH et al., 1988; NAZAROV et al., 1988; ELLIOT et al., 1989). The characteristics of these clay deposits reflect the characters of the smectite clay redeposited from adjacent areas. In the case of Jylland boundaries, the seawater column and sea bottom were apparently air saturated. WEHRLI and STUMM (1989) have estimated that the half-life of VO<sup>2+</sup> adsorbed on the surface of Al hydrous oxides (the smectite surface) and hydrolyzed as VO(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub> in a such (oxygen-rich) milieu is a matter of day or so. According to MCBRIDE (1979), the ESR spectrum of hydrolyzed VO<sup>2+</sup> adsorbed on the smectite surface, such as VO(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>, became much weaker after several days' exposure of the clay to air, indicating the conversion of V from the +4 to +5 oxidation state. In general, because of its susceptibility to oxidation, VO<sup>2+</sup> is almost everywhere altered to VO<sub>4</sub><sup>3-</sup> in the oxidizing milieu (EVANS and GARRELS, 1958). We deduced that heating of the carbonate-free fractions of the Jylland K/T sediments in air even at 600 K did not produce any change in the VO<sup>2+</sup> ESR intensity. VO<sup>2+</sup> ions incorporated into the Jylland boundary smectite structure as VO(OH)<sub>2</sub> owed their stability to an inaccessibility to oxygen. It is logical, therefore, to conclude that VO<sup>2+</sup> in the Jylland boundaries is detrital in the sense of having been brought into the basin of deposition already located in the smectite crystal structure. On the other hand, the fact that only about 3% (Nye Kløv) and 10% (Dania) of total V in the Danish boundary sediments is present as VO<sup>2+</sup> indicates that most of these ions (initially located in detrital smectite) were released and altered into hydrated oxides and/or vanadates which may be adsorbed on the smectite particles or precipitated in CaCO<sub>3</sub> (EVANS, 1978). These V species are relatively

labile and as such soluble in cold HCl (Table 1). The release and associated alteration had to occur at an early stage of the Danish K/T sedimentation in the oxygen saturated bottom seawater of Jylland.

At least two mechanisms thus have been involved in determining the VO<sup>2+</sup> content of the Danish boundary rocks:

1) VO<sup>2+</sup> ions were present in the suspended smectite particles accumulating to form the Jylland K/T boundary deposits, but most of these ions were released and altered through corresponding chemical redox processes into oxides and/or vanadates; and

2) most of VO<sup>2+</sup> ions were formed (through the reduction of mobile VO<sub>4</sub><sup>3-</sup> by humic substances) in the III sedimentary milieu and adsorbed by the III and IV smectite from the overlying and/or interstitial waters during earlier diagenesis.

#### Chromium

Table 3 lists the Cr concentrations observed in the four K/T boundary sediments from Denmark. Because a negligible portion of Cr is derived from biogenic CaCO<sub>3</sub>, the relevant data are those corrected for CaCO<sub>3</sub> (Table 3). The Cr contents of the carbonate fractions of the Danish boundary rocks are relatively small (Table 3). It is likely that most of Cr (>75%; Table 3) resides in the smectite phase, in harmony with the conclusion of SCHMITZ et al. (1988). The maximum Cr content is in the Nye Kløv sediment containing no FeS<sub>2</sub> or FeCO<sub>3</sub>, implying that the bulk of Cr in the Danish boundaries is not associated with these two Fe minerals. These results infer that Cr was incorporated into the Danish boundary smectite from its formation water. In a strongly sedimentary reducing realm (similar to those of the III and IV deposition sites; Fig. 6) the bulk of Cr would exist as CrOH<sup>2+</sup> (BROOKINS, 1988). It appears likely that Cr in this form was incorporated into the Danish K/T smectite.

In aerated seawaters (such as those of the Nye Kløv and Dania formations) Cr is predicted to occur in the +6 oxidation state, primarily as HCrO<sub>4</sub><sup>-</sup> (BROOKINS, 1988). As a consequence, the Cr species involved in adsorption process in oxic milieu appear to be anionic, resulting in a relatively low affinity for the clay particles (KRAUSKOPF, 1956). We suggest, therefore, that most (if not all) of Cr in the Jylland boundary rocks is detrital, having been transported to the deposition site already contained in smectite. Thus, we suggest that the CrOH<sup>2+</sup> (as VO<sup>2+</sup>) incorporation was an event that just preceded the redeposition of this smectite into the Jylland boundary basins.

The chemical analyses of III and IV indicate that there is a good correlation between Cr and Al. The Cr/Al ratio of these rocks ranges from  $1.0 \times 10^{-2}$  to  $1.2 \times 10^{-2}$  (NIKOLIĆ, 1992), and, even taking account of determinative errors in the Al and Cr contents, it is likely that this ratio could be considered constant, as would be expected if the bulk of Cr (as CrOH<sup>2+</sup>) was already present in smectite transported to the Stevns Klint basin of sedimentation. SCHMITZ et al. (1988) suggested that the process of the HCl leaching Cr in III followed the course of Mg. The Cr/Mg ratio of III and IV is rather constant, ranging from  $6.4 \times 10^{-3}$  to  $9.4 \times 10^{-3}$  (NIKOLIĆ, 1992). This is a further support that most of Cr is detrital and located in the smectite structure. Some minor

Table 3. Geochemical distribution of Cr ppm, Ni ppm, Co ppm, Ga ppm and Fe %<sup>a,\*</sup>.

| (a) III                | Sediment (wt%) | Cr  | Ni   | Ni/Cr | Co   | Ga  | Fe   |
|------------------------|----------------|-----|------|-------|------|-----|------|
| Acetate buffer         | 53             | 10  | 300  | —     | 30   | 1   | 0.10 |
| Boiling-HCl            | 19             | 550 | 1315 | —     | 130  | 20  | 5.50 |
| Smectite <sup>b</sup>  | 28             | 380 | 900  | 2.4   | 90   | 15  | 3.80 |
| Sediment <sup>b</sup>  | 100            | 110 | 405  | 3.7   | 40   | 4   | 1.2  |
| Corrected <sup>c</sup> | 47             | 230 | 860  | 3.7   | —    | —   | —    |
| (b) IV                 |                |     |      |       |      |     |      |
| Acetate buffer         | 79             | 10  | 55   | —     | 15   | 1   | 0.08 |
| Boiling-HCl            | 10             | 500 | 900  | —     | 100  | 30  | 5.00 |
| Smectite <sup>b</sup>  | 18             | 280 | 500  | 1.8   | 55   | 15  | 2.70 |
| Sediment <sup>b</sup>  | 100            | 60  | 135  | 2.3   | 20   | 4   | 0.70 |
| Corrected <sup>c</sup> | 21             | 290 | 645  | 2.3   | —    | —   | —    |
| (c) Nye Kløv           |                |     |      |       |      |     |      |
| Acetate buffer         | 69             | 60  | 15   | —     | 30   | 20  | 0.05 |
| Boiling-HCl            | 10             | 750 | 2800 | —     | 2500 | 150 | 5.00 |
| Smectite <sup>b</sup>  | 16             | 470 | 1800 | 3.7   | 1600 | 95  | 3.00 |
| Sediment <sup>b</sup>  | 100            | 115 | 295  | 2.7   | 280  | 30  | 0.90 |
| Corrected <sup>c</sup> | 31             | 370 | 950  | 2.6   | —    | —   | —    |
| (d) Dania              |                |     |      |       |      |     |      |
| Acetate buffer         | 75             | 15  | 10   | —     | 10   | 15  | 0.11 |
| Boiling-HCl            | 8              | 380 | 875  | —     | 65   | 125 | 8.00 |
| Smectite <sup>b</sup>  | 16             | 190 | 440  | 2.3   | 35   | 65  | 4.10 |
| Sediment <sup>b</sup>  | 100            | 45  | 80   | 1.8   | 15   | 20  | 0.85 |
| Corrected <sup>c</sup> | 25             | 180 | 320  | 1.8   | —    | —   | —    |

<sup>a</sup>The metal content determined by AAS.

<sup>b</sup>The sediment metal obtained by summation of fraction metal concentrations determined by AAS.

<sup>c</sup>Corrected for CaCO<sub>3</sub>.

\*Metal content in the HF fractions are less than 5% of total metal.

Cr (as CrOH<sup>2+</sup>) in the III and IV smectite phases appears to have been incorporated into these materials from overlying and/or interstitial seawaters of the Stevns Klint boundary. The Cr contents of the Danish boundary smectite range from 190 ppm (Dania) to 470 ppm (Nye Kløv; Table 3). These values are higher than the average content (90 ppm) in clays quoted by TUREKIAN and WEDEPOHL (1961).

#### Nickel

The Ni contents of the Danish K/T boundary sediments vary from 45 ppm (Dania) to 115 ppm (Nye Kløv; Table 3). The most striking feature of the Ni distribution in various fractions of these rocks is that the high proportion of the total Ni resides in the carbonate portions of III (38%; Table 3a) and IV (34%; Table 3b). It appears likely that its location is in CaCO<sub>3</sub> (Ni<sup>2+</sup> proxying for Ca<sup>2+</sup>) and/or in FeCO<sub>3</sub> (proxying for Fe<sup>2+</sup>). The maximum carbonate Ni<sup>2+</sup> occurs in III (300 ppm; Table 3a) containing both highest organic material (Table 3) and FeS<sub>2</sub>. It is suggested therefore that organic (humic) substances and/or FeS<sub>2</sub> played some role in the process of incorporation of Ni<sup>2+</sup> into the carbonate minerals of III through the adsorption of this ion from the seawater. The nature of this process remains in doubt until further data become available. The relatively high Ni content

in the boiling HCl-soluble fraction of III may indicate that Ni is associated with organic matter and/or FeS<sub>2</sub>. The relatively high Ni content of the boiling HCl-soluble part of Nye Kløv (containing minor amount of organic matter, Table 3c, and no FeS<sub>2</sub>), however, cannot be attributed to this cause. For this reason, we suggest that much Ni in the Danish boundaries must be located in smectite as Ni<sup>2+</sup>.

The Ni/Cr ratio for III (3.7; Table 3a) falls around the value for C1 chondrites (4.3; GILMORE et al., 1984); however, the Ni/Cr ratios for IV and the Jylland boundaries are distinctly lower than this value (Table 3b, c, and d). Figure 7 shows vertical distribution of the normalized values of Cr (a), as well as the Ni/Cr profile (b) across III and IV. Likewise, in the VO<sup>2+</sup> profile given in Fig. 5, incompatible amounts of Cr and high Ni/Cr value (6.3; close to the value for C1 chondrites, 4.3) of the basal 4 mm rapidly decrease upwards. SMIT and TEN KATE (1982) attributed this "tailing effect" to the secondary runoff from other (primary) fallout deposits.

#### Cobalt

Table 3 shows the distribution of Co among the four components of the Danish boundary rocks. The results show that the carbonate fractions of III, IV, and Dania contain 38, 50,

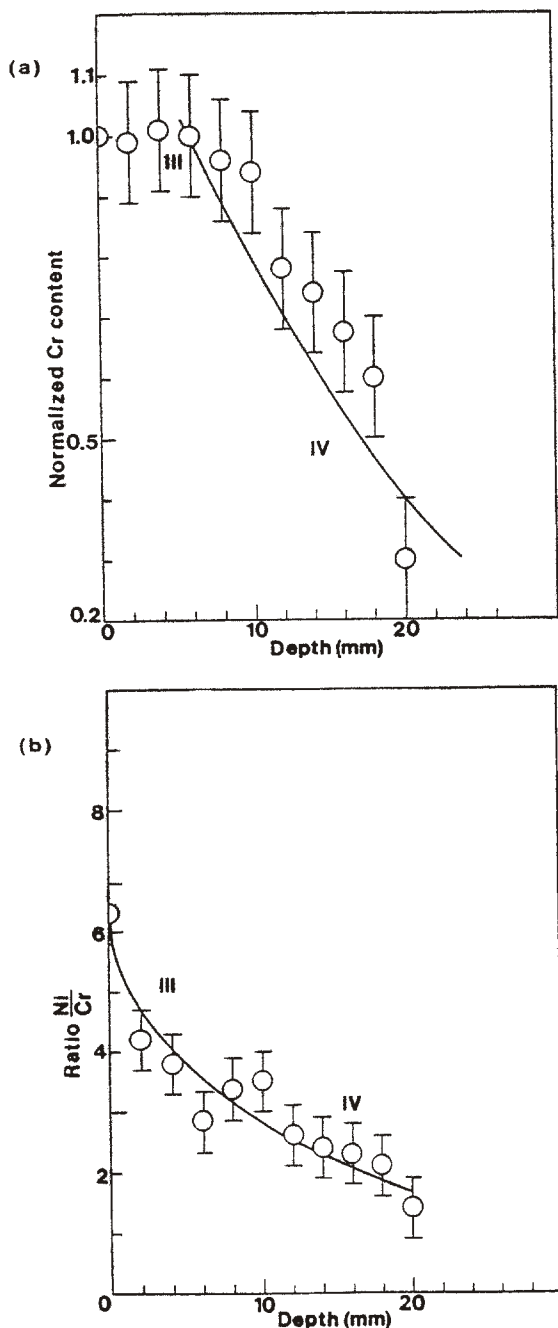


FIG. 7. Distribution of Cr (a): data are normalized to give depth 0 (mm) a value of 1; and the Ni/Cr ratio (b) across the III/IV boundary.

and 50% of the total Co, respectively. It is clear that the considerable proportion of this Co must be present in  $\text{CaCO}_3$  as  $\text{Co}^{2+}$ . It is highly likely that most of  $\text{Co}^{2+}$  in  $\text{CaCO}_3$  of these rocks is adsorbed from seawater. The carbonate fraction of the Nye Kløv sample contains only 8% of the Co (Table 3c). This indicates that the bulk of Co in the Nye Kløv rock resides in the smectite part. On the other hand, there is no evidence of any relationship between the contents of the noncarbonate Co and the contents of organic matter or  $\text{FeS}_2$  of the Danish boundaries, and it is clear that the bulk of this Co must be

present in the smectite material. Though siderophiles are enriched at selected K/T boundaries worldwide, Co is considered to be largely of terrestrial origin (STRONG et al., 1987).

Under the deduced physicochemical conditions of sedimentation of III and IV, Ni and Co may be present in solution only as sulfides:  $\text{NiS}$  and  $\text{CoS}$  (BROOKINS, 1988). If this is true then it is reasonable to conclude that (1) the bulk of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  in the smectite portions of III and IV is detrital; and, in addition, (2) the bulk of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  in the carbonate minerals ( $\text{CaCO}_3$  and  $\text{FeCO}_3$ ) of these sediments may be strictly detrital in nature. This may suggest that substantial proportions of the carbonate minerals are also detrital; i.e., they were transported into the basin of sedimentation of III and IV, which occurred simultaneously with redeposition of smectites. At present, this can be no more than a suggestion, but it is important to consider the total sedimentation conditions in any attempt to interpret the distribution of trace elements in any K/T boundary. Under oxic conditions (such as those of Nye Kløv and Dania) the bulk of Ni and Co in normal seawater ( $\text{pH} \sim 8$ ) should be present as  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  (BROOKINS, 1988).

#### Gallium

The Ga contents of the Danish boundary rocks range from 4 ppm (III) to 30 ppm (Nye Kløv; Table 3). Considerable quantities reside in the carbonate portions, though never more than 45% of the total Ga content (Table 3). Clearly, they were adsorbed from the seawater by  $\text{CaCO}_3$ . The excess of this metal would appear to be associated with smectite fraction. The fact that Ga is strongly diadochic with Al in nature (BROOKINS, 1988) suggests that (1) most, if not all, of  $\text{Ga}^{3+}$  is proxying for Al in the smectite structure, and (2) it is more probable that much of the Ga is strictly terrestrial in origin and detrital in character. The Ga contents of the carbonate portions of III and IV are rather low (1 ppm), and their smectite counterparts are twenty times higher. This is contrasted with the situation found in the Jylland sequences. The Ga in the carbonates varies from 15 ppm (Dania) to 20 ppm (Nye Kløv; Table 3). The Ga contents of their smectite fractions are rather high, ranging from 85 ppm (Dania) to 125 ppm (Nye Kløv; Table 3). These values are much higher than those recorded in the literature for argillaceous rocks: e.g., averages (19 ppm; TUREKIAN and WEDEPOHL, 1961). Finally, regardless of physicochemical conditions of sedimentation ( $E_h > 0$  or  $E_h < 0$ , i.e., oxic vs. anoxic milieu) in normal seawater, the bulk of Ga is present as  $\text{Ga}^{3+}$  ion.

#### Iron

Contents of this metal are high, and they are within the range 7000 ppm (IV) to 12000 ppm (III; Table 3). The contents of carbonate Fe are low ( $\leq 13\%$ ), and minor amounts of this element ( $< 5\%$ ) are present as  $\text{FeS}_2$  (III and IV) and as  $\gamma\text{-FeO}\cdot\text{OH}$  (Dania). Thus, the bulk of Fe ( $> 70\%$ ) must reside in the smectite material. An independent analysis of  $\text{Fe}_2\text{O}_3$  in III is in substantial agreement with this conclusion (SCHMITZ et al., 1988). The Fe contents of the Danish boundary smectites (Table 3) range between 2.7% (IV) to 4.1% (Nye Kløv); thus, these materials belong to the class of the so-called Fe-rich clays (COLE, 1985). Our chemical

and structural analyses of Fe in these clays indicate that most of this element is incorporated as  $\text{Fe}^{3+}$  into basic smectite skeleton (NIKOLIĆ, 1992). Very high Fe concentrations and their relatively small variations do accord with the detrital hypothesis for the Danish boundary smectite which was transported from its original (formation) site and was ponded in the Danish K/T boundary basins.

### Metal Enrichment of the Danish Boundary Smectites

From the preceding consideration of the distribution of Fe, Cr, Ni, Co, Ga, and their corresponding ions it appears that by lateral transport of the fine-grained smectite particulates, containing  $\text{Fe}^{3+}$ ,  $\text{CrOH}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ga}^{3+}$ , the bulk of these metals is distributed to the Danish K/T boundaries. After settling on the seafloor, detrital smectite and biogenic  $\text{CaCO}_3$  (especially those at Stevns Klint) may also scavenge additionally some of these metal ions.

Cr, Ni, Co, and V are present in the Danish K/T boundary smectite in concentrations considerably in excess of those in average smectite (CRONAN, 1969). Some elements, e.g., V, are only modestly enriched. Others, such as Cr, Ni, and Co, are strongly enriched (especially in Nye Kløv). The pattern of enrichment is similar to that found in recent and ancient metalliferous clays (HEATH and DYMOND, 1981). Although the majority are detrital, a significant proportion of the Fe-rich smectites are formed authigenically in the marine sediments. Three principal modes of formation are apparent for these smectites in recent marine sediments:

1) chemical interaction between biogenic  $\text{SiO}_2$  and Fe-oxyhydroxide at low temperature:

2) alteration of volcanic materials; and

3) direct precipitation from hydrothermal solutions (MILLOT, 1970).

The presence of labradorite (ELLIOT et al., 1989) and anatase (SPEARS and KANARIS-SOTIROU, 1979) in III would imply that the Danish boundary clay represents volcanoclastic material (probably ash along with some L.W.A. asteroid impact and local contributions) that subsequently weathered to the metalliferous smectite at original (marine) sites before the K/T event. Immediately after the K/T event this smectite was redeposited to the Danish K/T boundary sites.

Fine-grained, vitreous, volcanic debris is generally accepted as the source of the smectite clay. Devitrification and leaching of these materials as well as formation of smectite from this debris is likely in  $10^4$  to  $10^6$  years (MILLOT, 1970). Thus, we suggest that formation of the Danish K/T boundary smectite (at its original formation site) had probably occurred during a short period of time geologically, relatively soon

( $10^4$  to  $10^6$  years) after the volcanism that produced bed(s) of volcanoclastic rocks. If this concept is correct then it is likely that this volcanism was an event which preceded the K/T L.W.A. asteroid impact for at least  $10^4$  to  $10^6$  years. Recently, SCHMITT et al. (1991) proposed that intense, large scale volcanism before and after the K/T event, such as the Deccan Traps in India, may be responsible for metal enrichments of Shatsky Rise sedimentary rocks in the vicinity of the K/T boundary. These authors suggested that the dynamic atmospheric conditions and associated acidic rain generated by the Deccan-like volcanism would have increased surficial weathering, resulting in increased eolian inputs of clay and other fine detrital materials (including metals) to aquatic basins. Accordingly, the L.W.A. asteroid(s) impacts would generate climatic and weathering processes similar to those of Deccan volcanism. These researchers also reported that in addition to the metal (including Ir) enrichment peaks at the Shatsky Rise K/T boundary, metal enrichment peaks at ca. 0.2 Ma before K/T and several peaks ( $\geq 0.3$  Ma) after K/T were defined which exhibited no Ir enrichment peaks. Thus, if the multiple Deccan concept is correct, we suggest that most of the Danish K/T smectite clay (rich in V and other metals) is formed at its original site during the Deccan volcanic event at ca. 0.2 Ma before K/T. Recent  $^{40}\text{Ar}/^{39}\text{Ar}$  dating of K/T boundaries and Deccan Trap volcanics indicates that Deccan volcanism began before the K/T boundary event (MCWILLIAMS et al., 1992), which lends support to the proposed scenario.

### Non-Danish K/T Layers

The best evidence of the asteroid(s) impact concept, as noted, is the Ir enrichments found in  $>50$  K/T boundary clays from all over the world (ALVAREZ et al., 1984). In addition to the Stevns Klint (III) K/T sequence, we selected five boundary sites for which the trace V analyses were available (Table 4). The main criterion of selecting these sites is an Ir enrichment in the boundary clays by at least a factor of 5 at the majority of these sites (ALVAREZ et al., 1984).

The six highly metal-enriched boundary clays show striking similarities in sedimentology; all six boundary clays are associated with carbonate in forming gray-to-black shales enriched with pyrite, organic matter (SMIT and TEN KATE, 1982; GILMORE et al., 1984; KASTNER et al., 1984), and Ir (Table 4). The V contents of the K/T boundary layers do not show large variations: 112 ppm (Stevns Klint) to 210 ppm (Gubio, Italia; Table 4). Thus, it is reasonable to assume that even on the global scale local variables (sedimentation rate, marine vs. fresh water chemical environment, organic matter, etc.)

Table 4. Enriched Ir and V in bulk KT boundary clays.

| Locality     | Ir(ppb) | V(ppm)  | Reference               |
|--------------|---------|---------|-------------------------|
| Stevns Klint | 47.4    | 112     | Schmitz, 1985           |
| Caravaca     | 24.3    | 149     | Smit and ten Kate, 1982 |
| Biarritz     | 12      | 95.7    | Smit and ten Kate, 1982 |
| Gubio        | 9.1     | 210     | Alvarez et al., 1980    |
| Sugarite     | 3.2     | 175     | Gilmore et al., 1984    |
| Raton Basin  | 1.7     | 110-187 | Gilmore et al., 1984    |

may not have affected the process of concentrating V in the K/T sediments.

## CONCLUSIONS

From the results and considerations given in this paper the following conclusions can be drawn:

- 1) Most of V in the Danish boundaries is derived from terrestrial sources: crust or mantle. All  $\text{VO}^{2+}$  (determined by ESR) resides in the smectite structure of these rocks, probably as  $\text{VO}(\text{OH})_2$ . In the III and IV smectites, most of these ions were formed and adsorbed by the clay from the (overlying and/or interstitial) seawaters. These occurred under reducing physicochemical conditions of sedimentation through a chemical reduction of mobile  $\text{HVO}_4^{2-}$ ,  $\text{H}_2\text{VO}_4^-$ , and  $\text{NaHVO}_4^-$  ions to  $\text{VO}^{2+}$  by humic substances. The Eh and pH values for the coexistence of  $\text{VO}^{2+}$ ,  $\text{FeS}_2$ , and the carbonate ions in the III sedimentary milieu should be in the region of 0.0 V to -0.2 V and between 6 to 7, respectively. The boundaries at Nye Kløv and Dania were deposited in an oxic sedimentary realm with Eh > 0 and pH ≥ 7.
- 2) The main geochemical features of the Danish boundary smectite are relatively high concentrations of Fe, Cr, Ni, Co, and Ga. These metals are incorporated into the smectite structure mostly as  $\text{Fe}^{3+}$ ,  $\text{CrOH}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ga}^{3+}$ . The bulk of these ions in the Danish boundary clay are detrital in character; i.e., these ions were already present in the smectite which was redeposited into the basins of K/T boundary sedimentation.
- 3) Metal enrichment of the Danish K/T boundary smectite is characteristic for metalliferous clays. It is suggested that this smectite is detrital and was formed at the original site through weathering of volcanoclastic material along with some asteroid and local material. After the K/T event, the Danish boundary smectite was eroded from the original marine site and redeposited to the Danish K/T boundary sites.

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