

## Iron, manganese, vanadium, copper and zinc of the Cretaceous-paleogene boundary fish clay at the Kirkevig site (Højerup, Stevns Klint, Denmark)

M. G. Đorđević, P. I. Premović\*

Laboratory for Geochemistry, Cosmochemistry & Astrochemistry, University of Niš, P.O. Box 224, 18000 Niš, Serbia

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The marine shallow Cretaceous–Paleogene boundary (KPB) sections at Kirkevig consist of a very thin reddish smectite-rich carbonate-poor ejecta layer overlain by black marl. Similar sections with a thin reddish layer are found in other KPB sites at Stevns Klint. The metal oxide fractions of the ejecta layer have a relatively high Fe concentration (0.03 %) and trace concentrations of: Mn (30 ppm), Cu (45 ppm) and Zn (850 ppm). Most of these metals are located in this fraction: Fe (90 %), Mn (85 %), Cu (80 %) and Zn (90 %). Trace Mn, Cu and Zn were probably absorbed on the Fe oxides present. It is speculated that most of the Fe oxides were sourced by the chondritic component of the impact fallout. The smectite fraction includes lower Fe (10 %), Mn (15 %), Cu (10 %) and Zn (5 %) contents but a high V (90 %) content. This component is most likely of local (marine or terrestrial) provenance and was probably redeposited, after its formation, from the original site to its present location. The carbonate fraction of the ejecta layer shows minor concentrations of these metals.

**Keywords:** Cretaceous–Paleogene boundary, Ejecta layer, Trace metals, Smectite

### INTRODUCTION

In their seminal paper, Alvarez *et al.* [1] reported anomalously high Ir in the Cretaceous-Paleogene boundary (KPB) clays from Italy (Gubbio), Denmark (Stevns Klint) and New Zealand (Woodside Creek). According to these authors, this enhanced Ir concentration was produced by a large asteroid impact in the late Cretaceous that was probably largely responsible for one of the greatest biological extinctions in Earth history. It has been suggested that the impactor was a C1 chondrite-type body [2] and the impact occurred at Chicxulub (Yucatan Peninsula, Mexico) [3].

The Fish Clay is a thin grey-to-black marl forming KPB at Stevns Klint (eastern Denmark), Fig.1a. Here it occurs in small marine basins between the Cretaceous white chalk and the overlying calcareous Tertiary formation. The most prominent sites of the Fish Clay at Stevns Klint are near village of Højerup. Alvarez *et al.* [1] studied this clay from the most famous site near the Højerup old Church.

The Kirkevig boundary section is similar to the neighboring Højerup Church section in lithology. The Kirkevig boundary section is comprised of a dark clay with a basal Fe-rich (ejecta) red layer (Fig. 1b). The lower "reddish" unit (red layer) of this clay would be informally called the "ejecta layer" and the upper overlying "darkish" unit (black marl)

- the "boundary layer". The ejecta and boundary layers at Kirkevig are up to about 0.5 cm and up to 3 cm thick, respectively, (Fig. 1b). The contact between these two layers is generally sharp and records a significant change in depositional regime. Ejecta layer is underlain by a Maastrichtian bryozoan-rich chalk and the boundary layer is overlain by the lower Danian (Cerithium) limestone. In general, the Ir anomaly of the prominent marine and continental KPB clays is largely concentrated in the ejecta layers. Our preliminary results indicate that Ir is relatively abundant (ca. 15 ppm) in the ejecta layer of Kirkevig.

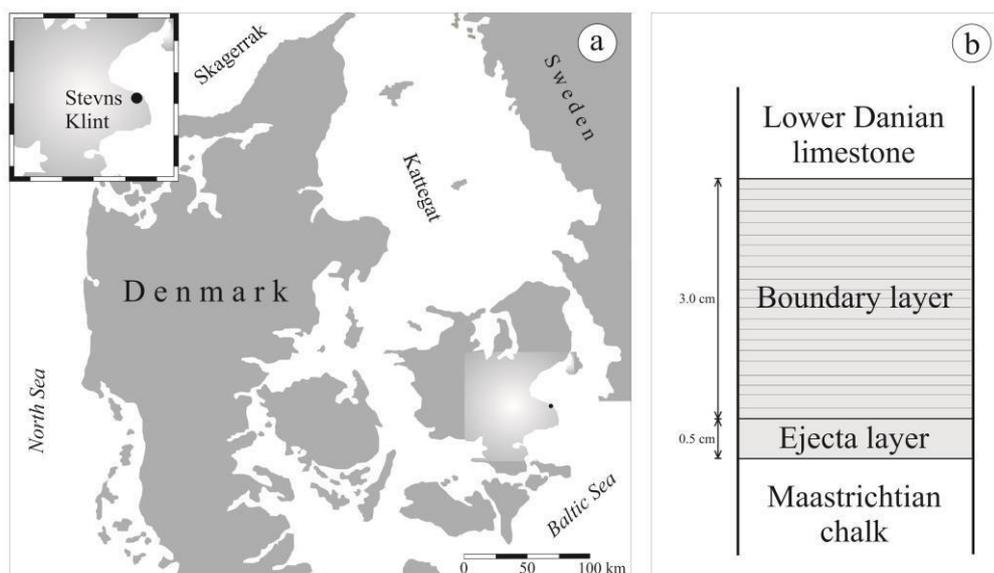
In this paper we focus our attention on Fe, Mn, V, Cu and Zn in the ejecta layer of the Kirkevig boundary section (hereinafter KEL) for which otherwise there are no previously published geochemical data. Essentially, this paper is complementary to our previous studies [5-7].

### EXPERIMENTAL

#### *Spectrochemical instrumentation*

*Inductively coupled plasma–optical emission spectroscopy (ICP–OES) analysis.* The various fractions of KEL were analyzed for Fe, Mn, V, Cu and Zn by a Spectroflame ICP–OES instrument using Ar as the plasma gas.

\* To whom all correspondence should be sent:  
E-mail: pavle.premovic@yahoo.com



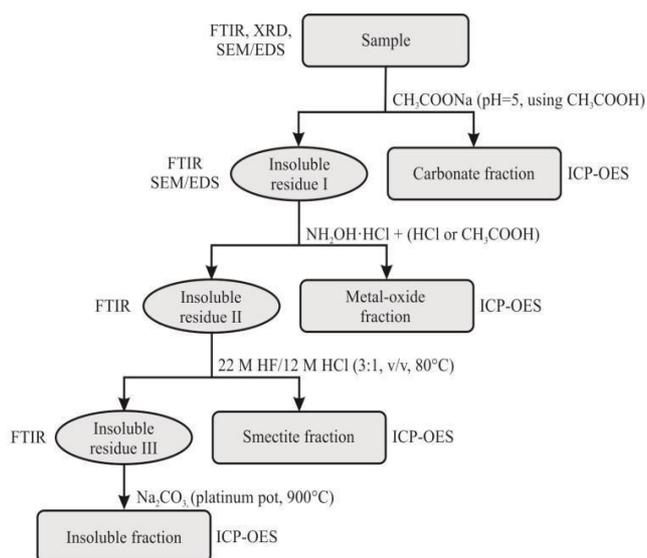
**Figure 1.** a) Geographic location map of the Fish Clay samples from Stevns Klint; b) a simplified lithological column of the KPB section at Kirkevig.

Relative error in the precision of the analyses ranged from 5 to 10 %. Total uncertainties (including accuracy errors) were up to 20 %.

**X-Ray diffraction (XRD) analysis.** XRD patterns were obtained with a Siemens D500 vertical goniometer using  $\text{CoK}\alpha$  radiation (35 kV, 20 mA). Powder diffractograms were acquired in the  $4\text{--}75^\circ 2\theta$  range, with 7–20 s counting per  $0.02^\circ 2\theta$  step. The samples were prepared using the back-loading procedure according to Moore and Reynolds [6], which provides significant disorientation of the clay layers.

**Fourier transform infrared (FTIR) spectrometry.** FTIR spectra were recorded in the absorbance mode using a BOMEM Michelson Series MB FTIR spectrometer set to give undeformed spectra. The resolution was  $4\text{ cm}^{-1}$  in the  $400\text{--}4000\text{ cm}^{-1}$  analyzed range. The spectra were obtained at room temperature from KBr pressed pellets prepared by mixing 1.5 mg of a KEL fraction (see below) sample with 150 mg of KBr.

**Scanning electron microscopy (SEM)-energy dispersive spectrometry (EDS).** All SEM-EDS work was carried out using a scanning microscope Philips XL 30 ESEM/TMP, coupled to an energy-dispersive spectrometer (EDAX type Sapphire). The backscattered electron (BSE) mode was done before microprobing. Analytical conditions were as follows: accelerating voltage 15 or 20 kV, probe current 60 nA, working distance *ca.* 1 cm, counting time 100 s. Individual parameters: acceleration of electron beam and magnification are printed on the photos. Samples were coated with gold and stuck to a carbon tape.



**Figure 2.** Flow chart of the selective extraction procedure.

### Analysis and fractionation

The modified fractionation procedure (selective extraction) of KEL was similar to that used by Premović [8], Tessier *et al.* [9] and Zakiri [10]. The flow chart in Fig. 2 outlines the major steps in preparing its four fractions.

Thus, powdered sample (1 g) was treated (room temperature, 12 h) with Na acetate using acetic acid (1 M, pH 5.0) to remove most of the carbonates. The soluble material constitutes the carbonate fraction. Carbonate removal was checked by FTIR/SEM-EDS analyses.

The insoluble residue (II) was demineralized with boiling hydrofluoric/hydrochloric acid HF/HCl

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(22 and 12M, respectively, 3:1 v/v, 80 °C, 12 h). This acid mixture removes SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

The removal of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> was checked by FTIR analysis. The soluble part constitutes the smectite fraction or phase.

The insoluble residue (III) was demineralized by annealing using sodium carbonate at high temperature (900 °C). The soluble part constitutes the insoluble fraction.

## RESULTS AND DISCUSSION

*Demineralization and ICP–OES analysis.* The first demineralization step (CH<sub>3</sub>COONa) removed only 10 wt. % of KEL. This mass loss was due to the total dissolution of carbonates. The second demineralization step (NH<sub>2</sub>OH-HCl) removed 35 wt. % of the sample, mainly Fe oxides. SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, the dominant constituents of the sample seem to have been unaffected by the demineralization steps. Geochemical analysis also indicated that 50

wt. % of the sample is the smectite fraction which was removed by the HF/HCl step.

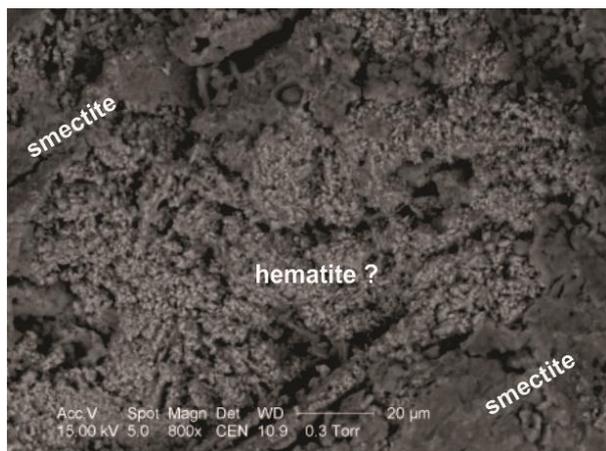
*Iron.* Simple chemical analyses showed that KEL is composed of carbonate (10 %), metal oxide (35 %), smectite (50 %) and insoluble (5 %) components. The distribution of Fe among these four fractions is also given in Table 1. This table shows that Fe was relatively abundant (0.03 %) and that about 90 wt. % of this metal was associated with the metal oxide phase. Indeed, the SEM-EDS analyses of KEL show also abundant presence of Fe oxides, probably hematite, Fig. 3.

The insoluble residue (I) was further demineralized by repeated treatment with hydroxylammonium chloride (NH<sub>2</sub>OH·HCl) in 0.25 M HCl and 25 % CH<sub>3</sub>COOH. This treatment removed metal oxides, including amorphous and crystalline Fe-oxides. The soluble part constitutes the metal-oxide fraction.

**Table 1.** Geochemical distribution of Fe, Mn, V, Cu and Zn in the sample fractions

Metal		Total	Carbonate	Oxide	Smectite	Insoluble
		[%]	[ppm]	[%]	[%]	[ppm]
Fe	ppm	0.03	<1	0.03	0.003	<1
	%	100	<1	90	10	<1
Mn	ppm	35	<1	30	5	<1
	%	100	<1	85	15	<1
V	ppm	110	<1	10	100	<1
	%	100	<1	10	90	<1
Cu	ppm	55	<1	45	5	5
	%	100	<1	80	10	10
Zn	ppm	940	40	850	45	5
	%	100	5	90	5	<1

Abundant Fe oxides in KEL indicate that its deposition probably occurred under well (aerated) oxygenated conditions.



**Figure 3.** SEM micrographs of Fe oxide (probably hematite) and smectite phase.



**Figure 4.** SEM micrographs of probably goethite-rich microspherules.

Premović [11] hypothesized that the massive amount of Fe oxides of the ejecta fallout is generated by the Chicxulub chondritic impactor. Indeed, SEM-EDS analyses of KEL show a presence of few Fe-oxide (probably goethite) microspherules, Fig. 4. Similar microspherules were found in Fish Clay near the Højerup Old Church which is interpreted to be derived from the Chicxulub impact fallout [12].

Premović [11] estimated that global fluency of Fe-oxides derived from the chondritic Fe was approximately  $20 \text{ g cm}^{-2}$ . He speculated that most of these oxides were probably originally deposited on the local (topographically high) oxic soils and then laterally transported to the KPB sites by the impact induced surface (acid?) waters. Indeed, Schmitz [13] reported that the ejecta layers at two of the worldwide most prominent KPB sites at Caravaca (Spain) and at Woodside Creek (N. Zealand) contain about 5 % of Fe. As KEL, both of these layers are

formed under well oxygenated conditions. For comparison, KEL contains about 8 % of Fe. This is about 10 times higher than in their underlying decarbonated latest Maastrichtian and overlying lower Danian limestone.

**Manganese.** Mn range in KEL is predominantly (85 %) associated with the metal oxide fraction. In a well oxygenated environment Mn geochemically behaves similar to Fe [14]. In this case, Mn shows only IV oxidation state, forming mainly oxide  $\text{MnO}_2$ . It is highly likely that in this form Mn is associated with the metal oxide fraction of KEL probably absorbed by its Fe oxides.

**Vanadium.** KEL contains a relatively high concentration (110 ppm) of V, Table 1. Most of this V (90 %) is incorporated within the smectite structure. The KEL vanadium content is comparable to the vanadium contents of ejecta layers of other Danish boundary rocks [5]. The study by Premović *et al.* [11] indicates that the smectite component of these rocks is most likely of local (marine or terrestrial) provenance and was probably redeposited, after its formation, from the original site to its present location. So there is no reason to believe that smectite of the Kikevig boundary section would be of different origin.

**Copper and Zinc.** We primarily selected to analyze KEL for Cu and Zn because of their distinctive (but relatively simple) geochemical activities and properties. Indeed, Zn and Cu show a similar geochemical behavior in sedimentary environments, which is distinctively different from the geochemical behavior of Fe and V [14].

Table 1 lists the KEL concentrations of Cu (55 ppm) and Zn (940 ppm). The concentration of Zn is much higher than the Zn content in the sedimentary rock which ranges from 100 to 120 ppm [14]. This table also shows that most of Cu (80 %) and Zn (90 %) reside in the metal oxide fraction containing mainly Fe oxides. They are most likely absorbed on these oxides.

## CONCLUSIONS

Main carrier of Mn, Cu and Zn in KEL is its metal oxide component enriched with Fe (0.03 %). These trace metals were probably adsorbed on the Fe oxides. Most V is associated with the KEL smectite component. This component is most likely of local (marine or terrestrial) origin and was probably redeposited, after its formation, from the original site to its present location.

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