# Geochemistry of Ni, Co and Zn in the Calcite Fraction of Organic Rich Layer at Cretaceous - paleogene Boundary from Caravaca (Spain)

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*Except the enhanced content of total meteoritic Ni (130 ppm), non meteoritic Co (35 ppm) and Zn (105 ppm) in the Caravaca KPB organic rich layer exists and relatively high concentration of these metals in the carbonate/calcite fraction. Geochemical analysis of the toxic Ni, Co and Zn in the carbonate fraction KPB layer at Caravaca (Spain) were undertaken. These metals were chosen primarily because of their relatively simple chemistry in natural waters and a similar geochemical behaviour. In a general discussion of the results, a geochemical model is describing the incorporation of Ni (70), Co (40) and Zn (55 ppm) in the biogenic calcite. We propose that most of the Ni, Co and Zn in this fraction of organic rich layer from Caravaca is of biological Ni, Co and Zn, i.e. the direct biochemical incorporation into the shells of calcerous microbiota during their metabolic uptake of seawater. Also, the origin of Ni is determineted as probably meteoritic, while Co and Zn are mainly of terrestrial origin.*

*Keywords: Cretaceous-Paleogene, Caravaca, calcite, geochemistry*

The study of trace metals in ancient sediments is important because on the basis of their geochemistry it is possible to reveal ancient geochemical records from the history of the planet Earth. Thanks to such studies of Ir in the Cretaceous-Paleogene boundary layers (KPB), it was revealed that the asteroid impact was most likely, the cause of the last major biological crisis [1]. Apart from well-know “Ir anomaly”, the world-wide KPB sedimentary rocks are enriched in other trace metals including Ni, Co and Zn [2-4].

The Caravaca KPB is marked by a 12-15 cm thick grey marl with a basal 1-3 mm thick rust-red layer, which contains the impact evidence. The mineralogy of the marl is comparatively simple, authigenic calcite, clays and quartz. Clay mineral assemblages also consist of smectites, illite and kaolinite [5, 6]. Lithostratigraphy of KPB layer was described by Schmitz [3]. This author has distinguished three important distinctive layers within this boundary section. The second layer is subdivided into a distinct rust-red layer (which was not analyzed, due to lower amount of biogenic calcite) at the base of the Danian and an organic rich layer (enriched in biogenic calcite).

The possibility of harmful (toxic) effects of heavy metals found in KPB calcite micro-organisms (carbonates; foraminifera) from Fish Clay (Stevns Klint; Denmark) was pointed by Premović et al. [7]. According to these authors trace metals, including Ni, Co and Zn, associated with the KPB at Stevns Klint show that one part of these metals is incorporated into biogenic calcite. A study of the mass extinction of planktonic foraminifera in Caravaca basin showed a percentage decrease in well-preserved specimens per gram in the lower Danian sediments [8, 9]. Indeed, Molina et al. [10] concluded on the basis of paleoenvironmental study that the percentage of planktic foraminifera that became extinct at the KPB Agost (located ~100 km to the east of the Caravaca) makes up to 90 % of the species. According to these authors, the benthic foraminifera did not suffer any mass extinction, although the drastic reorganization of their assemblages is in coincidence with the boundary and reflects important environmental changes. These changes are compatible with the castastrophic effects of a large asteroid impact that occurred just at the KPB. If we take this into account, we can conclude that the biogenic calcite was formed mainly of planktonic foraminifera.

## Experimental part

### *Inductively Coupled Plasma-Optical Emision Spectrometry*

Ni, Co and Zn of the whole-rock sample and its carbonate fraction were analyzed by ICP-OES. A Spectroflame ICP-OES instrument was employed and Ar was used as the plasma gas. Total uncertainty (including accuracy error) of the analysis ranges from 2 to 10 % for Ni, Co and Zn.

### *Fourier Transform Infrared (FTIR) Spectrometry*

Rock samples were powdered finely and dispersed evenly in anhydrous potassium bromide (KBr) pellets (1.5 mg/150 mg KBr). FTIR Spectra were taken at room temperature using a Bomem (Hartmann & Braun) MB-100 spectrometer set to give underformed spectra.

### *Scanning Electron Microscopy (SEM)/Energy Dispersive Spectrometry (EDS)*

All SEM/EDS analyses were carried out using a Jeol JSM-35 electron microscope equipped with a Tracor TN2000 energy dispersive X-ray spectrometer. Operating conditions for energy-dispersive analyses were at 25 keV accelerating voltage, 0.1 μA beam current and a beam spot diameter of approximately 3 μm.

### *Chemical analysis and fractionation*

All chemical collected bulk samples were collected from an outcrop 4 km south of the town of Caravaca de la Cruz (fig. 1). The rock sample was dried in an oven and carefully ground in an agate mortar. The experimental techniques/methods have already been described earlier [7, 11].

Powdered rock was treated (12 h) with acetate buffer: acetic acid (0.5 M)/sodium acetate (1 M) solution at *p*H 5.0 to remove most of the carbonates. The soluble material

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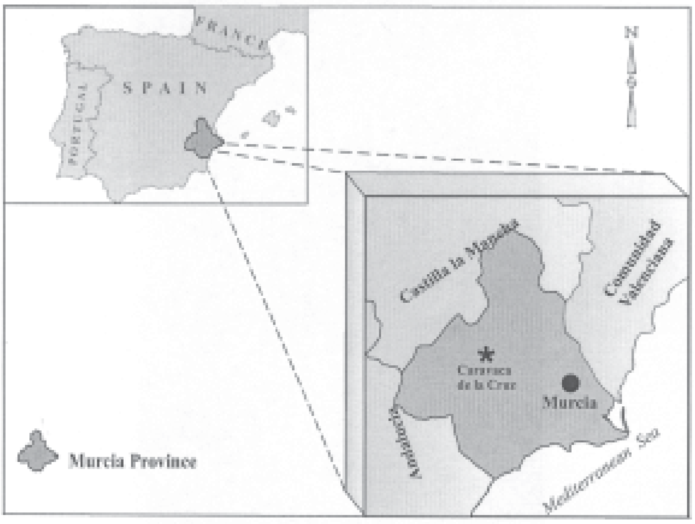

Fig. 1. Geographical location of Caravaca de la Cruz

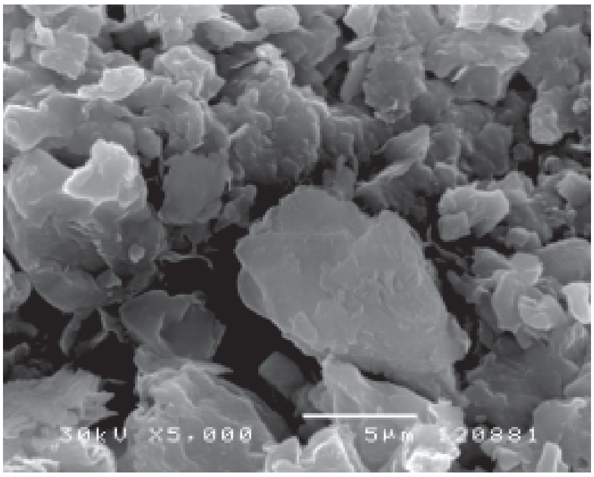

Fig. 3. SEM of bulk Caravaca sample

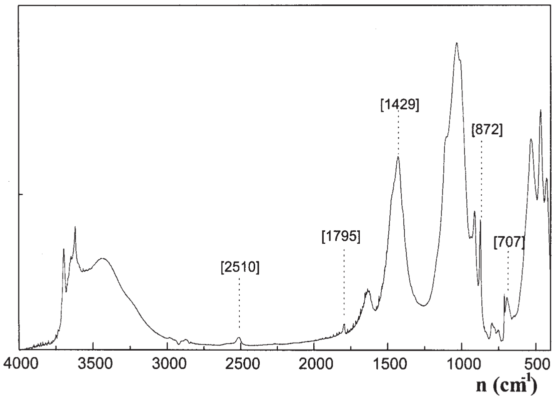

Fig. 2. FTIR spectrum of C-O vibration within CO$_3^{2-}$

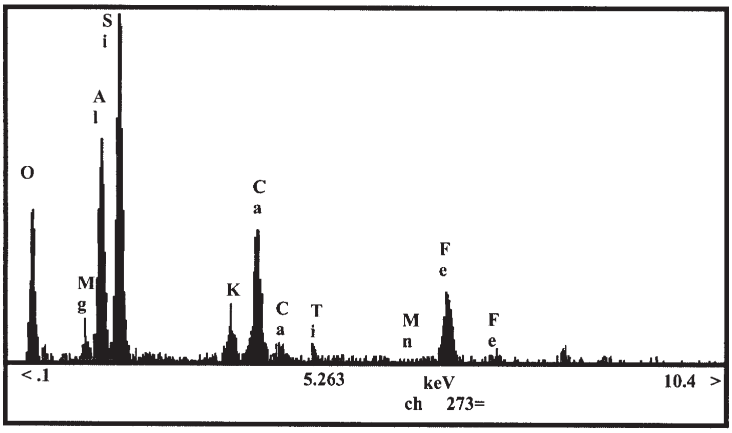

Fig. 4. EDS spectrum of bulk Caravaca Sample

constitutes the carbonate fraction. Carbonate removal was checked by FTIR/SEM/EDS analyses. The soluble portion constitutes the carbonate fraction analyzed for Ni, Co and Zn by ICP-OES. It appears that the treatment of the sediments with the acetic acid/sodium acetate is the most efficient and simple method for removing carbonates with a minimal damage to the clays present [12].

## Results and discussions

### *FTIR and SEM/EDS characterization*

Mineralogical characterization is based on FTIR analyses of CO$_3^{2-}$ vibrations in 4000-400 cm$^{-1}$ region, as a very useful and reliable method. The FTIR spectra of analysed samples show strong adsorption at 1429, 872 and 707 cm$^{-1}$ and weak peaks at 2510, 1795 and 872 cm$^{-1}$ (fig. 2) which are characteristic for C-O bands. FTIR spectra together with SEM and EDS results claimed that carbonate fraction of organic rich KPB layer from Caravaca is formed mainly of calcite (figs. 3, 4).

### *Trace metals content*

The content of trace Ni, Co and Zn in the sample has been determined by ICP-OES. The results of the total contetnt of these metals is in accordance with figure 5.

Except the enhanced content of total Ni (130 ppm), Co (35 ppm) and Zn (105 ppm) in the Caravaca KPB organic rich layer shows a relatively high concentration of these metals in the carbonate/calcite fraction (table 1). According to these results the KPB sample shows high percentage of carbonate fraction (37 %) with relatively high concentrations of Ni (70 ppm), Co (40 ppm) and Zn (55 ppm). These concentrations are much higher compared to the average concentrations of these metals in marine calcareous rocks [13] and normal seawater (table 1.). It appears that the distribution of Ni, Co and Zn in biogenic calcite is about 23 , 43 and 19 % of whole metal content (table 1).

Evidently, the abrupt injection of high Ni, Co and Zn (and other toxic metals) into the surface seawater would be particularly vulnerable to marine flora. Possible mechanism of the toxic effects of these metals is explained in the works of Sunda and Huntsman [16] and D. Munsel, *et al.* [17]. According to these authors, toxic metals such as Ni, Co or Zn inhibit Mn uptake, when Mn is present in low concentrations. In terms of chemical competition, Mn binding is blocked by (toxic) trace metals, which bind to the receptor sites on transport-specialised membrane proteins designed for the acquisition of nutrients.

Therefore, we propose that most of the Ni, Co and Zn content in the carbonate fraction of organic rich layer Caravaca represents biological Ni, Co and Zn, i.e. the direct biochemical incorporation of Ni$^{2+}$, Co$^{2+}$ and Zn$^{2+}$ of the divalent cations calcareous into the shells of calcareous microbiota during their metabolic uptake of seawater (fig. 3). If most of the Ni, Co, and Zn reside in biogenic calcite, then their calcite shells are most likely their hosts; they could be introduced into the shell structure through inorganically controlled incorporation of their divalent cations. These ions may substitute for the Ca$^{2+}$ ions in the calcite matrix since Ni$^{2+}$ (0.70 A$^{o}$), Co$^{2+}$ (0.65 A$^{o}$) and Zn (0.75 A$^{o}$), have similar ionic radius/the same charge as Ca$^{2+}$ (1.00 A$^{o}$). Of course, the incorporation could take place only in the ordinary oxygenated seawater already highly enriched in the Ni$^{2+}$, Co$^{2+}$ and Zn$^{2+}$ ions

**Table 1**
GEOCHEMICAL CONCENTRATION AND DISTRIBUTION [PPM] OF Ni, Co AND Zn IN THE CARBONATE FRACTION OF ORGANIC RICH LAYER

| Percentage | Metal | | |
|---|---|---|---|
| | **Ni** | **Co** | **Zn** |
| **Concentration** | 70 | 40 | 55 |
| **Distribution*** | 25 | 15 | 20 |
| **%** | 23 | 43 | 19 |
| **Total$^{**}$** | 130 | 35 | 105 |
| **NS (ppt)** | 118 | 0.6 | 3.3 |
| **CC** | 11000 | 500 | 312 |

*The percentage of the whole sample: carbonate [37 %], HCl-cold [13.5 %], Smectite [12.5 %], HCl insoluble fraction [37 %].

**The total metal content was obtained by summation of its fraction.

NS: Normal seawater [14];

CC: Average carbonaceous chondrite [15].

*Origin of Ni, Co and Zn*

Interestingly, the Ni/Co ratio in the organic rich layer is about 3. This is consistent with the assumption that the same IEF is likely to be responsible for their Ni and Co enrichments. For comparison, the Ni/Co ratio for ordinary seawater and C1 chondrite is about 197 and 22, respectively (these two values are calculated using the data given in table 1). According to Strong et al.[18] the low Ni/Co ratio (1.1) in the KPB deposit at Flaxbourne River (New Zealand) shows that the Co is largely of terrestrial origin. Based on these assumptions it can be concluded that most of Zn is mainly also of terrestrial origin (Ni/Zn ratio about 1; table 1). Thus, it seems very likely that Ni within the biogenic calcite structure Caravaca is indeed a time marker, representing the sudden airfall of the impact-derived materials in the Caravaca Basin.

## Conclusions

We interpreted the high/abrupt increase of presumably meteoric Ni and non meteoric Co and Zn in the calcite of the organic rich layer as a result of the asteroidal impact and associated impact-related superacid rainfall. We proposed that most of the toxic Ni, Co and Zn in the carbonate fraction of organic rich layer Caravaca represents biological Ni, Co and Zn, i.e. the direct biochemical incorporation of $Ni^{2+}$, $Co^{2+}$ and $Zn^{2+}$ of the divalent cations calcareous into the shells of calcerous microbiota (e.g. planctonic foraminifera) during their metabolic uptake of seawater.

Based on the Ni/Co and Ni/Zn ratios in carbonaceous chondrites and Caravaca carbonate fraction it was determined the asteroid origin of Ni and terrestrial origin of Co and Zn.

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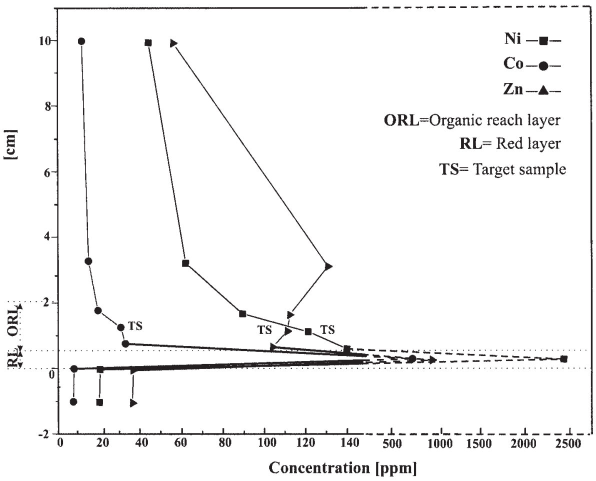

Fig. 5. Concentration profiles of Ni, Co and Zn (ppm) in the Caravaca section (based on the Kyte et al. [2])

## References

1. ALVAREZ, L. W., ALVAREZ, W., ASARO, F., MICHEL, H. V., Science, **208,** 1980, 1095-1108
2. KYTE, F. T., ZHOU, Z., WASSON, J. T., Earth Planet. Sci. Lett., **73,** 1985, 183-195
3. SCHMITZ, B., Geology **16**, 1988, 1068-1072
4. SHUKOLYUKOV, A., LUGMAIR, G. W., Science, **282,** 1998 927-930
5. ORTEGA-HUERTAS, M., MARTINEZ-RUIZ, F., PALOMO, F., CHAMLEY, H., Sediment. Geol. **94,** 1995, 209-227
6. MARTINEZ-RUIZ, F., ORTEGA-HUERTAS, M., PALOMO, M., 6th Workshop Impact Markers in the Stratigraphic Record, Granada (Spain), 2001.
7. PREMOVIĆ, P. I., NIKOLIĆ, N.D., PAVLOVIĆ, M. S., TODOROVIĆ, B. Z., DORDEVIĆ, D. M., NIKOLIĆ, R. S., LOPEZ, L., LO MONACO, S., J. Serb. Chem. Soc., **66,** 2001, 647-670
8. KAJIHO, K., LAMOLDA, M. A., Geology, **27,** 1999, 355-358
9. ARZ, J. A., ARENILLAS, I., MOLINA, E., SEPULVEDA, R., Andean Geology, **27,** 2000, 355-358
10. MOLINA, E., ALEGRET, L., ARENILLAS, J. I., ARZ, A., J. Iber. Geol., **31,** 2004, 135-148
11. PREMOVIĆ P. I., TODOROVIĆ B. Z., STANKOVIĆ M. N., Geologica Acta, **6,** 2008, 2008369-382
12. LYLE M., HEATH R. G., ROBINS J. M. Geochim. Cosmochim. Acta, **48,** 1984, 1705-1715
13.BOWEN, H. J. M., Environmental Chemistry of the Elements. Academic Press Inc., Ltd, London, 1979
14. BRULAND, K. W., Trace elements in seawater. Academic Press Inc., Ltd, London, 1983
15. ANDERS, E., GREVESE, N., Geochim. Cosmochim. Acta, **53,** 1989, 197-214
16. SUNDA, W. G., HUNTSMAN, S. A., Sci. Total Environ., **219,** 1998a, 165–181
17. MUNSEL, D., KRAMAR, U., DISSARD, D., NEHRKE, G., BERNER, Z., BIJMA, J., REICHART G.-J., NEUMANN, T., Biogeosciences, **7,** 2010, 2339-2350
18. STRONG, C. P., BROOKS, R. R., WILSON, S. M., REEVES, R. D., ORTH, C. J., MAO, X.-Y., QUINTANA, L. R., ANDERS. E., GEOCHIM. Cosmochim. Acta, **51,** 1987, 2769-2777

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