COMPOSITION AND ORIGIN OF NI-RICH SPINEL FROM CRETACEOUS-TERTIARY BOUNDARY.
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Introduction: Extraterrestrial spinel is a magnetic mineral that is found in melted micrometeorites, in the fusion crust of meteorites and meteoroid ablation droplets, and in various impact-derived spherules more or less preserved in marine sediments. This mineral can be distinguished from terrestrial spinel on the basis of high Ni content and a high ferric/ferrous ratio resulting from crystallization in an O_2-rich environment, i.e. the Earth's atmosphere [1-4]. Ni-rich spinel is a specific marker of extraterrestrial material which can be used as a tracer of cosmic events in the sedimentary record.

Previous Work: The existence of Ni-rich spinel crystals in K/T boundary clays was revealed by [5, 6]. Regional and local (i.e., from site to site) variations in spinel compositions have been also reported (e.g., [7, 8]); mostly variations in Cr, Fe, Mg, Al, and Ni content.

It has been shown that the composition of spinel depends primarily on ambient oxygen fugacity and on the initial composition of the crystallizing material [3,4], but their exact formation mechanism is still controversial (e.g., [3, 9, 10]). Two different modes of formation are invoked: condensation in the impact vapor plume [7] and atmospheric ablation of the projectile [1].

Recently, [11, 12] have shown that some impact spinel, so far only for K-T boundary spinel crystals from Bidart (France) and Caravaca (Spain), display compositional zoning from core to rim, with a core depleted in Fe, Ni, and Ti, and enriched in Cr, Al, and Mg. Similar zonations have been reported in spinel crystals present in impact horizons of Upper Eocene sections [13] and from meteorite fusion crusts [3, 12, 14], but these have never been studied in detail.

Compositional zoning was recognized using a scanning electron microscope (SEM), [11, 12]. The contact between the Cr-rich core and the Fe-rich rim is very well defined (i.e., sharp), in both, impact spinel and spinel from meteorite fusion crust. Additionally, the depletion in nickel observed in the core of the crystals indicates that the chemical zoning is primary rather than the result of alteration. Ferrière and Robin [11, 12] have suggested that either the variation of the Fe^{3+}/Fe_{total} ratio from core to rim indicate an increase of the oxygen fugacity (f_{O2}) during the crystallization of the spinel (with chromite precipitation at low f_{O2} and subsequent magnetite overgrowth at higher f_{O2}) or it may reflect the presence of relict chromite with subsequent magnetite overgrowth.

Aims, Methods, and Expected Results: The main objective of our study is to characterize, at the nanometric scale, the internal microstructure of Ni-rich spinel from the K/T boundary, to better understand and constrain their formation conditions. The transmission electron microscope (TEM) observations of impact spinel crystals will give us the possibility to elucidate the origin of the chemical zoning. The precise nature and composition of the core vs. rim will also permit us to better constrain formation conditions (i.e., temperature, ambient oxygen fugacity, crystal growth velocity, stress, etc.) of impact spinel.

In order to prepare our samples for TEM observations, Ni-rich spinel crystals from two K-T boundary sites, Bidart (France) and Caravaca (Spain) have been investigated with SEM; X-ray maps and compositional profiles across some of the zoned crystals were created (Fig. 1). For comparison, a few spinel from the fusion crust of the meteorite Beni M'hira (L6) were also documented.

The Focused Ion Beam (FIB) technique will be used for the preparation of TEM foils at the GeoForschungsZentrum (GFZ) Potsdam (Germany). FIB foils of 15 x 5–10 µm extent and about 150 nm thickness will be prepared following the method described by [15]. This technique will allowed us to "cut" precisely the part of the spinel crystal that we are interested in, like the "contact zone" between "core" and "rim". The TEM investigations, including observations and conventional bright-field imaging, as well as energy-dispersive X-ray microanalyses and mapping, will also be performed at the GFZ. The results of our TEM investigations will be presented at the conference.

We expect to provide observations that will help to determine if one or both of the hypotheses of spinel formation are applicable (i.e., condensation in the impact vapor plume v.s. atmospheric ablation of the projectile).

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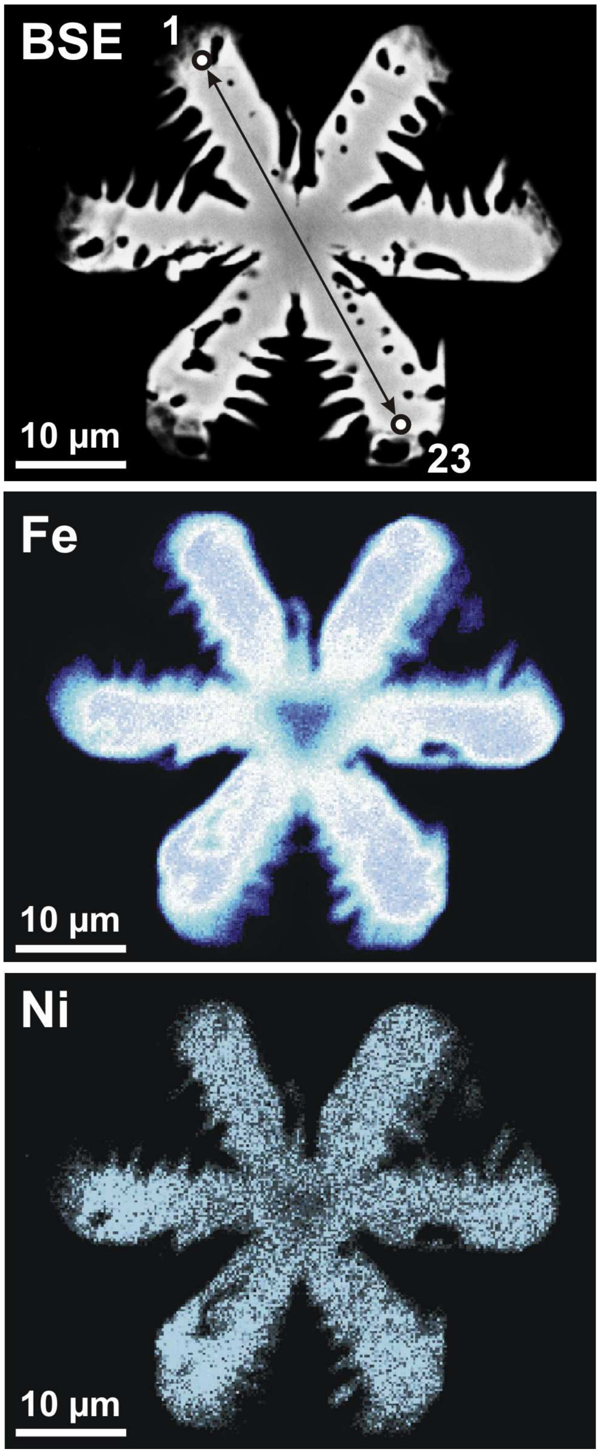
References: [1] Robin E. et al. (1992) *Earth Planet. Sci. Lett.*, *108*, 181–190. [2] Gayraud J. (1995) PhD of the Univ. of Paris-sud, Orsay, France, 301p. [3] Gayraud J. et al. (1996) *GSA Special Paper* #307, 425–443. [4] Toppani A.

and Libourel G. (2003) *Geochim. Cosmochim. Acta*, *67*, 4621–4638. [5] Montanari A. et al. (1983) *Geology*, *11*, 668–671. [6] Smit J. and Kyte F. T. (1984) *Nature*, *310*, 403–405. [7] Kyte F. T. and Smit J. (1986) *Geology*, *14*, 485–487. [8] Robin E. et al. (1999) *LPS XXX*, Abstract #1601. [9] Siret D. and Robin E. (2003) *LPS XXXIIII*, Abstract #1865. [10] Ebel D. S. and Grossman L. (2005) *Geology*, *33*, 293–296. [11] Ferrière L. and Robin E. (2005) *Meteoritics & Planet. Sci.*, *40*, A47. [12] Ferrière L. and Robin E. (2006) *Meteoritics & Planet. Sci.*, *41*, A55. [13] Robin E. and Molina E. (2006) *Meteoritics & Planet. Sci.*, *41*, 1231–1248. [14] Genge M. J. and Grady M. M. (1999) *Meteoritics & Planet. Sci.*, *34*, 341–356. [15] Wirth R. (2004) *Eur. J. Mineral.*, *16*, 863–876.



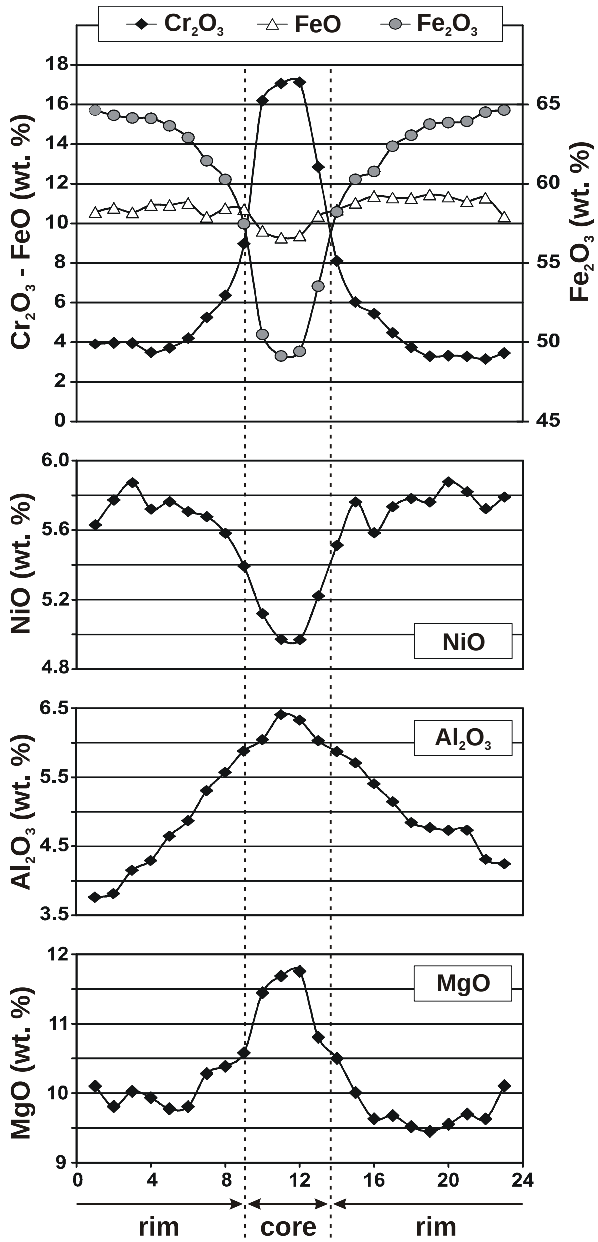


Fig. 1: Transect and X-ray mapping of a large zoned skeletal spinel crystal from Caravaca (Spain) with an enrichment in Cr, Al, and Mg in the core. The core is also clearly depleted in Fe and Ni comparatively to the rim.