ON THE ORIGIN OF CRETACEOUS-TERTIARY BOUNDARY SPINELS. E.
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Introduction. Ni-rich spinels (1), also named magnetites (2-4), and magnesioferrites (5), have now been found worldwide in Cretaceous-Tertiary (K-T) boundary rocks: in marine emerged sections in Italy (1-3), Spain (3-5), New Zealand (5), Tunisia (6) and Haiti (7), in a nonmarine section in North America (8), and in deep sea sites in Pacific (1,2,5), Atlantic (1) and Indian (4,6) oceans. These minerals, often clustered in flattened spheroids (1-4), display dendritic, skeletal, cruciform and octahedral morphologies, which are characteristics of primary components rapidly crystallized from a high temperature melt. Their composition, with relatively high NiO (1-10%) and low TiO₂ (<1%) content, is quite unusual for terrestrial spinels (9). Because Ni-rich spinels have no analogs in terrestrial rocks, they are considered as relics of the alleged K-T impact (1,2,5).

Mode of formation of Ni-rich spinels. The formation of Ni-rich spinels requires oxidation of chondritic material under relatively high oxygen fugacities, above 10⁻⁵ atm (10). Three oxidation steps can be distinguished (10, 11): 1) weak oxidation during atmospheric entry of micrometeoroids; 2) intermediate oxidation of molten chondritic droplets produced by ablation of large meteoroids; 3) extensive oxidation of oceanic impact products. Direct condensation of spinel crystals during cratering events (1,5) is very unlikely because of the reducing conditions that prevailed in the impact vapour cloud. Reducing conditions during cratering events are demonstrated by the systematically reduced state of iron in impact-generated products, i.e. tektites (12) and impactites (13-15), which indicates oxygen fugacities as low as 10⁻¹⁴ atm (16). Reducing conditions are also demonstrated by the presence of metallic phases in tektites (17), impactites (18) and in fractured rocks beneath some impact craters (19,20). On the other hand, if spinel crystals could be formed directly by condensation from a vapour cloud, they should be abundant on the Moon, which has experienced recurrent micrometeoroid, meteoroid and asteroid impacts. This is not the case: all spinels found in lunar soil samples are extremely reduced, with no Fe³⁺ (21). Micrometeorite spinels are generally depleted in Ni relative to other "cosmic" spinels (10, 11). They also display lower iron oxidation state, with Fe³⁺/Fe_total ratio ranging from 65-75 atom% (figure) whereas this ratio ranges from 75-90% in spinels of meteorite fusion crusts and meteoroid ablation material (figure). These lower iron oxidation states are attributed to deceleration and oxidation of micrometeorites in the upper atmosphere, under oxygen fugacities comprised between 10⁻⁵-10⁻³ atm, whereas meteoroids are decelerated and oxidized deeper in the atmosphere, under higher oxygen fugacities (10). The maximum Fe³⁺/Fe_total ratio of spinel crystals that formed in the atmosphere is 90%, corresponding to an oxidation close to the ground, under the maximum oxygen fugacity of 0.2 atm existing at sea level. Formation of spinels with Fe³⁺/Fe_total>90% require still higher oxygen fugacities (10). The discovery of highly oxidized Ni-rich spinels in Eltenin glassy spherules (22), with Fe³⁺/Fe_total=97% (figure), indicates that such conditions can exist during oceanic impact. One very attractive explanation is that oxygen fugacities higher than 0.2 atm can be produced by decomposition of sea water in its atomic components. If so, spinel crystals with Fe³⁺/Fe_total>90% would be indicative of oceanic impacts.
K-T Boundary spinels: Robin E. et al.

Origin of K-T spinels. The systematically high Fe\(^{3+}/Fe_{total}\) ratio of K-T spinels suggests that they do not arise from the oxidation in the upper atmosphere of microparticles (figure). They rather derived from meteoroid ablation material and oceanic impact products. This result is rather difficult to reconcile with a single impact event (23). Indeed, all of a bolide of 10 km in diameter, the expected size of the K-T asteroid (23), would be vaporized upon the impact (24). Only material in the form of microspherules that condensed in the cloud of vaporized projectile and target material (25), can be ejected worldwide on ballistic orbits, but their subsequent oxidation during atmospheric re-entry would lead to the formation of spinels with low iron oxidation states, comparable with the one observed in micrometeorites. Therefore, it is difficult to avoid the conclusion that multiple events occurred at the end of the Cretaceous. The geographical study of the iron oxidation state of K-T spinels suggests that those from the European regions would derive from ablation of large meteoroids (Fe\(^{3+}/Fe_{total}<90\%\)) while those from Pacific and Indian ocean would derive from oceanic asteroid impacts (Fe\(^{3+}/Fe_{total}>90\%\)). The collision of a comet fragmented by tidal forces (26) or the encounter with meteoroid and asteroid swarm would better explain the worldwide dispersion of highly oxidized Ni-rich spinels at the K-T boundary than a single asteroidal collision.