K-T BOUNDARY SIGNATURES IN THE MANGANESE NODULE ZETES-3D:
A. V. Murali, Lunar and Planetary Institute, 3303 NASA Road 1, Houston, TX 77058, **D. P. Blanchard,** NASA/Johnson Space Center, Houston, TX 77058, **B. L. K. Somayajulu,** Physical Research Laboratory, Ahmedabad 380 009, India, **P. P. Parekh,** Wadsworth Center for Laboratories and Research, New York State Department of Health, Albany, NY 12201.

Hydrogenous manganese nodules form on the ocean floor by slow authigenic precipitation (1-6 mm/Ma) of the oxyhydroxides of manganese and iron that continuously scavenge trace elements from the marine environment. Consequently, these nodules represent independent marine deposits useful for the study of the chemical signatures of the paleomarine environments. Although the global nature of the K-T boundary event is evident from the reported iridium anomalies in ~95 marine and continental K-T sections all over the world (1), no attempt has been made to look for the record of this event in hydrogenous manganese nodules except our earlier work on the nodule Zetes-3D (2, 3). This is probably due to the difficulty in obtaining nodules covering a growth span of $\geq$70 Ma because large nodules (>10 cm) are likely to break up or get subducted at the plate boundaries.

We continued the study of the nodule Zetes-3D from the Pacific Ocean (40^{o} 16'N; 170^{o} 20'E). Zetes-3D is a large (24 x 17 x 10 cm) hydrogenous nodule whose slow growth rate of 1.3 mm/Ma (4) indicates that it existed on the ocean floor for the last 100 Ma. Study of the samples collected from different layers of the nodule (Fig. 1) confirmed the following observations reported earlier (2, 3): (1) The chemical signatures of the top (1, 2, 3 and 4) and bottom (8) layers are comparable in terms of their siderophile and REE abundances and patterns (Fig. 1 and Fig. 2). (2) The samples taken from the region covering the 50- to 69-Ma are distinctly different in that they are depleted (values in wt%) in Fe (~30%), Sc, and REE (~40-50%) but are enriched in Mn, Co and Ni (~20-40%). (3) A positive cerium anomaly is observed throughout the nodule; this anomaly nearly triples (from 3x to ~9x) in 50- to 69-Ma layers (Fig. 2).

The Ir content of these samples was determined employing the HPGe-coincidence/NaI(Tl)-anticoincidence spectrometry (5, 6), which indicated a sharp Ir spike (37 $\pm$ 6 ppb) in the sample corresponding to 54-62 Ma (Fig. 2). The chemical signatures of the K-T event (65 $\pm$ 1 Ma) are expected in the sample covering the 62- to 69-Ma span (#7) deduced from our ^{10}Be age extrapolation. However, in view of the errors in the ^{10}Be age technique (> $\pm$10%) and the propogated errors due to the sample selection based on an *a priori* assumption of uniform growth rate of the entire nodule, we consider that sample #6 could be the actual K-T boundary layer in the nodule. In fact, the presence of the high Ir spike in the nodule layer (which is observed globally in the K-T sections) within ~10% outside the extrapolated K-T layer in the nodule proves that our age (^{10}Be) extrapolation is more or less valid.

Iridium anomaly: The Ir content of the deep-sea manganese nodules (average value ~9 ppb) is considered to be derived from the interplanetary dust particles (7). In fact, cosmic spherules and flakes with high siderophile elements are also reported from the manganese nodules (8). The average Ir content of the Zetes-3D (excluding sample #6) is $\leq$10 ppb (Fig. 2), which is consistent with the reported average in various manganese nodules (7). The sudden increase in the Ir flux (~4 times the background level) in the Zetes-3D layer corresponding to the K-T event supports the bolide impact hypothesis (1).

Cerium anomaly: In the marine environment, Ce^{+3} is oxidized to insoluble Ce^{+4} that is precipitated as CeO_2 or $Ce(OH)_4$ in the manganese nodule. The pH of the sea water is the main controlling factor for the Ce anomaly in the marine environment and has been related to the Pco_2 of the atmosphere; *i.e.,* higher cerium anomalies in the nodule indicate a lower pH of the sea water, reflecting an increase in the Pco_2 content of the atmosphere (9). Although Deccan volcanism seems to have contributed too little Ir to account for the global Ir anomaly (10), it is evident that the voluminous eruptive pulses of this volcanism spanning at least >72 to 59 Ma could have released tremendous amounts of co_2, so_2, etc., into the atmosphere (11). The resultant acid rains might have accelerated the weathering of the continental regions and enhanced the fluvial transport/input of the cerium (and other REE) into the oceans. The combined effects of the pH reduction of the open ocean and the enhanced continental weathering would account for the sudden increase in the cerium anomalies and absolute Ce abundances (Fig. 2) in the nodule layers covering 69- to 50-Ma layers. Thus the chemical signatures in the manganese nodule support the hypothesis that the bolide impact(s) occurred during the time of the Deccan eruptive episodes (10). We believe that it is not either "bolide impact" or "volcanism", but both have contributed to the K-T scenario. Study of the carbonate samples from the Shatsky rise (12) supports these conclusions.

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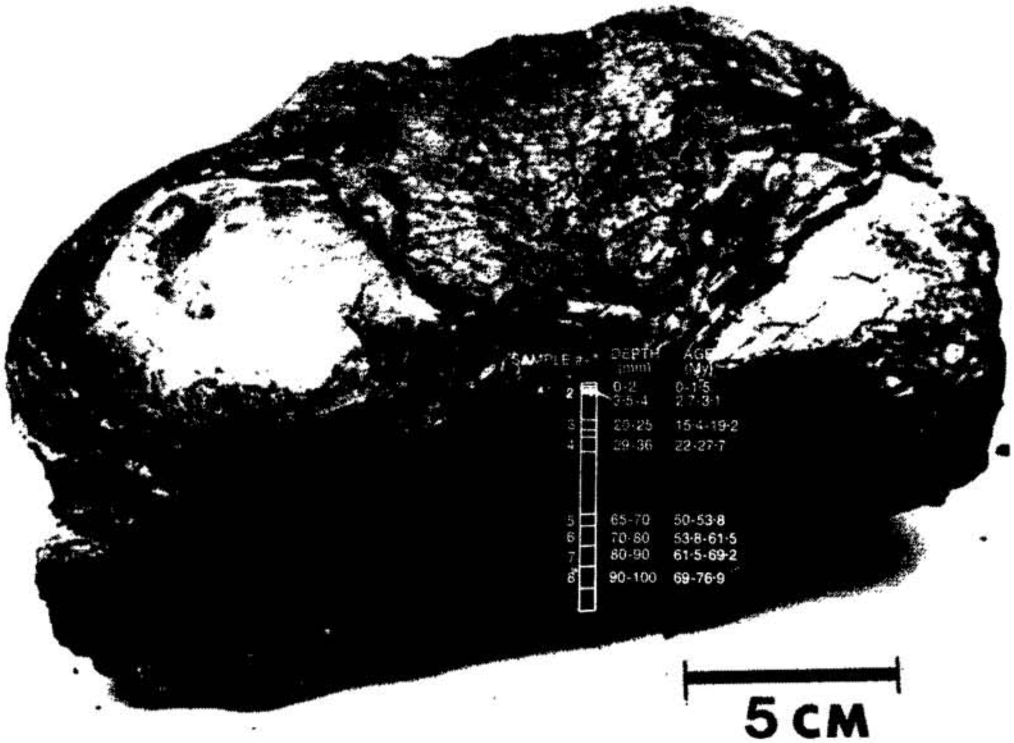

Fig. 1. Fresh interior of Zetes-3D vertically cut for sampling. Sample depths and their ^{10}Be (extrapolated) ages are also shown (original size 24 x 17 X 10 cm).

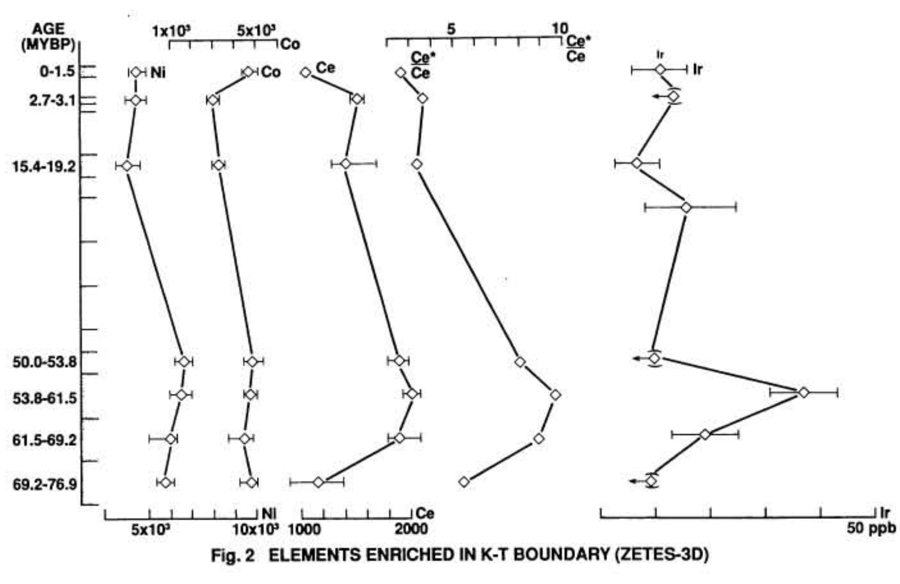

Fig. 2 ELEMENTS ENRICHED IN K-T BOUNDARY (ZETES-3D)