ABSENCE OF Zn, As, AND Sb ENRICHMENTS RELATIVE TO NORTH AMERICAN SHALE COMPOSITE IN 11 WORLDWIDE K/T BOUNDARY CLAYS AND IN SHATSKY RISE K/T BOUNDARY CLAYS TORPEDOES HYDROTHERMAL-SMOKER POISONING HYPOTHESIS FOR THE OCEANIC MASS EXTINCTION MECHANISM AT K/T; Y.-G. Liu\(^1,2\) and R.A. Schmitt\(^1,4\), \(^1\)The Radiation Center and Departments of \(^2\)Chemistry and \(^3\)Geosciences, and \(^4\)College of Oceanography, Oregon State University, Corvallis, Oregon 97331

It has been reported that three trace elements (Zn, As, and Sb) relative to C\(_1\) chondrites are strongly enriched with Ir in the worldwide K/T boundary clays [1,2]. Asteroid impact ejecta has been proposed as the origin for the Ir enrichments. Other possible sources which also have been proposed include seawater and volcanism. Schmitz [3] reported the results from continental K/T boundary layers and found As and Sb were enriched but Zn showed ordinary concentrations. The continental As and Sb enrichments are explained by the close spatial association of the boundary layers with coal and the abundant weathering products of pyrite.

In studies of Shatsky Rise (S.R.) carbonate sedimentary samples, we have observed a series of elemental enrichment peaks in the vicinity of the K/T boundary [4,5]. In addition to the peak at the K/T boundary, peaks at -0.2 Ma before K/T, -0.3 Ma after K/T, and five peaks at -1.1 to 1.3 Ma after K/T have been defined. The abundance ratios of nine elements, Al, V, Cr, Fe, Rb, Cs, Hf, Ta, and Th, all with different chemical properties, are the same in the detrital clays before, after and in those peaks, and essentially overlap the N.A.S.C. (North American Shale Composite), except for Cr and Fe in the S.R. K/T samples because of the bolide fallout contribution. The reported Zn, As, and Sb enrichments at many K/T boundary layers prompted us to determine these elements in S.R. samples at the neighborhood of the K/T boundary. We found that Zn, As, and Sb are not only enriched at the K/T boundary, but also are enriched with many other elements at other positions. For example, As reaches 0.9 and 1.6 ppm at the K/T peak and the 0.2 Ma peak before K/T, respectively, with background levels of -0.3 ppm. For comparison, elemental abundances are expressed in the detritus assuming these elements are all in the clay component (-0.5-6%) in carbonate sediments. Results are tabulated in Table 1 and plotted in Fig. 1, along with eleven K/T clays by Gilmour and Anders [2]. Two sets of background S.R. Hole 577 data at 59 and 61 Ma and 1.0, 3.5 and 4.5 Ma are also listed.

Though Zn, As, and Sb show concentration peaks at K/T and other positions, their N.A.S.C. normalized abundances remain essentially the same at all peaks, K/T included, and off-peak background samples, and are similar to the N.A.S.C. composition. The normalized high Co, Ni, and Zn abundances at the peaks also overlap the background, but are consistently higher than N.A.S.C. This is attributed to adsorption of these elements from seawater onto the detritus. Fe and Cr are essentially the same as N.A.S.C. at the peaks and background samples except they are higher at the K/T boundary due to the bolide (asteroid or comet) contribution. The average abundances in the 1.0, 3.5, and 4.5 Ma detrital clays are consistently lower than in 59 and 61 Ma clays, which reflect different oceanic environments in the Pliocene and the Paleocene. Our data overlap those reported by Gilmour and Anders [2] for the worldwide K/T boundary clays within a reasonable range.

These results suggest that elemental enrichments of Zn, As, and Sb are not unique at the K/T boundary. There are a series of enrichment peaks in the vicinity of K/T boundary. The compositions of detrital clay materials are essentially the same at the elemental enrichment peaks, including K/T, and at the off-peak background samples. We [5] have proposed that the intense, large scale volcanism during this time period [6,7], such as the Deccan Traps in India, may be responsible for the peaks of elemental enrichments. Large amounts of CO\(_2\), SO\(_2\), HCl and other gases released by volcanism [8] would have accelerated the climatic and weathering processes on the continents, resulting in increased inputs to the oceans by dissolved and suspended fluvial loads, and by eolian processes for transport of N.A.S.C.-like fine detrital materials from the continents. Specifically, for the K/T peak, the dynamic atmospheric conditions and associated acidic rain [9,10] generated by the L.W. Alvarez bolide impact would result in similar climatic conditions as those produced by Deccan Trap volcanic pulsings at 0.2 Ma before K/T (= 66.4 Ma), 0.3 Ma after K/T, and 1.1 to 1.3 Ma after K/T [5]. The acidic rain at K/T only increased the Ce\(^3+\) (Ce
ABSENCE OF Zn, As and Sb: Liu Y.-G. and Schmitt R.A.

anomaly) in the Pacific Ocean from \( \approx 0.045 \) (immediately before and after K/T) to \( \approx 0.060 \) within the FWHM of the K/T peak (the present Ce\(^A\) = 0.06 ± 0.01 [11]); therefore, we suggest that the pHs of only the -100 m mixed layers were affected by the acidic rain.

One of us [12] proposed an intensified hydrothermal-smoker mechanism, triggered by the L.W.A. bolide impact, to account for the elemental enrichments such as Zn, As, and Sb (constraint #23 of reference 1) at the K/T boundary and the poisoning of the Earth's oceans as one of the primary factors responsible for the extinction of selected marine families. From the absence of Zn, As, and Sb enrichments in K/T boundary samples, it is highly probable that the hydrothermal-smoker hypothesis has been torpedoed into oblivion and obscurity!