EVIDENCE FOR NON-CHONDRITIC SIDEROPHILE ELEMENTS AND VOLCANOGENIC TRACERS AT THE EL KEF K-Pg BOUNDARY.

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Introduction: There are two hypotheses for the cause of the K-Pg extinction: asteroidal impact and volcanism [1-5]. The key piece of evidence supporting the impact hypothesis was the discovery of high concentrations of Ir in the K-Pg boundary clay [e.g., 1], but subsequent recognition of high Ir in volcanic aerosols rendered the Ir evidence ambiguous [6]. Very few studies have provided multi-element siderophile abundances of the K-Pg boundary to assess the difference between a chondritic and volcanic aerosol input of Ir [7]. Recent geochronology has shown that the K-Pg extinction was synchronous with the end of the Poladpur phase of the Deccan eruption (Fig. 1) [8]. Outgassing of trace elements, e.g. Cd and Re [9] could be evident in sediments deposited at this time [9]. To examine the synchroneity of major Deccan eruption pulses, Ir layers and nannofossil stratigraphy, we analyzed sediments from the El Kef K-Pg stratotype by laser ablation ICP-MS [9].

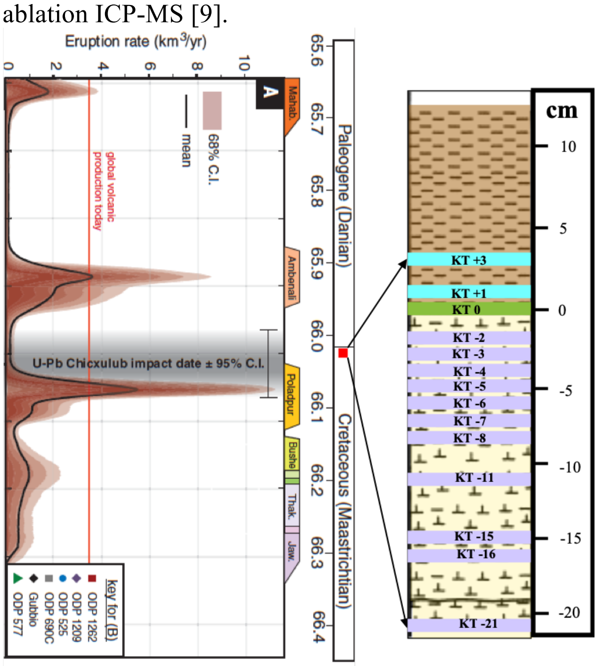

Fig. 1: Stratigraphy at El Kef showing position of samples compared with Deccan chronology [8].

Analytical Methods: Polished sections of epoxy impregnated sediments taken from 3 cm above to 21 cm below the K-Pg boundary at El Kef (Fig. 1) were analyzed by LA-ICP-MS using an ESI™ New Wave™ UP193FX laser ablation system coupled to a Thermo Element XR™ at the Plasma Analytical Facility at FSU [10]. Samples were analyzed with line scans using 100 µm spot sizes and 50 Hz repetition rate. Standards used were GSD-1g, NIST SRM 610, pyrite, calcite, gypsum and the Hoba (IVB) iron meteorite.

Results: Averaged compositions of about 70 elements for each sediment were obtained and the results for key elements are shown in Figs. 2 and 3. An elemental profile across an Fe-oxyhydroxide vein is shown in Fig. 4 with the averaged siderophile element composition of the same vein shown in Fig. 3.

Marl or marly limestones occur above or below the K-Pg boundary, while the boundary is comprised of three components: clay, gypsum and Fe-oxyhydroxides [11]. The gypsum and Fe-oxides appear to have been introduced diagenetically [11]. Since the mixing ratios of the three components are likely to be different between samples, agreement in abundances is not to be expected. The highest enrichments of highly siderophile elements (HSE) are found in the boundary clay. Average Ir abundances for two separate samples of the boundary clay yielded 6 and 7 ppb of Ir that is higher than the 1.7 ppb Ir previously reported [12], but proportionate to the amounts of Fe-oxides (4.7 wt. % [12] vs. 22 and 34 wt. %, this study). Since most of the siderophile elements are in the Fe-oxyhydroxide component (Fig. 4) the abundances of the siderophile elements are proportionately higher in this study compared with [12]. However, the Ni/Co ~6 is similar for both studies.

The Fe-oxyhydroxides contain the highest Se concentrations of the three components. The Fe/Se (~10^4) is the same in both studies [12] and is consistent with the Fe-oxyhydroxides being weathered pyrite. Pyrite was originally abundant in the K-Pg clay [1, 3].

Discussion: Eruption of the Poladpur formation was synchronous with the end-Cretaceous extinction (Fig. 1). When volcanic aerosols [13] are added to sediment of upper continental crustal (UCC) composition, the largest enrichments are seen in Cd, Re and Os [9]. Fig. 2 shows that the sediments at or below the K-Pg boundary at El Kef are systematically enriched in both Cd and Re relative to UCC in proportions identical to that found in the Erta Ale aerosols [13]. A sample taken 3 cm above the K-Pg boundary (KT +3) does not show an enrichment in Cd or Re (Fig. 2), which indicates it was likely deposited between the Poladpur and Ambenali eruptions. Fig. 3 shows that many of the El

Kef sediments have a super-chondritic Os/Ir ratio, inconsistent with a cosmochemical origin, that likely reflects volcanic input [13]. The $^{187}Os/^{188}Os$ ratio in late Cretaceous marine sediments drops below the seawater value (~0.5) interpreted to be the result of Deccan eruptions [5, 14]. The high Os/Ir ratio corroborates a volcanic origin for the coeval $^{187}Os/^{188}Os$ anomaly.

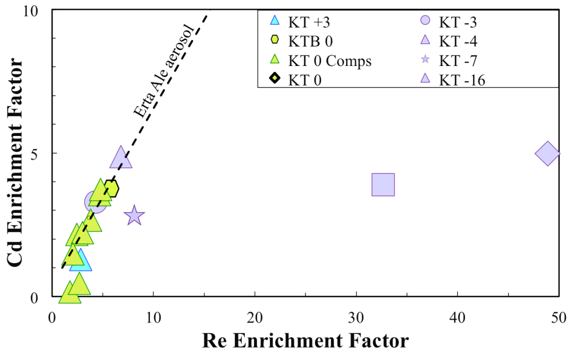

Fig. 2: Enrichments of Cd and Re in the El Kef sediments relative to UCC. The line represents mixing between Erta Ale aerosol [13] and sediment [15].

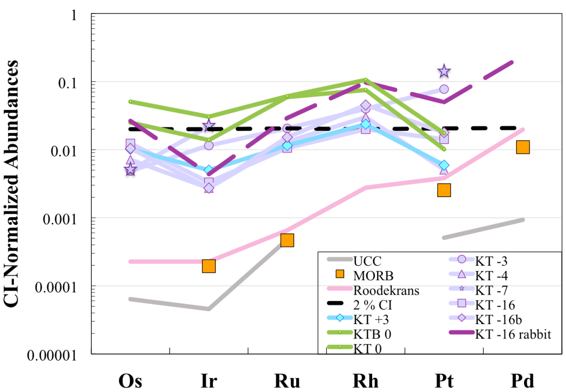

Fig. 3: Siderophile element patterns for the El Kef KT sediments compared with patterns for MORB [16], UCC [15] and basalt [17]. The black dashed line represents a 2% CI chondritic mixture with UCC [7].

The Ir abundances in the El Kef sediments are comparable to percentage level contamination of UCC with CI chondrite material [12]. However, the highly siderophile element patterns of sediments above, within and below the K-Pg boundary are distinctly terrestrial (Fig. 3). Clearly, terrestrial siderophile elements have been concentrated in the Fe-oxyhydroxides. Further evidence for a potent siderophile element concentration mechanism in sediments is provided by microanalysis of an Fe-oxyhydroxide vein located within marl 16 cm below the K-Pg boundary (Fig. 4). This vein locally contains extreme enrichments of Co, Ni, Pd and Os, with Pd reaching chondritic abundances of over 500 ppb. Altered pyrites converted to Fe-oxyhydroxides acted as ion exchangers sequestering metallic anions from percolating ground water. Trace levels of HSEs in solution are subsequently concentrated by factors of $\sim 10^6$ or more.

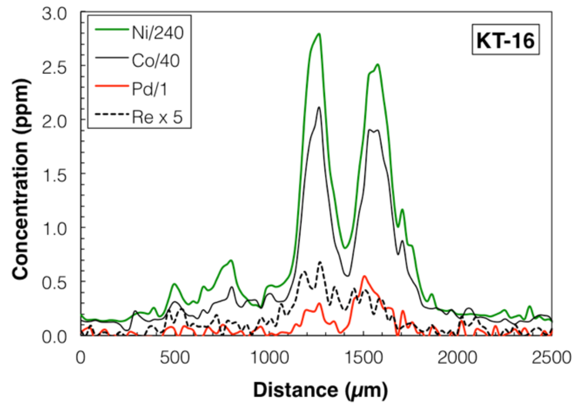

Fig. 4: Elemental profile across KT-16 Fe-oxyhydroxide vein.

Conclusions: We detected volcanic aerosol signatures (Cd, Re) from the Poladpur eruption in sediments deposited at or below the K-Pg boundary at El Kef, but not in the sediment above the K-Pg boundary. We detected high concentrations of PGEs in sediments above, on and below the K-Pg boundary at El Kef that had basaltic patterns, possibly from diagenetic fluids which percolated through the clays at the K-Pg boundary. Local enrichments to chondritic levels of Pd in Fe-oxyhydroxide veins demonstrate that such veins concentrated siderophile elements from percolating ground waters. The emphasis placed on Ir alone [e.g., 1] failed to recognize the terrestrial nature of the siderophile enrichments at the K-Pg boundary.

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