

REDUCING CONDITIONS IN THE PACIFIC OCEAN BEFORE, AT, AND AFTER THE K/T (CRETACEOUS/TERTIARY) BOUNDARY, III; Roman A Schmitt, Departments of Chemistry and Geology, the Radiation Center, and the College of Oceanography, Oregon State University, Corvallis, OR 97331.

In a previous paper [1], Jin and I calculated the ratio of an oxidizable element Mn to a detrital element Al in a variety of pure Pacific marine carbonates, <1-100 Ma. In this paper, I report a more meaningful ratio of Mn/La because with exposure to seawater, $\text{MnO}_{1.8-2.0}$ and LaPO_4 , as a typical REE phosphate, will grow in the Fe-Mn-Al-Ti-oxyhydroxide coatings of sedimentary carbonates. A measure of the Mn content in carbonates is related to the oceanic oxidizing environment.

The attached table lists Mn/La ratios for <1-97 Ma pure carbonates ($\leq 7\%$ detrital clay). For <1-35 Ma and ~70-97 Ma carbonates, Mn/La ratios varied from 35-117. During the Paleocene (58-65 Ma), the Mn and La in Hole 316 carbonates, >4 km deep seawater, were 1150 ± 160 ppm and 18 ± 7 ppm, respectively, for 5 samples and in Hole 577, Mn and La were 240 ± 120 ppm and 12 ± 5 ppm, respectively, for 3 samples. The average La values overlap within their σ s. Comparing these ratios to the 316 and 577 data in the Neogene, I conclude that the Mn/La ratios in Hole 316 remained fairly uniform while the Mn contents and the Mn/La ratios in the S.R. (Shatsky Rise) carbonates were ~4X lower during the Paleocene. I suggest that the S.R. depth was considerably shallower, say at ~1000 m, during the Paleocene and subsequently subsided to its present depth of ~2700 m. At a shallower depth, the seawater reducing environment may have slowed the formation of $\text{MnO}_{1.8-2.0}$.

At K/T time the net integrated Mn/La ratio for Hole 577B-1 [2] at 6.6 is the same as the ratio of 6.5 for Hole 577, as expected. Just before and after the Mn and La peaks at K/T time, the ratios increase slightly to 7.4-8.6, and these ratios are ~2.5-3.0X less relative to the 577 ratios during the Paleocene. Also the absolute average Mn abundance of 112 ± 16 ppm for samples before and after the K/T peak is ~2.1X lower relative to Mn in the 577 Paleocene samples. These ratios and absolute values suggest a more reducing oceanic environment associated with the K/T event per se.

The net integrated Mn and La abundances and their ratios in the -0.2 Ma peak (66.6 Ma) and in the +1.2 Ma peak (65.2 Ma) overlap the corresponding values observed in 577 Paleocene carbonates. Finally, for the ~0.6 Ma interval before K/T time, the average Mn of 150 ± 20 ppm and Mn/La of 9 ± 1 in five samples indicate a oceanic reducing environment less severe than that existent at K/T time.

The global dispersal of partially unoxidized carbonaceous matter in the periphery of CEEA and SACC events from dirty cometesimals, i.e. rich in carbonaceous matter, was invoked [1] for providing the requisite reducing matter for inhibition of Mn oxidation at K/T time. This rationale is ruled out by complete oxidation of carbonaceous matter in CEEA fireballs [3].

Within the context of my general theory of mass extinctions [4], I suggest that the enhanced hydrothermal-smoker activities and associated lower oceanic pHs will provide a reducing environment conducive for inhibiting Mn^{+2} oxidation at K/T time such that the Mn/La ratio in K/T carbonates was only increased by ~2X relative to the average Mn/La ratio of ~3 in the present Pacific ocean. When more normal seawater oxidation conditions returned in the Paleocene as reflected over the S.R., the Mn/La ratio in the carbonates increased by ~6X relative to the present seawater ratio. Then in the Pliocene and Pleistocene, the ratio increased by ~14-37X, which I attribute to normal deep seawater redox conditions.

The low Mn/La ratio of 6.6 in carbonates at K/T time is even more remarkable when one considers that hydrothermal-smoker solutions will be enriched in Fe and Mn by $\sim 2 \times 10^6$ and $\sim 3 \times 10^6$ X, respectively, their relative soluble seawater contents [5,6]. However, such copious additions of Fe and Mn will not mask the addition of C1 like CEEA fallout into the upper oceanic mixed layer because of the oxidation of Fe^{+2} and Mn^{+2} in the oceanic bottom layers followed by precipitation of Fe-Mn-Al-Ti-oxyhydroxides near the ridges as the smoker plumes are diluted in the bottom oceanic regime [7].

Among the 24 elements measured by [2] and the 32 elements measured by us [8], both via INAA, the trace element U allows one to circumscribe the reducing potential within a broad limit. As discussed previously [1], when marine carbonates are deposited in shallow seas rich in organics (e.g. the oil rich Saudi Arabian platform at ~80-200 Ma ago), the U abundances may be enriched in carbonates up to ~100X relative to carbonates deposited in the deep oceans (e.g. Hole 316, ~4460 m depth). An organic rich sediment will favor reduction of a small fraction of the UO_2^{+2} carbonate complexes to U^{+4} . Because the U/Th ratio is ~30,000 in seawater, U/Th changes in carbonates (coatings) may be attributed to small fractions, say $\sim 10^{-3}$, of UO_2^{+2} reduction followed by hydrogenous coprecipitation of the highly insoluble $\text{U}(\text{OH})_4$, $K_{sp} \sim 10^{-56}$.

The U abundances in the 577B-1 K/T peak [2], the 577 K/T peak, the -0.2 Ma peak [8], and before and after these peaks indicate no significant changes in the U/Th ratios relative to carbonates deposited in normal deep Pacific ocean (Hole 316) and Laytonville Limestones. Also the absolute U abundances in carbonates before and after the K/T peak at ~0.05 ppm are similar to U abundances observed in normal deep sea carbonates. In conclusion, these observations indicate no significant reduction of $\text{UO}_2(\text{CO}_3)_2$ or

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$\text{UO}_2(\text{CO}_3)_3^{4-}$ to $\text{U}(\text{OH})_4$ before, during, and after the K/T event.

From a chemical redox perspective, the above U and Mn observations are consistent. Calculating the Es under seawater conditions for the couples $\text{UO}_2(\text{CO}_3)_3^{4-}/\text{U}(\text{OH})_4//\text{H}_2\text{O}/\text{O}_2$, $\text{UO}_2(\text{CO}_3)_2^{2-}/\text{U}(\text{OH})_4//\text{H}_2\text{O}/\text{O}_2$, and $\text{MnO}_2/\text{Mn}^{2+}/\text{H}_2\text{O}/\text{O}_2$, and using a modified E^0 for the $\text{H}_2\text{O}/\text{O}_2$ couple [10], I find that the reducing potentials for reduction of the uranyl carbonates are ~0.6V lower than the modest reducing potential required for MnO_2 reduction.

REFERENCES: [1] Jin G.-Y. and Schmitt R.A. (1989) *Lunar and Planet Sci.* XX, 464-465; [2] Michel et al. (1985) *Init. Repts. D.S.D.P.* 86, 533-538; [3] Anders E. (1989) *Nature* 342, 255-257; [4] Schmitt R.A. (1990) II., this volume; [5] Von Damm et al. (1985) *G.C.A.* 49, 2197-2220; [6] Nojiri et al. (1989) *Nature* 342, 667-670; [7] Lyle et al. (1987) *Geophys. Res. Letts.* 14, 595-598; [8] Jin G.-Y. and Schmitt R.A. (1989) *Lunar and Planet Sci.* XX, 460-461; 462-463; [9] Zachos et al. (1985) *Init. Repts. D.S.D.P.* 86, 513-532; [10] Liu et al. (1989) *G.C.A.* 52, 1361-1371.

Mn/La Ratios in Pacific Marine Carbonates (CaCO_3)
Over the Past 100 Ma

Sample/D.S.D.P. Hole ^a	Age (Ma)	Mn (ppm) ^b	La (ppm) ^b	Mn/La	Sample/D.S.D.P. Hole ^a	Age (Ma)	Mn (ppm) ^b	La (ppm) ^b	Mn/La
316	<1	750	6.4	117					
577	-1.0	580	5.2 (4.4) ^c	112 (132) ^c	After Peak 577	66.3-65.9	130	17	7.6
577	3.5	450	6.3 (5.3) ^c	71 (85) ^c	K/T Peak 577	66.4	1,120	171	6.5
577	4.5	590	13.7 (9.8) ^c	43 (60) ^c	K/T Peak A577B-1	66.4	1,310	199	6.6
316	7	350	8.3	42	Before Peak 577	66.4	100	13.5	7.4
316	35	410	7.5	55	Before Peak A577B-1	66.4	107	12.5	8.6
316	55	980	14.5	68	577	66.5-67.1	150	17	9
577	58	370	16.9	22	After Peak 577B-1	66.6	330	22	15
577	59	147	8.0	18	-0.2 Ma Peak 577B-1 ^d	66.6	1,100	193	32
316	60	1,400	30.2	46	Before Peak 577B-1	66.6	250	23	11
316	61	1,190	15.5	77					
577	63	197	11.4	17	316	-70	860	19.4	44
316	64	1,090	16.8	65	316	70	910	16.6	55
316	64	1,100	14.5	76	316	71	730	14.7	50
316	-65	980	14.1	70	316	71	650	15.1	43
After Peak A577B-1	=65.1	590	27	22	316	-75	730	20.9	35
+1.2 Ma Peak A577B-1 ^d	=65.2	1,480	1,480	18	Laytonville Limestones	-93	740	11.2	66
Edge of Peak 577	=65.3	1,060	47	22	Laytonville Limestones	-93	790	9.0	88
Before Peak A577B-1	=65.4	500	21	24	Laytonville Limestones	-97	510	9.0	57
577	=65.8	220	21	10.5	Laytonville Limestones	-97	810	7.8	104
					Pacific Seawater				3

^a Hole 316 is ~2,300 km S. of Hawaii at ~4,460 m depth. Holes 577 and 577B-1 are ~60 m apart and are on the Shatsky Rise at ~2,680 m depth and ~2,200 km ESE of Japan. Laytonville Limestones were deposited in ~500-2,000 m depth in the central-eastern Pacific. INAA data for Holes 316, 577, and 577B-1 (-0.2 Ma peak) were obtained by M.R.U. Miah, G.-Y. Jin, and R.A. Schmitt.

^b The Mn and La in each sample were corrected for N.A.S.C.-like detrital clay by assuming all Al in carbonates is detrital and Al=9.9%, Mn=460 ppm, and La=31 ppm in N.A.S.C. Net integrated values for peaks at -0.2 Ma, K/T and +1.2 Ma were obtained by subtracting background values.

^c If the REE concentrations in the clay detritus were higher by ~20% and ~50% relative to N.A.S.C. in the 1.0 Ma sample and in the 3.5 and 4.5 Ma samples, respectively, the La* values are lower and the corrected $\text{Ce}^{\text{A*}}$ values are ~0.06, in line with normal $\text{Ce}^{\text{A*}}$ values for normal oceanic redox environments.

^d Using Zachos et al. [9] sedimentation rates, the peaks at -0.2 Ma and +1.2 Ma before and after K/T times, respectively, replace the -0.5 Ma and +1.5 Ma peaks of our previous works cited in [1,8].

^Δ L.B.L. data from Michel et al. [2].