EARTH'S PARTIAL PRESSURE OF CO_2 OVER THE PAST 120 Ma; EVIDENCE FROM Ce ANOMALIES IN THE DEEP (>600 m) PACIFIC OCEAN, I;

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

We [1] have found that Ce serves as a chemical tracer of paleo-oceanic redox conditions. It has been shown [2-6] that the unoxidized and soluble Ce^{3+} in modern seawater exhibits a negative anomaly relative to the other soluble REE^{3+}. We [1] derived an expression of soluble Ce^{3+} in seawater that was ~1900X greater than the average observed Ce in 600-5000 m Pacific seawater [7]. Since $Ce(CO_3)^+$ and $Ce(CO_3)_2^-$ complexes greatly exceed the $Ce(PO_4)^\circ$ complexes in seawater [8], we have followed the formulations of [1] using carbonate complexes and have found that the calculated Ce and observed concentrations in the deep 600-5000 m Pacific Ocean agree within the uncertainties of the thermodynamic data. As expected, the calculated Ce concentrations are a strong function of pH and found to be lesser functions of CO_3^{2-} activities.

Cerium depletion in seawater is expressed in a relative way by a defined anomaly, Ce^{A*} = observed Ce abundance normalized to N.A.S.C. (North American Shale Composite)/Ce expected abundance interpolated between La and Nd, normalized to REEs in N.A.S.C. [9]. Abundances of the light REE in average fluvial input to the oceans are approximately proportional to N.A.S.C. abundances [10-12]. Because seawater pH is controlled by $P(CO_2) \propto [H^+]^2$, the Ce^{A*} is in turn governed mainly by $P(CO_2)$.

The seawater REE pattern is preserved in relatively pure $CaCO_3$ sediments [1]. Correcting for the contributions of small amounts of aeolian or other N.A.S.C.-like clay particulates in the whole rock carbonate specimens, we observe that generally 95-98% of the total observed REEs in the carbonate sediments of this study precipitated from seawater onto the Fe-oxyhydroxide coatings of the $CaCO_3$ grains and onto the clay particulate surfaces during the 10^4-10^6 year exposure of the sediment to direct seawater and interstitial seawater. Therefore, the observed Ce^{A*}s in the carbonates equal the Ce^As of the parental oceans.

If we assume that the REE concentrations in seawater remained constant at times 1 and 2, the following expression is used for estimations of pHs at times 1 and 2.

$$\log (Ce_2^{A*}/Ce_1^{A*}) = [0.50 \log (a^3_{CO_3^{2-}}) - 0.50 \log (a_{Ce(CO_3)_2^-}/a_{Ce(CO_3)^+})$$
$$-\log (0.33\, pH-2.0) -0.25 \log P_{O_2} -3.0\, pH]_2 - [0.50 \log (a^3_{CO_3^{2-}})$$
$$-0.50 \log (a_{Ce(CO_3)_2^-}/a_{Ce(CO_3)^+}) -\log (0.33\, pH-2.0) - 0.25 \log P_{O_2} -3.0\, pH]_1$$

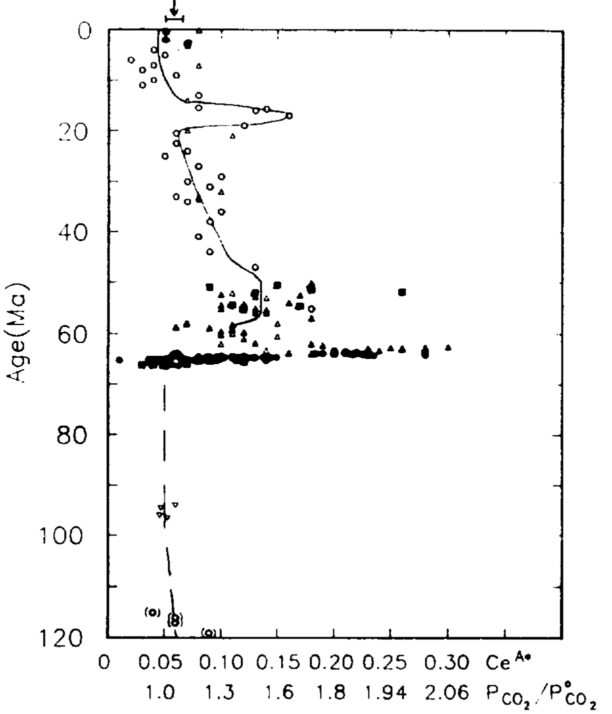
For calculations of pHs at 1 and 2, we will assume that P_{O_2} changes during the Phanerozoic were trivial relative to $P(CO_2)$ changes. Also the buffering effects and formulas [13] were utilized for estimations of $P(CO_2)$. Therefore, from experimentally determined Ce^{A*} in marine carbonates of different ages and associated paleo-pH values atmospheric $P(CO_2)$ values are calculated relative to present deep sea conditions as a reference.

Using INAA, we have determined 26-32 elements in ~205 carbonate samples. We have also calculated the Ce^{A*} for 60 carbonates, 63.4-65.1 Ma, L.B.L. Hole 577B data [14]; ~40 samples were mostly under the full K/T Ir peak.

Observations shown in Figs. 1 and 2 are summarized as follows: 1. From 0-14 Ma, the Ce^{A*}s and $P(CO_2)$ are equal to the present values. 2. Between 15-19 Ma, the Ce^{A*} peak at ~17 Ma corresponds to a $P(CO_2)$ ~1.6X $P^\circ(CO_2)$. Within age uncertainties, this peak corresponds to the flooding time of Columbia River Basalts (CRBs). 3. From ~20-50 Ma, the Ce^{A*}s and $P(CO_2)$s appear to increase uniformly. 4. In the 50-57 Ma interval, early Eocene, the data from three Pacific sites indicate an average Ce^{A*} of 0.13 and $P(CO_2) \approx 1.5 \pm 0.2$X. 5. In Fig. 2, we have expanded the Paleocene and upper-upper Maastrichtian to emphasize relationships to the K/T Ir peak at 64.7 Ma [15] and the floodings of the Deccan Traps that began before the K/T Ir peak [15]. The K/T Ir peak in Shatsky Plateau samples has been defined at 65.0 Ma for calculation of other relative ages. Ce^{A*}s and $P(CO_2)$ increase uniformly from ~58-62 Ma. From 62.5-64.3 Ma, the Ce^{A*} and $P(CO_2)$ reached their maxima, with an average $P(CO_2)$ ~1.9X over this interval. 6. At 64.3 Ma, the Ce^{A*} and $P(CO_2)$ decline abruptly, with a $P(CO_2)$ ~1.3X at 64.5 Ma. 7. At K/T Ir peaking, the Ce^{A*}s and $P(CO_2)$ are identical to the present Pacific Ocean. Phenomena that caused the celebrated K/T observations did not affect significant changes in the Earth's $P(CO_2)$. 8. The K/T Ir peak is flanked by Ce^{A*} and $P(CO_2)$ peakings at 64.6 Ma and 65.2 Ma yielding $P(CO_2)$ values of ~1.6X and ~1.5X, respectively. 9. From 65.3-66.2 Ma, the deep Pacific regime was identical to the present. If the Deccan Traps (DTs) began before the K/T Ir peaking event [15] and flowed over a ~0.5 Ma interval, the voluminous DTs' emissions of CO_2, SO_2, HCl etc. gases were insufficient to change the Pacific Ocean's pH. Because the DTs are considerably more voluminous relative to the CRBs, the tentative conclusion reached in #2 above is questionable. 10. At 95 Ma, the Ce^{A*} and $P(CO_2)$ were identical to present conditions. 11. The four Hole 316 data between 115-119 Ma represent carbonates deposited in shallow to intermediate depths, i.e. <200 m - ~500 m (?) [16]. For such suggested depths, the observed Ce^{A*} and $P(CO_2)$ correspond to the present values. 12. In the interval 69-76 Ma, we have analyzed 24 carbonates, yielding an average Ce^{A*} = 0.16±0.05. Because some or most of these samples may have derived from turbiditic flows from nearby edifices, i.e. carbonates deposited in shallow seawater, we are not able to use a definite seawater reference. For example, the present geometric mean Ce^{A} in shallow Pacific seawater is ~0.22, with a range from 0.10-0.43. If the above 24 carbonates were deposited in shallow seawater, the best estimate of $P(CO_2)$ in the 69-76 Ma would be the present value. 13. Paleosol carbonate data yield estimates of $P(CO_2)$ ~5-10X at ~120 Ma [17] and <2X throughout the Tertiary [18]. These estimates at 120 Ma are clearly at variance with our estimate of ~1.0X. Our $P(CO_2)$ estimate at ~3 Ma agrees with [19]. 14. Our $P(CO_2)$ estimates contrast sharply with the theoretical modeling of [20] who calculated $P(CO_2)$ values of 6^{+6}_{-4}X at ~120 Ma, $4^{+6}_{-2.5}$X at 95 Ma, and $2^{+1.5}_{-0.8}$X at K/T time. At these three times, our Ce^{A}s and $P(CO_2)$s of the Pacific Ocean were identical to the present values.

References: [1] Liu Y.-G. et al. (1988) G.C.A. 52, 1361-1371. [2] Goldberg E.D. et al. (1963) J.G.R. 68, 4209-4217. [3] Høgdahl O.T. et al. (1968) Adv. Chem. Ser. 73, 308-325. [4] Elderfield H. and Greaves M.J. (1982) Nature 296, 214-219. [5] Klinkhammer G. et al. (1993) Nature 305, 185-188. [6] De Baar H.J.W. et al. (1985) G.C.A. 49, 1943-1959. [7] Piepgras D.J. and Jacobsen S.B. (1992) G.C.A. 56, 1851-1862. [8] Lee J.H. and Byrne R.H. (1992) G.C.A. 56, 1127-1137. [9] Gromet L.P. (1984) G.C.A. 48, 2469-2482. [10] Goldstein S.J. and Jacobsen S.B. (1988) E.P.S.L. 88, 241-252; 89, 35-47. [11] McLennan S.M. (1989) Rev. Min. 21, 169-200. [12] Elderfield H. et al. (1990) G.C.A. 54, 971-991. [13] Stumm W. and Morgan J.J. (1981) Aquatic Chem., Chapter 4. [14] Michel H. et al. (1985) Init. Repts. D.S.D.P. 86, 533-538. [15] McWilliams M.O. (1992) EOS 73, No. 14, 363; the K/T Ir age is probably closer to 64.9 Ma, priv. com. from McWilliams. [16] Kauffman E.G. (1973) Init. Repts. D.S.D.P. 33, 503-535. [17] Cerling T.E. (1984) E.P.S.L. 71, 229-240; Am. J. Sci. (1991) 291, 377-400. [18] Cerling T.E. et al. (1992) EOS 73, No. 43, 95. [19] Raymo M.E. and Rau G. (1992) Ibid. [20] Berner R.A. (1990) Science 249, 1406-1409.

Pacific Ocean deep sea carbonates ($CaCO_3$) sediments: Manihiki Plateau Holes 317A, 317B ○, Shatsky Plateau 577 ▲, 577A ■, 577B ●; Laytonville Limestones ▽; Hole 316 △. Ce anomalies (Ce^{A*}) of carbonates equal Ce^{A} of Pacific Ocean. Present Ce^{A} in 600-5000 m Pacific Ocean [7].



Pacific Ocean Shatsky Plateau deep sea (> 1800 m) carbonate ($CaCO_3$) sediments. Ce anomalies (Ce^{A*}) of carbonates equal Ce^{A} of Pacific Ocean. Present Ce^{A} of 600-5000 m Pacific Ocean [7].