EARTH'S PARTIAL PRESSURE OF CO₂ OVER THE PAST 120 Ma; EVIDENCE FROM Ce ANOMALIES IN THE DEEP (> 600 m) PACIFIC OCEAN, I; Y.-G. Liu¹² and R.A. Schmitt¹⁴.¹ The Radiation Center and Departments of Chemistry and Geosciences, and ²College 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 Ce³⁺ in modern seawater exhibits a negative anomaly relative to the other soluble REE³⁺. We [1] derived an expression of soluble Ce³⁺ in seawater that was ~1900X greater than the average observed Ce in 600-5000 m Pacific seawater [7]. Since Ce(CO₃)²⁺ and Ce(CO₃)⁻ complexes greatly exceed the Ce(PO₄)²⁺ 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 CO₃²⁻ activities.

Cerium depletion in seawater is expressed in a relative way by a defined anomaly, CeA⁺ = 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 atmospheric P(CO₂) = [H⁺]², the CeA⁺ is in turn governed mainly by P(CO₂).

The seawater REE pattern is preserved in relatively pure CaCO₃ 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 CaCO₃ grains and onto the clay particulate surfaces during the 10⁴-10⁶ year exposure of the sediment to direct seawater and interstitial seawater. Therefore, the observed CeA⁺ in the carbonates equal the CeA⁺ 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.

\[
\log \left( \frac{\text{CeA}^+}{\text{CeA}^+} \right) = 0.50 \log \left( \frac{a_{\text{Ce}^3+}}{a_{\text{Ce}^+}} \right) - 0.50 \log \left( \frac{a_{\text{Ce}^3+}}{a_{\text{Ce}^+}} \right)^x - 0.50 \log \left[ \frac{\text{P(CO}_2)}{3.0 \text{ pH}^{-2.0}} \right] \]

Where \( x \) is 2, the CeA⁺ is in turn governed mainly by P(CO₂). Therefore, from experimentally determined CeA⁺ in marine carbonates of different ages and associated paleo-pH values atmospheric P(CO₂) 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 CeA⁺ 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 CeA⁺s and P(CO₂) are equal to the present values. 2. Between 15-19 Ma, the CeA⁺ peak at ~17 Ma corresponds to a P(CO₂) ~1.6X P(CO₂). Within age uncertainties, this peak corresponds to the flooding time of Columbia River Basalts (CRBs). 3. From ~20-50 Ma, the CeA⁺s and P(CO₂)s appear to increase uniformly. 4. In the 50-57 Ma interval, early Eocene, the data from three Pacific sites indicate an average CeA⁺ of 0.13 and P(CO₂) = 1.5±0.2X. 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. CeA⁺s and P(CO₂) increase uniformly from ~58-62 Ma. From 62.5-64.3 Ma, the CeA⁺ and P(CO₂) reached their maxima, with an average P(CO₂) ~1.9X over this interval. 6. At 64.3 Ma, the CeA⁺ and P(CO₂) decline abruptly, with a P(CO₂) ~1.3X at 64.5 Ma. 7. At K/T Ir peaking, the CeA⁺s and P(CO₂) 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(CO₂). 8. The K/T Ir peak is flanked by CeA⁺ and P(CO₂) peakings at 64.6 Ma and 65.2 Ma yielding P(CO₂) 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 CO2, SO2, 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 CeA* and P(CO2) 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 CeA* and P(CO2) correspond to the present values. 12. In the interval 69-76 Ma, we have analyzed 24 carbonates, yielding an average CeA* = 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 CeA 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(CO2) in the 69-76 Ma would be the present value. 13. Paleosol carbonate data yield estimates of P(CO2) ~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(CO2) estimate at ~3 Ma agrees with [19]. 14. Our P(CO2) estimates contrast sharply with the theoretical modeling of [20] who calculated P(CO2) values of 6.4+8X at ~120 Ma, 4.6±X at 95 Ma, and 2.6±X at K/T time. At these three times, our CeA's and P(CO2)s of the Pacific Ocean were identical to the present values.