

**EARTH'S PARTIAL PRESSURE OF CO<sub>2</sub> OVER THE PAST 120 Ma; EVIDENCE FROM Ce ANOMALIES IN THE DEEP (> 600 m) PACIFIC OCEAN, I; Y.-G. Liu<sup>1,2</sup> and R.A. Schmitt<sup>1,4</sup>, <sup>1</sup>The Radiation Center and Departments of <sup>2</sup>Chemistry and <sup>3</sup>Geosciences, and <sup>4</sup>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<sup>3+</sup> in modern seawater exhibits a negative anomaly relative to the other soluble REE<sup>3+</sup>. We [1] derived an expression of soluble Ce<sup>3+</sup> in seawater that was ~1900X greater than the average observed Ce in 600-5000 m Pacific seawater [7]. Since Ce(CO<sub>3</sub>)<sup>+</sup> and Ce(CO<sub>3</sub>)<sub>2</sub><sup>-</sup> complexes greatly exceed the Ce(PO<sub>4</sub>)<sup>o</sup> 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<sub>2</sub><sup>2-</sup> activities.

Cerium depletion in seawater is expressed in a relative way by a defined anomaly, Ce<sup>A\*</sup> = 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<sub>2</sub>) ∝ [H<sup>+</sup>]<sup>2</sup>, the Ce<sup>A\*</sup> is in turn governed mainly by P(CO<sub>2</sub>).

The seawater REE pattern is preserved in relatively pure CaCO<sub>3</sub> 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<sub>3</sub> grains and onto the clay particulate surfaces during the 10<sup>4</sup>-10<sup>6</sup> year exposure of the sediment to direct seawater and interstitial seawater. Therefore, the observed Ce<sup>A\*</sup>s in the carbonates equal the Ce<sup>A\*</sup>s 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.

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

For calculations of pHs at 1 and 2, we will assume that P<sub>O<sub>2</sub></sub> changes during the Phanerozoic were trivial relative to P(CO<sub>2</sub>) changes. Also the buffering effects and formulas [13] were utilized for estimations of P(CO<sub>2</sub>). Therefore, from experimentally determined Ce<sup>A\*</sup> in marine carbonates of different ages and associated paleo-pH values atmospheric P(CO<sub>2</sub>) 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<sup>A\*</sup> 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<sup>A\*</sup>s and P(CO<sub>2</sub>) are equal to the present values. 2. Between 15-19 Ma, the Ce<sup>A\*</sup> peak at ~17 Ma corresponds to a P(CO<sub>2</sub>) ~1.6X P<sub>o</sub>(CO<sub>2</sub>). Within age uncertainties, this peak corresponds to the flooding time of Columbia River Basalts (CRBs). 3. From ~20-50 Ma, the Ce<sup>A\*</sup>s and P(CO<sub>2</sub>)s appear to increase uniformly. 4. In the 50-57 Ma interval, early Eocene, the data from three Pacific sites indicate an average Ce<sup>A\*</sup> of 0.13 and P(CO<sub>2</sub>) = 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. Ce<sup>A\*</sup>s and P(CO<sub>2</sub>) increase uniformly from ~58-62 Ma. From 62.5-64.3 Ma, the Ce<sup>A\*</sup> and P(CO<sub>2</sub>) reached their maxima, with an average P(CO<sub>2</sub>) ~1.9X over this interval. 6. At 64.3 Ma, the Ce<sup>A\*</sup> and P(CO<sub>2</sub>) decline abruptly, with a P(CO<sub>2</sub>) ~1.3X at 64.5 Ma. 7. At K/T Ir peaking, the Ce<sup>A\*</sup>s and P(CO<sub>2</sub>) 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<sub>2</sub>). 8. The K/T Ir peak is flanked by Ce<sup>A\*</sup> and P(CO<sub>2</sub>) peakings at 64.6 Ma and 65.2 Ma yielding P(CO<sub>2</sub>) 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<sub>2</sub>, SO<sub>2</sub>, 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<sup>A\*</sup> and P(CO<sub>2</sub>) 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<sup>A\*</sup> and P(CO<sub>2</sub>) correspond to the present values. 12. In the interval 69-76 Ma, we have analyzed 24 carbonates, yielding an average Ce<sup>A\*</sup> = 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<sup>A</sup> 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<sub>2</sub>) in the 69-76 Ma would be the present value. 13. Paleosol carbonate data yield estimates of P(CO<sub>2</sub>) ~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<sub>2</sub>) estimate at ~3 Ma agrees with [19]. 14. Our P(CO<sub>2</sub>) estimates contrast sharply with the theoretical modeling of [20] who calculated P(CO<sub>2</sub>) values of 6<sup>+6</sup><sub>-4</sub>X at ~120 Ma, 4<sup>+6</sup><sub>-2.5</sub>X at 95 Ma, and 2<sup>+1.5</sup><sub>-0.8</sub>X at K/T time. At these three times, our Ce<sup>A</sup>s and P(CO<sub>2</sub>)s of the Pacific Ocean were identical to the present values.

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