

EARTH'S PARTIAL PRESSURE OF CO₂ OVER THE PAST 100-500 Ma; EVIDENCE FROM Ce ANOMALIES IN MOSTLY SHALLOW SEAS (<200m) AS RECORDED IN CARBONATE SEDIMENTS, II; Y.-G. Liu^{1,2}, J.W. Reinhardt⁵, and R.A. Schmitt^{1,4}, ¹The Radiation Center and Departments of ²Chemistry and ³Geosciences, and ⁴College of Oceanography, Oregon State University, Corvallis, Oregon 97331, USA; and ⁵Institute for Paleontology, Universität Erlangen, Erlangen, Ger. Present at Myanma Shell-Burma, 2501 An The Hague, The Netherlands.

In a previous abstract in this volume [1] we reported the direct relationship of Ce anomalies, Ce^{A*}, recorded in 0.2-119 Ma CaCO₃ sediments to the Ce anomalies, Ce^A, in the parental Pacific deep seawater and their relationship to atmospheric P(CO₂) relative to the present P^o(CO₂). Because carbonate samples from ocean basins, obtained from D.S.D.P. and O.D.P., are restricted to <130 Ma, we have analyzed via INAA [1] continental CaCO₃ samples that were deposited in ancient oceans and shallow sea platforms <200 m over central USA, central Europe, China, and Saudi-Arabian/Oman. Shallow sea conditions over continents as well as platforms may have been subjected to more localized variations because of their complex chemical regimes as well as being at higher temperatures relative to the <200 m Pacific Ocean's mixed layer. This has been observed in the spread of trace elements in ~250 Ma China carbonates and in carbonates from the ~150 Ma oil-rich Arab Formation.

Although many dolomites were analyzed, they were excluded from P(CO₂) calculations in order to avoid unknown dolomitization effects. Although we adopted such a conservative approach, examination [2] of REE and Nd geochemistry of regionally dolomitized carbonates indicates dolomitization does not affect their geochemistry during diagenesis. Comparison of our dolomite and limestone data from the same formations support the [2] observations.

It has been noted that carbonates with low U/Th ratios and low U abundances (e.g. 0.16±0.10 ppm in Central Pacific deep sea carbonates) may be utilized as diagnostic indicators for obtaining reliable Ce^{A*} measurements [3]. Because of associated organic debris in shallow sea platforms, considerable reduction of UO₂²⁺ - U⁴⁺ is expected (U/Th > 3x10⁴ in seawater) with adsorption of U(OH)₄ onto oxyhydroxide coatings of carbonate minerals; e.g. the average U in 16 Arabian limestones was 1.4±0.9 ppm. Regimes favoring reduction of UO₂²⁺ could also inhibit Ce³⁺ - Ce(OH)₄ oxidation. However, the absence of significant Ce^{A*} - U correlations at many shallow sea sites indicates that Ce^{A*} values obtained from shallow sea deposited carbonates may be considered reliable for ΔpH and P(CO₂) calculations.

We have plotted the Ce^{A*} values over the 75-470 Ma interval. For P(CO₂) calculations, we assumed as a reference standard, the <200 m mixed Pacific Ocean with a Ce^A geometric mean of 0.22 and a range of 0.10-0.43 [4]. Five China carbonates at 250, 261, and 280 Ma that are shown as (♦) were deposited in deeper open platforms, say up to ~1000 m and therefore exhibit quite reliable Ce^{A*} and P(CO₂) values. Their actual Ce^{A*} values were 0.28, 0.19, 0.19, 0.10, and 0.08 which are consistent with the Ce^A in Pacific intermediate seawater, 200-600m [4]; we normalized these actual values to the average Ce^A in shallow seawater for depiction, i.e. multiply by 0.22/0.10. Another 430 Ma China deeper ocean platform sample was 0.74, which corresponds to a P(CO₂) ~2.7X P^o(CO₂). This more reliable value of 2.7X relative to an average of P(CO₂) ~1.9X for two USA 430 Ma shallow seawater samples is in line with lower CO₂ solubilities expected from higher temperatures, say ≥30°C, in the <100 m shallow sea over the central USA during the early Silurian period.

Observations are summarized below.

1. Because P(CO₂) values obtained from reliable deep Pacific Ocean carbonates [1] in the 67-119 Ma interval were similar to the present P^o(CO₂) values, we have drawn a 1.0 ratio for that interval. Two of three Saudi-Arabian 75-106 Ma carbonates fall within the Ce^A range for the present Pacific Ocean mixed layer. Coincidentally, a 90 Ma Oman carbonate yielded Ce^{A*}=0.18. This Ce^{A*} for a shallow sea platform agrees well with the Ce^{A*}s of the 95 Ma Laytonville Limestones deposited in deep seas [1], both yielding P(CO₂) ~1.0X.
2. Although there is considerable scatter among the ~150 Ma carbonates, the average Ce^{A*} value suggests that P(CO₂) increased during the early Cretaceous, i.e. 1.0X at ~120 Ma to ~1.4X at ~150 Ma.
3. At ~250 Ma, the average Ce^{A*} in 13 shallow sea China carbonates agrees well with the single and more reliable ~250 Ma China carbonate (♦) deposited in deeper open platform. We suggest that P(CO₂) ranged from 1.4-1.7X over the Jurassic and Triassic periods.

4. At ~280 Ma, three China carbonates deposited in deeper open platforms and therefore considered more reliable are consistent with a European carbonate, which indicate Ce^A and P(CO₂) values similar to the present. The minimum at ~280 Ma corresponds to the great Permo-Carboniferous glaciation. Modeling levels of atmospheric CO₂ over the past 570 Ma predicts a P(CO₂) ~1.0±0.2 at 280 Ma [5].

5. From 280 Ma to 470 Ma, the trend favors increasing Ce^{A*} and corresponding P(CO₂) values between 1.9-2.7X, with a more reliable value closer to 2.7X at 430 Ma because of the unknown higher (>30°C relative to ~20°C in the present Pacific's mixed <200 m layer between ±20° latitude) temperature in the <100 m seawater over continental USA which was located just south, ~15° S, of the equator at ~430 Ma [6].

For comparison, paleosol carbonate data yield considerably higher P(CO₂) estimates of ~5-10X P°(CO₂) at ~120 Ma, ~5-9X at ~140 Ma, ~7-13X at ~200 Ma [7], and ~3-5X at ~370 Ma and ~11-16X at ~410 Ma [8]. Corresponding theoretical models indicate P(CO₂) values of 6⁺⁶X at ~120 Ma, 4⁺²_{-2.5}X at ~140 Ma, 4⁺³_{-1.5}X at ~200 Ma, 8⁺⁵₋₅X at ~370 Ma, 11⁺⁷₋₇X at ~410 Ma, and 14⁺⁷₋₁₀X at ~470 Ma [5]. During the Cretaceous, a predicted P(CO₂) ~2.3X was reported [9].

The greenhouse effect induced by increasing CO₂ seems to be an important factor contributing to Earth's climatic changes [10,11]. The P(CO₂) trend is in general consistent with climatic changes noted in the past: glaciation during the Carboniferous-Permian periods, warmer climates through the Mesozoic, and a temperature decline during the Paleogene [12]. The P(CO₂) patterns of our work are similar to a "best guess" by [13].

The geochemical cycles that control atmospheric CO₂ have been discussed by [14,15,9]. Plate tectonics, which affects both metamorphic-magmatic decarbonation and changes in continental land area, is one of the major controls of atmospheric CO₂. Climatic changes induced by CO₂ have been limited to the intensity of sea-floor hydrothermal activity induced by tectonic rearrangements of sea-floor spreading center; e.g. in the early Eocene [16]. The estimated P(CO₂) values of ~1.5X [1] for that epoch support their [16] suggestion. During the Mesozoic, similar P(CO₂) values could be related to the breakup of Pangaea starting with the separation of North America and Gondwanaland in the late Triassic (~230 Ma) followed by the breakup of Gondwanaland during the late Jurassic (~150 Ma) and Cretaceous [17,6,18].

We acknowledge the following persons and institutions for supplying carbonate samples: Arabian-American Oil Co. (Aramco), S.D. Bower (and D.G. Hadley and D.L. Schmidt of the U.S.G.S.) for Saudi-Arabian/Oman samples; Illinois State Geol. Survey, R.D. Norby and M.W. Leighton for Illinois and Iowa samples; Ohio Dept. Nat. Res., D.A. Stith for Ohio samples; U.S.G.S., H.E. Cook for Laytonville Limestones; and D.S.D.P. and O.D.P. personnel for Pacific carbonates.

References: [1] Liu Y.-G. and Schmitt R.A. (1993), this volume. [2] Banner J.L. et al. (1988) *J. Sed. Pet.* **58**, 415-432. [3] Liu Y.-G. et al. (1988) *G.C.A.* **52**, 1361-1371. [4] Piepgras D.J. and Jacobson S.B. (1992) *G.C.A.* **56**, 1851-1862. [5] Berner R.A. (1990) *Science* **249**, 1406-1409. [6] Ziegler A.M. (1981) *Paleobot. Paleoecol., and Evol.* **2**, 231-266. [7] Cerling T.E. (1991) *Am. J. of Sci.* **291**, 377-400. [8] Mora C.I. and Driese S.G. (1992) *EOS* **73**, No. 43, 95; Mora C.I. et al. (1991) *Geol.* **19**, 1017-1020. [9] Walker J.C.G. (1988) *Ind. J. Rad. Space Phys.* **17**, 147-154. [10] Walker J.C.G. et al. (1981) *J.C.R.* **86**, 9776-9782. [11] Marshall H.G. et al. (1988) *J.G.R.* **93**, 791-801. [12] Frakes L.A. (1979) *Climates Throughout Geol Time* (Elsevier). [13] Kasting J.F. (1987) *PreCamb. Res.* **34**, 205-229. [14] Berner R.A. et al. (1983) *Am. J. Sci.* **283**, 64-83. [15] Berner R.A. (1992) *G.C.A.* **56**, 3225-3231. [16] Owen R.M. and Rea D.K. (1985) *Science* **227**, 166-169. [17] Seyfert C.A. and Sirkin L.A. (1973) *Earth History and Plate Tectonics* (Harper & Row). [18] Ziegler A.M. et al. (1983) *Tidal Friction and Earth's Rot.* **II**, 240-252.

Shallow Sea deposited carbonate (CaCO₃) sediments: Saudi-Arabian Platform ●; China Platform ◆, Europe ■, USA (Ill., Iowa, Ohio) ✦. Range and geom. mean Ce^{A*} in <200 m Pacific Ocean [4]

