Elevated Eocene Atmospheric CO_2 and Its Subsequent Decline

Tim K. Lowenstein* and Robert V. Demicco

Quantification of the atmospheric concentration of carbon dioxide ($[CO_2]_{atm}$) during warm periods of Earth's history is important for predicting global warming, because over the next 100 years burning of fossil fuels may produce $[CO_2]_{atm}$ approaching 1000 parts per million by volume (ppm) (*1*). One such warm period, the early Eocene [~56 to 49 million years ago (Ma)], had the highest prolonged global temperatures of the Cenozoic, peaking ~52 to 50 Ma during the early Eocene climatic optimum (EECO) (*2*). However, the relation between atmospheric CO_2 concentrations and greenhouse climates of the early Eocene is uncertain because proxy measurements from paleosols (*3*, *4*), marine boron isotopes (*5*), and leaf stomatal indices (*4*) give estimated $[CO_2]_{atm}$ concentrations between 100 and 3500 ppm.

Estimates of ancient $[CO_2]_{atm}$ can be determined from the equilibrium assemblage of sodium carbonate minerals precipitated from waters in contact with the atmosphere (*6*). At present $[CO_2]_{atm}$ of ~380 ppm, trona ($NaHCO_3$•Na_2CO_3•$2H_2O$) crystallizes at temperatures above ~25°C in at least a dozen modern alkaline saline lakes worldwide. Natron (Na_2CO_3•$10H_2O$) forms at lower temperatures, but nahcolite ($NaHCO_3$) is rare because it is predicted to precipitate only under elevated $[CO_2]$ (Fig. 1A). The preponderance of trona in modern systems indicates that sodium carbonate deposition follows thermodynamic predictions.

During the EECO, long-lived lakes in the western United States deposited oil shale and sodium carbonate evaporites of the Wilkins Peak member of the Green River Formation and equivalents. The dominant sodium carbonate mineral of the Piceance Creek Basin, Colorado, is nahcolite up to ~300 m thick, which in places occurs as microcrystalline chemical mud finely interlayered with halite (NaCl). This nahcolite, confirmed by x-ray diffraction analysis, contains textures diagnostic of precipitation in contact with atmospheric CO_2 at the air-water interface of a perennial lake (fig. S1). The minimum $[CO_2]$ at which pure nahcolite precipitates, determined experimentally, is ~1330 ppm; however, coprecipitation with halite (Fig. 1A) requires a lower minimum $[CO_2]$, anchoring minimum early Eocene $[CO_2]_{atm}$ at >1125 ppm (Fig. 1B) (*6*). Estimates of paleotemperatures from the Green River basin before and after evaporite deposition suggest surface water temperatures varied seasonally from ~20° to 35°C [Supporting Online Material (SOM) text]. Precipitation of nahcolite plus halite at those temperatures fixes minimum early Eocene $[CO_2]_{atm}$ between 1125 and 2985 ppm.

Trona, rather than nahcolite, is the major sodium carbonate in the coeval Green River Formation, Green River Basin, Wyoming. The reaction

$$2NaHCO_3\ (\text{nahcolite}) + 2H_2O + Na^+ \leftrightarrow NaHCO_3{\bullet}Na_2CO_3{\bullet}2H_2O\ (\text{trona}) + H^+$$

indicates that trona forms instead of nahcolite under conditions of high activity of Na^+ (a_{Na^+}) and high pH, suggesting different brine chemistries in the Green River and Piceance Creek basin lakes.

The only other economic accumulation of nahcolite is the Anpeng deposit, Henan Province, China, also Eocene in age (SOM text). Trona is the principal sodium carbonate in younger deposits (Fig. 1B), indicating atmospheric $[CO_2]_{atm}$ dropped below 1125 ppm after the Eocene. Atmospheric $[CO_2]$ closer to modern values by the Miocene is suggested by the trona in the Beypazari deposit, Turkey (21.5 Ma). Trona is also the dominant sodium carbonate in the Pleistocene deposits of Searles Lake, California.

Primary nahcolite in the Green River evaporites gives firm geochemical evidence for elevated $[CO_2]_{atm}$ (>1125 ppm) in the early Eocene. These data support a causal connection between CO_2 and global warmth in the EECO and clarify the history of atmospheric CO_2 over the past 60 million years (My) (Fig. 1B). Estimates of early Eocene atmospheric CO_2 from Green River sodium carbonates are in the same range as those predicted by geochemical models (*7*). By ~20 Ma, all available data (*8*) suggest $[CO_2]_{atm}$ was at or near modern concentrations.

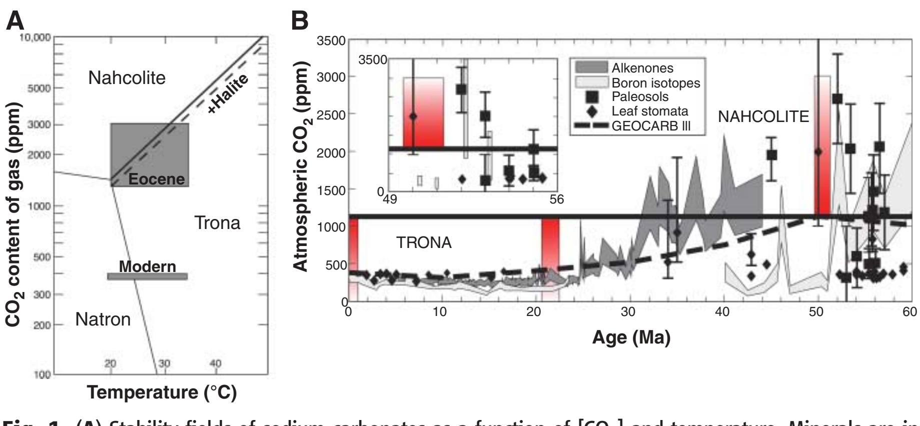

Fig. 1. (**A**) Stability fields of sodium carbonates as a function of $[CO_2]$ and temperature. Minerals are in equilibrium with solution and gas at 1 atm total pressure (*6*). Dashed line shows that addition of halite lowers $[CO_2]$ of the gas in equilibrium with nahcolite plus trona to 1125 ppm at 20°C (*6*). Shaded areas mark environmental boundaries (~20° to 35°C) for precipitation of sodium carbonate minerals today ($[CO_2]_{atm}$ ~ 380 ppm) and during the early Eocene. (**B**) Atmospheric $[CO_2]$ over the past 60 My, estimated from $\delta^{11}B$ of foraminifera (*5*), alkenone $\delta^{13}C$ (*8*), stomatal densities [compilation of (*4*)], paleosol carbonates [(*3*), compilation of (*4*)], and predicted GEOCARB III values (*7*). (Inset) Details for 56 to 49 Ma. The horizontal line at 1125 ppm is the minimum $[CO_2]_{atm}$ necessary to precipitate nahcolite. Probable $[CO_2]_{atm}$ values during deposition of Green River nahcolites (51.3 to 49.6 Ma), Beypazari trona (21.5 Ma ± 0.9 Ma), and Searles Lake trona (<1 Ma) are shaded red. Errors shown are discussed in (*3*–*5*) and (*8*).

References and Notes

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Supporting Online Material

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Fig. S1

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Department of Geological Sciences and Environmental Studies, State University of New York at Binghamton, Binghamton, NY 13902, USA.

*To whom correspondence should be addressed. E-mail: lowenst@binghamton.edu