

ATMOSPHERIC SCIENCE

Can climate feel the pressure?

Changes in atmospheric pressure may be an important long-term climate forcing mechanism

By Daniel J. Peppe¹ and Dana L. Royer²

Atmospheric carbon dioxide (CO₂) concentrations are widely held to be the main driver of climate change through the Phanerozoic (the past 541 million years), with warm intervals corresponding to high CO₂ concentrations and cold intervals having low CO₂ concentrations (1) (see the figure). However, paleoclimate models often cannot match proxy estimates of temperature and precipitation unless unrealistic CO₂ concentrations are prescribed (2, 3). The solution may come from an unexpected direction: atmospheric oxygen (O₂), which is not a greenhouse gas and thus provides no direct greenhouse forcing. On page 1238 of this issue, Poulsen *et al.* (4) report model results that identify O₂ as an important climate driver through its contribution to total atmospheric pressure.

O₂ has varied through the Phanerozoic from ~10 to 35% (see the figure), affecting the evolution and diversification of plants, animals, and insects (5, 6). Yet the possible influence of O₂ on climate has been underappreciated. Poulsen *et al.* show that changes in atmospheric density caused by geologically reasonable variations in O₂ partial pressure affect the scattering of incoming solar radiation. At high atmospheric pressure, shortwave scattering intensifies, leading to a weaker greenhouse forcing and a reduction in atmospheric water vapor, global precipitation, and surface temperatures; at low atmospheric pressure, the reverse patterns are seen. These results mark an important advance in thinking about climate over geologic time and may address a long-standing problem in paleoclimate research: disagreements between model results and proxy reconstructions of climate.

The authors focus on the Cenomanian (100 to 94 million years ago). Climate models for this time period consistently predict lower increases in temperature and moisture than seen in climate proxies, especially at mid- and high latitudes, given that CO₂ concentrations are constrained to between 500 and 2000 ppm (parts per million) by proxies and long-term carbon cycle models

(see the figure). Under a scenario in which O₂ is at the low end of the range of estimates (see the figure), these differences between climate models and proxy data largely disappear. The results have important implications for assessing climate during other times in Earth history.

The early Paleogene (66 to 50 million years ago) is one of the best-studied intervals of a hothouse planet, with proxy records

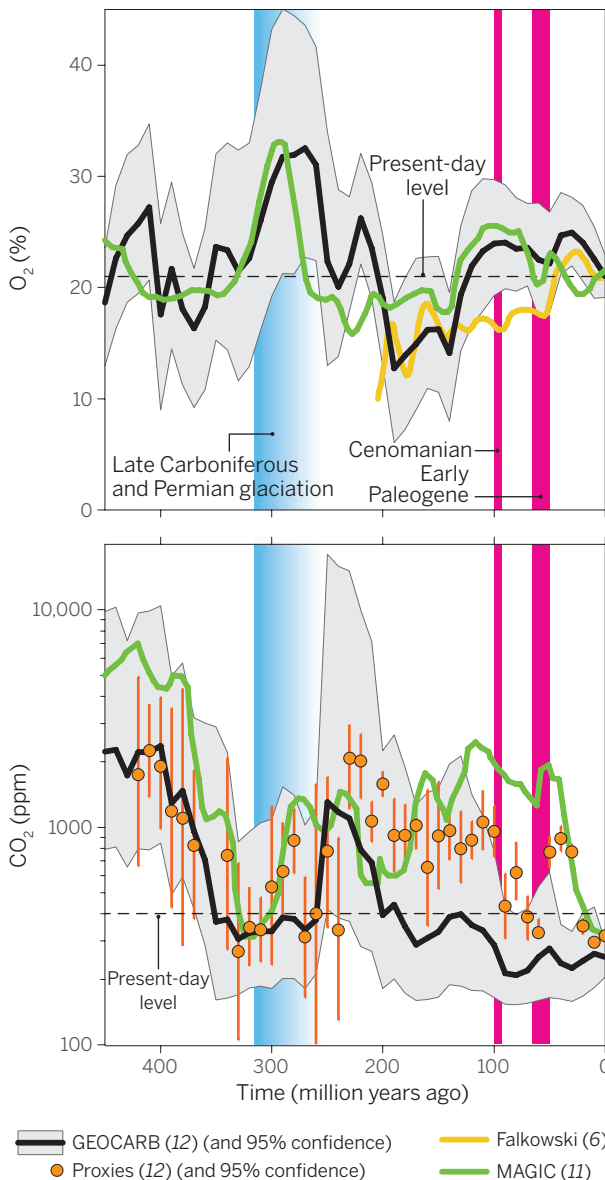
indicating very warm and wet conditions in mid-latitude and polar regions (2, 7) and CO₂ levels below 2000 ppm (1) (see the figure). Despite decades of intensive research, climate models predict too cool and too dry climates, especially in polar regions (2), unless CO₂ concentrations greater than 2500 ppm are used. O₂ during this time was probably between ~15 and 25% (see the figure). If the low-end O₂ estimates are correct (~15%), the

reduced density of the atmosphere relative to today would elevate surface temperatures and precipitation, particularly at the poles, likely reducing the model-proxy differences.

During the late Carboniferous and Permian (315 to 255 million years ago), Earth experienced the largest and longest glacial period of the Phanerozoic (8), coincident with high O₂ (as much as 35%) and low CO₂ (~350 ppm) (see the figure). Climate models require CO₂ to drop below 560 ppm to initiate ice sheet growth (8) and are thus broadly compatible with CO₂ constraints from proxies and long-term carbon cycle models. Nevertheless, climate model results should be revisited in light of Poulsen *et al.*'s findings, because the high-pressure atmosphere at this time likely caused additional

Poulsen *et al.*'s model results (4) indicate that oxygen-driven changes in atmospheric density cause changes in atmospheric water vapor, precipitation, and surface temperature. The model may help provide a mechanism that at least partially explains the cold temperatures during the late Carboniferous and Permian glaciation, when atmospheric pressures were high, as well as the warm temperatures during the Cenomanian and early Paleogene, when atmospheric pressures may have been lower (6, 11, 12).

Long-term record of O₂ and CO₂



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cooling and reduced precipitation. Additional cooling may provide a mechanism for near-tropical glaciation, because ice in the tropics cannot be modeled using radiative forcing from only CO₂ (3).

Both climate modelers and paleoclimate researchers most commonly express CO₂ in terms of volume fraction (such as parts per million by volume, or ppmv). However, if total atmospheric pressure is changing, these CO₂ estimates mean different things in terms of radiative forcing. For example, if the partial pressure of atmospheric CO₂ remains constant but the total atmospheric pressure decreases because of a drop in the partial pressure of atmospheric O₂, CO₂ concentrations (expressed in ppmv) will increase, even though the CO₂ radiative forcing will not have changed. Thus, if climate models prescribe CO₂ ppmv estimates informed from proxies from a time period with a different atmospheric pressure from today's (such as the Carboniferous or early Paleogene; see the figure), the modeled radiative forcing from CO₂ may be incorrect. There would be great benefit to developing a common language for use in modeling and proxy work—for example, reporting whenever possible the sea-level partial pressure of CO₂ along with the total atmospheric pressure of CO₂. Additionally, because all CO₂ proxies have been developed at modern atmospheric pressure, it will be crucial to test the sensitivity of CO₂ proxies at differing atmospheric pressures.

A critical limitation of exploring the climatic effects of Poulsen *et al.*'s model in the geologic past is that paleo-O₂ records are uncertain (see the figure). During the Cenomanian and early Paleogene, O₂ levels may have been lower or higher than today. New O₂ proxies are in development (9, 10), but as with any new proxy system, they must be tested thoroughly. Poulsen *et al.*'s study provides a convincing argument for the importance of developing a robust history of atmospheric O₂. ■

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NANOMATERIALS

Economical routes to colloidal nanocrystals

A new precursor library yields high-quality quantum dots for device applications

By Zeger Hens

Colloidal semiconductor nanocrystals (NCs) or “quantum dots” offer exquisite control of absorption and emission colors for device applications by tuning their size and shape (1). The proliferation of NC applications has been enabled by the “hot-injection” synthesis, which can tightly control the particle size to achieve pure colors (2). However, current hot-injection synthesis recipes are largely incompatible with low-cost, large-area remote phosphor applications of NCs. Reagents are too expensive, reaction mixtures too dilute, and conversion yields too low, especially if size tuning is accomplished by adjusting the reaction time. On page 1226 of this issue, Hendricks *et al.* (3) report on a radical improvement of the hot-injection synthesis economics of metal sulfide NCs by introducing a library of inexpensive thioureas as reagents.

The hot-injection synthesis is a homogeneous nucleation and growth reaction (4) initiated by the rapid mixing of reagents at elevated temperatures in apolar solvents. By stopping growth at a specific time, NCs of different sizes and thus different properties are readily obtained (see the first figure). Hendricks *et al.* introduce substituted thioureas as an alternative sulfur precursor for the formation of metal sulfide NCs, such as sulfides of lead (PbS), cadmium, zinc, and copper, by hot injection. As generic synthesis recipes for most of these NCs have been proposed before (5), this result may not seem particularly groundbreaking. However, unlike other approaches, the authors focus on reactions that have nearly quantitative chemical yield.

They manage to control the final NC size by adapting the reactivity of the thioureas through subtle changes of their composition (see the second figure, panel A). This size-tuning scheme relies on the most recent understanding of the several steps that turn injected precursors into NCs, especially the finding that NCs do not form by the separate

incorporation of the injected precursors, thiourea and a metal carboxylate. Instead, these precursors react to form the actual solute, and it is the solute supersaturation that initiates the nucleation and drives the growth of NCs (6).

This two-step reaction mechanism has important consequences. First, the rate of solute formation sets the rate of solute consumption by nucleation of new nuclei or growth of existing nuclei into larger NCs (see the second figure, panel B). Second, hot-injection synthesis becomes a zero-sum game where solute consumption by growth



Color shift. Colloidal nanocrystals have size-dependent optical properties. For example, photoluminescence of CdSe nanocrystals shifts from blue to red with increasing diameter.

can only increase at the expense of nucleation. Faster solute formation benefits nucleation, such that more NCs are formed by the time growth arrests nucleation (7). If all precursors injected are transformed in more NCs, their size at the end of the reaction will be smaller, which makes for an effective mechanism for size tuning at full yield (8).

By proposing an easily implemented chemical approach to adjust the rate of solute formation, Hendricks *et al.* likely make the best possible use of this tuning scheme. The vast possibilities for substitution make for an astonishing range of reactivities and thus a library of precursors fit to synthesize

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