Using the Past to Predict the Future?
Gabriele C. Hegerl, *et al.*
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by the concentration of the precursors and by temperature. Size control is important for exploiting quantum effects of NPs, such as the size-dependent fluorescence of semiconductor NPs. Current size control methods enable the production of NPs with size distributions sufficient to crystallize and form 2D and 3D lattices (*5–8*) (see the figure, panel B). Protocols for the synthesis of NPs of most inorganic materials already exist. In order to keep NP colloids stable, their surfaces are typically covered with charged molecules or with molecules that provide steric repulsion (ligands). These ligand molecules can be highly ordered, so that x-ray diffraction structures of crystallized ligand-coated NPs can be recorded. Even when proteins adsorb onto the NP surface under physiological conditions, the so-called protein corona possesses remarkable order (*9*).

By performing NP synthesis in templates or by making use of the fact that different crystalline facets of NPs can grow with different speeds, control of the NP shape is also possible (see the figure, panel C). Besides spherical NPs, NPs in the shape of rods (*10*), disks (*11*), cubes, and prisms (*12*) have been demonstrated, as have hollow (*13*) and branched NPs. Moreover, the material composition of NPs can be locally tuned. This began with core-shell structures, whereby the NP core and shell are composed of different materials and culminate in rod- or tetrapod-shaped NPs with attached spherical NPs (*14*) or branched structures of different materials (see the figure, panel D). The diversity of examples illustrates the control of material, size, shape, and composition of NPs that is now possible.

González *et al*. use a combination of all degrees of control, in addition to using clever concepts. One such concept is based on galvanic deposition. If a material (such as a metal) in reduced state A is present in a solution of atoms or molecules of B^+ in its oxidized state, which have a higher electrochemical potential, then the surface of the material A will be oxidized ($A \rightarrow A^+$) and driven to solution, whereas atoms or molecules from solution are reduced and deposited at the surface ($B^+ \rightarrow B$). For example, this process occurs for the case of an iron nail placed in a solution of copper ions. Some iron on the surface will go to solution, whereas the surface of the nail will be covered with elemental copper. On the other hand, the Kirkendall effect, which is based on different diffusion rates of a diffusion couple, has been used to create NPs with defined cavities (*13*). González *et al*. report a protocol in which they first synthesize Ag NPs and then create, by subsequent application of the Kirkendall effect and galvanic deposition, controlled cavities and coating of the Ag surface with Au (see the figure, panel E). By addition of Pd, even a third material could be integrated in the NPs.

Taking into account all the different parameters for the designed growth of colloidal NPs, we can conclude that modern synthesis techniques allow for excellent control of geometry and composition with maze-like interiors that are not available to physical growth techniques such as molecular beam epitaxy. Colloidal NPs may never be amenable to atom-by-atom control as demonstrated for small 2D assemblies, but larger 3D objects can be obtained in parallel. This paves the way for designing NPs to perfectly match their desired application.

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CLIMATE CHANGE

Using the Past to Predict the Future?

Reconstructions of climatic conditions on Earth during the Last Glacial Maximum may help to constrain the likely magnitude of global warming.

Gabriele C. Hegerl and Tom Russon

Predictions of future climate change are subject to considerable uncertainty, for two main reasons: Future factors that may influence climate—such as emissions of greenhouse gases, volcanic eruptions, and changing solar activity—are uncertain; and knowledge of how strongly the climate system responds to external influences, particularly increases in greenhouse gases, is incomplete. One way to summarize this latter type of uncertainty is by estimating the equilibrium climate sensitivity (ECS), which is defined as the equilibrium response of global surface temperature to a doubling of the atmospheric CO_2 concentration. On page 1385 of this issue, Schmittner *et al*. (*1*) report that the use of spatially more complete paleoclimate data for the Last Glacial Maximum (LGM) shows promise for narrowing the ECS uncertainty ranges relative to previous estimates.

School of GeoSciences, University of Edinburgh, Edinburgh EH9 3JW, UK. E-mail: gabi.hegerl@ed.ac.uk

The lower limit for ECS values is quite well constrained. A range of observational data shows a substantial change in global temperature in response to changes in Earth's energy balance (*2*, *3*). However, the upper limit has proven more difficult to estimate. This is reflected in the conclusions of the Intergovernmental Panel on Climate Change (IPCC) that the ECS "is likely to be in the range 2 to 4.5°C with a best estimate of about 3°C, and is very unlikely to be less than 1.5°C. Values substantially higher than 4.5°C cannot be excluded, but agreement of models with observations is not as good for those values" (*2*). This situation makes it difficult to rule out large temperature increases in response to greenhouse gas increases, or to estimate the atmospheric CO_2 concentrations that would allow certain warming thresholds to be avoided (*4*, *5*).

Estimates of ECS can be obtained from climate models, observations of modern climate change, and reconstructions of past climatic (paleoclimatic) conditions. The usefulness of paleoclimatic constraints has been questioned because the uncertainties associated with proxy-based climate information are much greater than those within the observational record. Furthermore, there may be no paleoclimatic analogs for the forcing or boundary conditions of the current cli-

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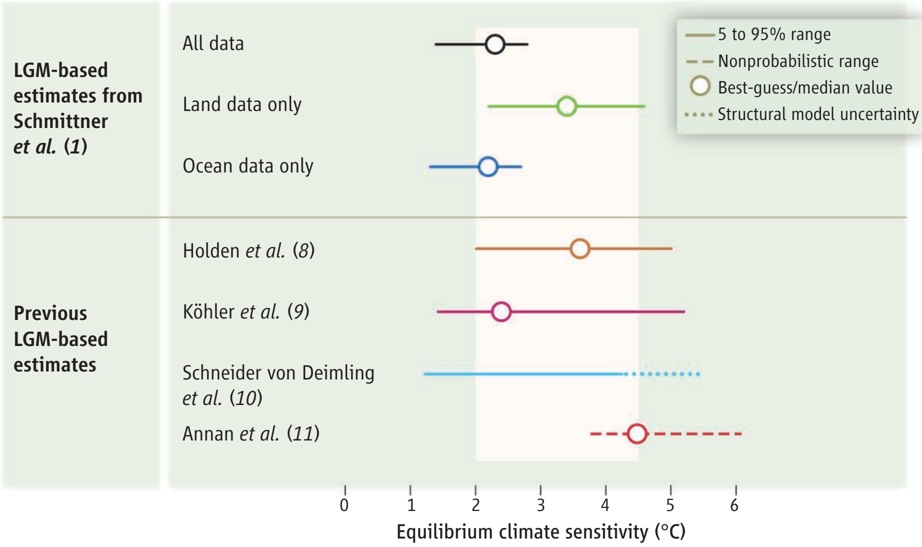
mate system (*6*). However, the paleoclimatic record also has substantial promise because it includes periods of change in climate conditions that were close to equilibrium. Part of the difficulty in estimating ECS from recent data is that the climate system is not in equilibrium over the relatively short duration of the observational period. Also, the paleoclimate record includes changes that are much larger than those seen in the observational record. Paleoclimate records can therefore provide a glimpse of the climate system's equilibrium response to large and long-term changes in Earth's radiative balance.

Schmittner *et al*. present estimates of ECS based on recent compilations of spatially reconstructed surface ocean and land temperatures at the LGM. The LGM occurred around 21,000 years ago, when the Northern Hemisphere was strongly glaciated, atmospheric dust levels were higher than today's, and atmospheric CO_2 was ~100 parts per million by volume lower than preindustrial levels; all of these factors contributed to climate cooling. It is difficult to estimate ECS by directly comparing the reconstructed global average temperature response to the total climate-forcing change, because the feedbacks that enhance the direct temperature response in a much colder climate are different from those that operate during increasing greenhouse gas conditions (*7*, *8*). Instead, Schmittner *et al*. performed a large range of simulations of LGM climates using multiple versions of the University of Victoria (UVic) Earth System Model of intermediate complexity; each version assumed a different model ECS value. They then compared the simulations with the LGM climate reconstructions to determine which ECS values best matched the LGM climate.

The LGM climate reconstruction data sets used in the present study offer more spatial coverage than has been available for earlier climate sensitivity estimates (*8*–*11*), including those that pioneered this modeling approach (*10*, *11*). The increased availability of data outside the tropics yields the possibility of a tighter constraint on ECS in the new work and may reduce the model sensitivity of the result (*12*). Indeed, the new uncertainty range (5 to 95% probability range) is narrower than that seen in most previous paleoclimatic estimates of ECS and has a median value at the lower end of the "likely" (66% probability) range identified by the IPCC (*2*) (see the figure). Only versions of the UVic model with ECS values between 1.3° and 4.6°C broadly reproduce the features and magnitude of LGM surface cooling. These results offer prospects for narrowing estimates of ECS and for shortening the long tail of upper-limit estimates.



Climate sensitivity estimates from paleodata. Estimated uncertainty ranges (90% probability, except for one estimate that is not strictly probabilistic) and best estimates of ECS as based on LGM climate reconstructions (*1*, *8*–*11*). The "all data" estimate from Schmittner *et al*. is based on a spatially more complete compilation of proxy data and has a narrower range than do previous estimates. However, it does not explicitly include estimates of structural model uncertainty. The gray shaded area is the "likely" (≥66% probability) range for ECS identified by the IPCC (*2*), based on results from studies and expert opinion on the possible impact of remaining uncertainties.

However, important caveats remain. First, the results only strictly apply to ECS in one particular climate model of intermediate complexity. Different feedback strengths, yielding different results, may be obtained in another climate model, particularly one that represents the physics of the atmosphere more completely. Future work with a range of models would serve to strengthen the current results (*11*).

The second caveat is that it remains challenging to fully quantify the uncertainties in the forcing terms—for example, those associated with the distributions of LGM ice sheets and vegetation. Higher sensitivities than estimated may be consistent with the data if the true forcing is smaller than that used in the study.

The third caveat relates to Schmittner *et al*.'s finding that the LGM ocean temperature reconstructions exert a far stronger control on the ECS estimate than do the land reconstructions (see the figure). Even the most recent proxy LGM ocean data compilations remain biased toward the low-latitude ocean and the North Atlantic. Further increases in the spatial coverage of the reconstructions would help to reduce this uncertainty.

The work of Schmittner *et al*. demonstrates that climates of the past can provide potentially powerful information to reduce uncertainty in future climate predictions and evaluate the likelihood of climate change that is larger than captured in present models. However, given the remaining uncertainties, which the authors discuss in their paper, a firm upper boundary is still elusive. The study also shows that to take advantage of the opportunity offered by past climates for understanding future climate change requires not just high-quality data but also appropriate physical climate models and statistical modeling. This is not an easy challenge, but it is an important one.

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