

*et al.*³ postulate that the product of Cnx1G, the molybdopterin-AMP, is cleaved by domain E of Cnx1, which also transfers the Mo to the molybdopterin sulphur groups to produce Moco. Understanding domain E and its interplay with domain G will now be crucial in completing the picture of this biosynthetic pathway.

Second — and perhaps most important — is the observation of copper binding to the two sulphur groups of the molybdopterin (Fig. 1). These sulphur atoms are potentially reactive and some mechanism is required to protect them until they actually coordinate Mo. The copper ion was not added to the protein during the experiment, but rather seems to have been picked up from the bacterial expression system used to produce the protein, which suggests that the levels of copper present in culture are sufficient for the purpose. The implication is that *in vivo* Cnx1 binds copper, probably for a combination of

reasons: a metal ion complexed to the reactive sulphur groups would not only protect them, but would also provide a mechanism to assist in the insertion of Mo into the cofactor as the metals are exchanged. The suggestion of a direct link between Cu and Mo biology is highly intriguing and will spur further investigations to delineate the relationship between these essential metal ions. ■

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Climate change

Models change their tune

Thomas F. Stocker

Climate models are usually tuned to match observations. A new approach, in which the models are detuned instead, increases our confidence in projections of future warming.

In 2001, the Intergovernmental Panel on Climate Change published its report stating that the Earth will warm by between 1.4 °C and 5.8 °C by the end of the twenty-first century¹. Many argue that this range is too large to justify action to reduce the rising concentrations of greenhouse gases, principally carbon dioxide, in the atmosphere. Two factors are responsible for the wide estimated range: uncertainty in our understanding of the physical processes that influence climate and our ability to model them; and uncertainty over the so-called ‘emissions path’ — how the demographic, technological and ecological development of human societies will affect energy consumption and greenhouse-gas emissions.

Murphy and colleagues (page 768 of this issue)² have used a climate model to estimate the uncertainty associated with modelling the physical processes. Climate modellers use mathematical formulations, called parameterizations, to describe processes that cannot be resolved because of their scale or complexity, or that are not well understood. Murphy *et al.* quantify how the choice of parameterizations affects the results of modelling the evolution of temperature, precipitation and other climate variables when the greenhouse-gas concentration increases. The good news for the modelling community is that none of these choices alters the basic response of the model to a common

scenario, a doubling of CO₂ concentration: all simulations show consistent warming worldwide, most likely between 2 °C and 3 °C, with the characteristic amplification of warming at high latitudes of the Northern Hemisphere. So this is a robust result over a wide range of parameterizations.

Simplifications are unavoidable when trying to capture the climate system — with its cascades of scales in time and space — in a finite numerical model. Some of these parameterizations may be rigorously derived from fundamental physical principles³, but many contain poorly constrained parameters that are used to complete the mathematical construct. Although it is often true that (in John von Neumann’s words) “the justification of such a mathematical construct is solely and precisely that it is expected to work”, practical data from instruments must be used to set limits on the physically realistic range for these parameters.

Murphy and colleagues’ model² consists of a state-of-the-art atmospheric general circulation model coupled to a ‘slab’ ocean. The latter provides a rudimentary lower boundary condition for the atmospheric model, with lateral fluxes of heat being suggested and kept fixed, while sea surface temperatures are allowed to change. Ocean dynamics are not taken into account, which precludes projections of such considerations as changes in sea-ice cover in the Arctic and

Antarctic, or in the ocean uptake of CO₂. In predicting climate changes in the next several decades — the transient climate response — the ocean cannot be neglected^{4,5}. However, the equilibrium climate sensitivity, a key value in characterizing a climate model, can be reasonably estimated using this reduced set-up. Climate modellers are sometimes preoccupied with ‘tuning’ their models to achieve best agreement with observations, but Murphy *et al.* take the opposite tack: instead of aiming for a best estimate by careful tuning, they quantify the range of outcomes that results when parameter values are changed. This detuning is a neat way of perturbing some of the physics of the climate model.

Within given bounds, they varied 29 parameters, one by one, and analysed the results from 20-year simulations under present-day and doubled CO₂ conditions. In this linear approach, perturbing each parameter in turn, it is assumed that the effect of combinations of changed values of different parameters can be roughly estimated by adding their results. Murphy *et al.* define a climate prediction index, or quality index, which weighs the simulated fields against observations, and permits an objective determination of the critical parameters in the perturbation experiments. It is no surprise that fields associated with the hydrological cycle, particularly cloud processes, show the widest spread in this quality index. In consequence, the partitioning of the radiative fluxes (short-wave versus long-wave radiation, downwards versus upwards) varies widely when the parameterizations are perturbed. This was expected from earlier comparisons⁶; it indicates that the models must be improved if they are to be reconciled with high-precision data on components of the radiative balance⁷.

In a further step, Murphy *et al.* calculate probability density functions for climate sensitivity; this is defined as the estimated increase of global mean temperature in doubled CO₂ conditions. Earlier studies have produced such estimates with either small ensembles of comprehensive models⁴ or simplified climate models⁸. Depending on the various model simulations to which the quality index is applied, and giving more weight to those that show better agreement with observations, the warming in the 5–95% probability range is between 2.4 °C and 5.4 °C. In spite of the relatively wide range of systematic parameter variation, the fundamental response of the climate model is consistent with the range reported by the Intergovernmental Panel^{1,9}.

Uncertainty is inherent in any prediction. The public have become used to probabilities reported in weather forecasts. But the public, and decision makers, have yet to accept that a similar approach is necessary to guide steps to reduce and mitigate the impact

of climate change. Work such as that of Murphy *et al.* and other initiatives will reduce these uncertainties to a point where the dominating uncertainty remains the choice of emission path used in modelling. This is already the case for predictions that look at the second half of this century¹⁰. To shift that time horizon closer to the present will require improved climate models that can be compared in a systematic way¹¹, larger model ensembles for testing^{12,13}, and a systematic exploration of uncertainties in the radiative balance. ■

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Materials science

Flame-broiled alumina

Paul F. McMillan

A method for preparing aluminate glasses and glass-ceramic composites opens up new possibilities for generating mechanically strong structural components and high-hardness coatings.

Shattered glass and cracked dinnerware: ceramics are brittle materials that fail catastrophically when they are stressed. However, strategies are being developed for creating ceramics, including glasses, that are toughened against fracture¹. The best of these techniques use nanometre-size crystals that are formed by devitrification of a glassy matrix² — that is, the formation of ordered crystalline regions throughout the amorphous, non-crystalline glass. On page 761 of this issue, Rosenflanz *et al.*³ describe a new method: micrometre-size beads of aluminate glasses are formed using a flame-spray technique; the glassy beads are then sintered into bulk glasses; further heating produces toughened, hard ceramics in which nanocrystalline alumina-rich phases are dispersed throughout a glassy matrix.

Alumina — aluminium oxide, Al₂O₃ — is the basis of many important ceramic systems, such as optical fibres. Alumina ceramics are also the industry standard for structural applications at high temperatures, especially in chemically reactive environments. Fracture-resistant aluminas are ideal for use in gas turbines, as protective tiles on space probes, and as supports for catalytic reactor systems. These applications all involve forming the ceramics into complex, dense shapes. The best way to do that is to first prepare the materials in an amorphous form, such as glass, and then devitrify them.

However, aluminate glasses form only within a narrow range of compositions because of their high melting temperatures, low viscosity on melting, and the competing

crystallization kinetics of their components. No one has yet prepared a bulk glass from pure alumina liquid using standard melt-quenching techniques (the same is true of water and silicon). But Rosenflanz and colleagues' flame-spray method yields glassy microspheres containing more than 80% alumina³. The flame-spray technique consists of feeding oxide powder into a high-temperature hydrogen-oxygen flame and then cooling it rapidly (quenching) to produce the glassy beads for sintering. The authors suggest that the technique could be extended to produce glasses in other 'reluctant' glass-forming systems.

Aluminate glasses formed in combination with calcium or zirconium oxides, or rare-earth oxides (REOs), are remarkable materials: they are mechanically strong and hard, and have some of the highest sound speeds of any glassy system⁴. Interestingly, devitrified samples containing mechanically weak REO components have hardness values that are almost as high as those of dense polycrystalline alumina. This reflects the importance of the interfaces between the components for toughening the glass-ceramics^{5,6}: the energy of a crack propagating through the material may be deflected or absorbed at such an interface, adding to its strength. So controlling the overall texture in these materials is the key to designing and developing composite ceramics that are both hard and strong.

Rosenflanz *et al.*³ present another important observation from their study of the REO-containing composite gadolinium

aluminate (Al₂O₃-Gd₂O₃); this observation is linked to the physical properties of alumina-rich liquids, rather than to materials research. Molten aluminates are highly 'fragile', in that the relationship between their temperature and viscosity does not follow Arrhenius' law⁵. This is correlated with the large configurational entropy in these systems, reflecting the wide variety of structural states that they can adopt: for example, Al³⁺ ions occur in multiple coordination environments (tetrahedral, octahedral, 5-coordinate, and so on), and rare-earth metal ions have coordination numbers ranging from 6 to 10. The result is a rapidly changing structure within the high-temperature liquids.

An intriguing consequence of this behaviour is that aluminate liquids and glasses can exhibit 'polyamorphism' — different liquid phases or glasses are possible that, although they have the same chemical composition, have different structures and thermodynamic properties⁶. This results in an unusual new phenomenon for the liquid state: density- or entropy-driven liquid-liquid phase transitions can appear as the pressure and temperature change. These transitions are analogous to the temperature- and pressure-driven structural transformations seen in crystalline solids, such as the diamond-graphite transition or the transitions between the quartz, cristobalite, coesite and stishovite polyamorphs of silicon dioxide.

When heating their gadolinium-aluminate glass, Rosenflanz *et al.*³ noticed an exothermic — heat producing — feature that could indicate the presence of polyamorphism in the supercooled aluminate liquid. Similar features have already been observed among yttrium-aluminate (Y₂O₃-Al₂O₃) liquids that are known to exhibit low- and high-density polyamorphs possessing different values of hardness and other physical properties^{7,8}. Controlling the polyamorphism in glassy aluminates and the resulting ceramic microtextures provides a new way to tailor the mechanical properties, including hardness, of families of composite materials. ■

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