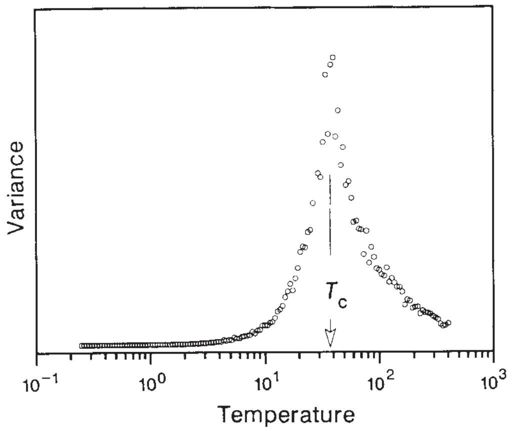

FIG. 4 Variance of the cost function of NbF_4 during the annealing process. The arrow indicates the 'crystallization' temperature.

simple cost function used. First, the 'naive' second term of the cost function we used performs well for ionic compounds that can be described as a close packing of spherical atoms but fails when applied to cations that form strongly directional bonds. For the same reason the cost function is not suited to structures exhibiting face-sharing polyhedra with highly charged cations (such as α-Al_2O_3). Second, within the accuracy of the valence-bond rule (and parameters), different topological configurations are sometimes obtained for some compounds. This emphasizes the weakness of current empirical expressions used to correlate bond valence and bond lengths: their accuracy is adequate to check the validity of an experimentally determined atomic arrangement[6] but we found that it is not always sufficient for reliable *ab initio* structure prediction. Other expressions such as that recently introduced by Hoppe *et al.*[16] to calculate charge distributions in crystals may provide interesting alternatives. Another fruitful approach would be to explore the apparent similarity[17] of the bond valence network to electric circuits and introduce the analogue of Kirchhoff's voltage law in the cost function. This ring sum rule, advocated by O'Keeffe[18], provides further constraints which could complement or even replace the electrostatic term now used in the cost function.

Despite the current limitations, the results mentioned above demonstrate that the simulated annealing approach to structure prediction is a promising method for exploring the possible arrangements that are compatible with a set of prescribed building rules within the limits of a given unit cell. As such, the method is of general applicability: the challenge is to conjecture the empirical or semi-empirical rules that govern the architecture of the solids. ☐

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Phase transition in polymer gels induced by visible light

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PHASE transitions and critical phenomena in polymer gels have attracted much attention because of their scientific interest and technological significance[1–3]. Phase transitions accompanied by a reversible, discontinuous volume change as large as several hundred times, in response to infinitesimal changes in environmental conditions, have been observed universally in gels made of synthetic and natural polymers[1–9]. Phase transitions have been induced in gels by varying temperature, solvent composition, pH, ionic composition and a small electric field[10]. Recently, gels sensitive to ultraviolet light were also reported[11]. The ultraviolet light initiates an ionization reaction in the gel, creating internal osmotic pressure which induces swelling. In the absence of this light, the equilibrium tends towards the neutral polymer system and the gel collapses. This transition process is slow, as it depends on the photochemical ionization and subsequent recombination of ions, and it is technologically desirable that the transition be induced by faster mechanisms. Also, visible light is less harmful and more abundant than ultraviolet in sunlight. Hence we now report the phase transition of gels induced by visible light, where the transition mechanism is due only to the direct heating of the network polymers by light, which is an extremely fast process. Such systems might be used as photoresponsive artificial muscles, switches and memory devices.

Gels containing *N*-isopropylacrylamide (main constituent) and the light-sensitive chromophore, trisodium salt of copper chlorophyllin (Fig. 1), were formed by free-radical copolymerization as follows: 7.8 g of recrystallized *N*-isopropylacrylamide (Kodak), 0.67 g of *N,N'*-methylenebisacrylamide (cross-linker, Bio-Rad), 0.72 g of chlorophyllin (Aldrich) and 240 μl of tetramethylethylenediamine (accelerator, Bio-Rad) were dissolved in 100 ml of degassed water at 0 °C, to which 0.2 g of ammonium persulphate (Mallinckrodt) was added to initiate the polymerization. Capillaries of ~100-μm inner diameter were

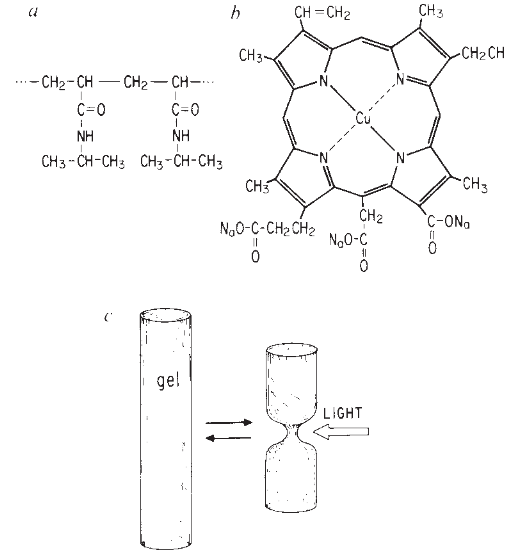

FIG. 1 Chemical structures of *N*-isopropylacrylamide (*a*) and trisodium salt of copper chlorophyllin (*b*). Chlorophyllin has a double bond that can be covalently connected to the polymer network. *c*, The collapse of the gel under illumination.

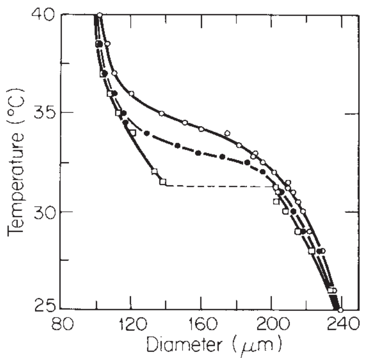

FIG. 2 Diameter of *N*-isopropylacrylamide/chlorophyllin copolymer gel as a function of temperature. Open circles, $I=0$ mW; solid circles, $I=60$ mW; squares, $I=120$ mW 488-nm radiation.

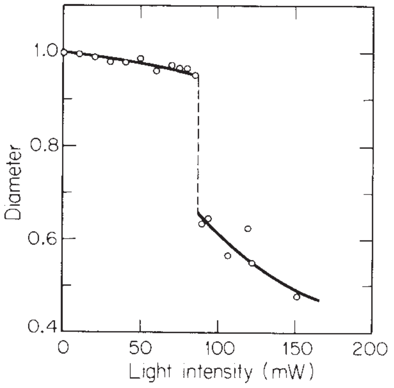

FIG. 3 Diameter of *N*-isopropylacrylamide/chlorophyllin copolymer gel as a function of intensity at 31.5 °C. The data were taken on the gels with the same composition but with an initial diameter different from the one used in Fig. 2.

inserted into the solution. After gelation, the cylindrical samples were removed from the capillaries and dialysed extensively with distilled deionized water. A gel sample was then immersed in water (pH 5.8) or a NaOH solution (pH 11.9) and sealed in a rectangular glass microcapillary, the temperature of which was regulated to within ±0.1 °C. Argon-ion laser radiation at 488-nm was used, and the light intensity at the gel was varied from 0 to 150 mW using a polarizer. The incident beam, gaussian diameter ~7 mm, was focused to 20 μm (focal depth 0.8 μm) at the sample using a lens of 19-cm focal length. The size and shape of the gel were then monitored and analysed using an image processor (Model C1966, Hamamatsu Photonics).

Figure 2 shows the equilibrium volume of the gel at pH 11.9 as a function of temperature for three values of light intensity. In the absence of illumination, the gel underwent a sharp but continuous volume change at ~35 °C. At a light intensity of 60 mW, the volume change became more pronounced and the 'bulk' equilibrium transition temperature was lowered to 33 °C. At an intensity of 120 mW the gel showed a discontinuous volume transition at 31.5 °C. The data in Fig. 2 show that the light-sensitive polymer gel is swollen in the absence of irradiation but collapses when illuminated with light of visible wavelength. Light shrank the gel over the entire temperature range, but the largest effect was seen in the transition region. These features were observed at both pHs. The results indicate that at an appropriate 'bulk' equilibrium temperature the gels should undergo a discontinuous transition when the light intensity is varied, as we observed when we fixed the temperature at 31.5 °C and varied the intensity from 0 to 150 mW (Fig. 3). The light intensity at the transition varies from gel to gel, as seen in the difference between Figs 2 and 3. The differences in the ratios of gel and beam diameters, or in the bleaching conditions may be responsible for the variation.

Two interesting features of the light-induced phase transition are that irradiation causes the originally continuous transition to become discontinuous and causes the transition temperature to be lowered. These can be explained using the Flory-Huggins equation of state. The swelling curve given by the condition of zero osmotic pressure for the gel is[8,12]

$$\frac{1}{T}=\frac{\Delta S}{\Delta H}+\frac{k}{\Delta H}\left[\frac{v_1\nu_e}{N\phi^2}\left\{(2f+1)\left(\frac{\phi}{\phi_0}\right)-2\left(\frac{\phi}{\phi_0}\right)^{1/3}\right\}-\frac{2}{\phi}-\frac{2\ln(1-\phi)}{\phi^2}\right] \quad (1)$$

where T is the absolute temperature, ΔS and ΔH are the entropy and enthalpy of polymer-polymer contact, k is the Boltzmann

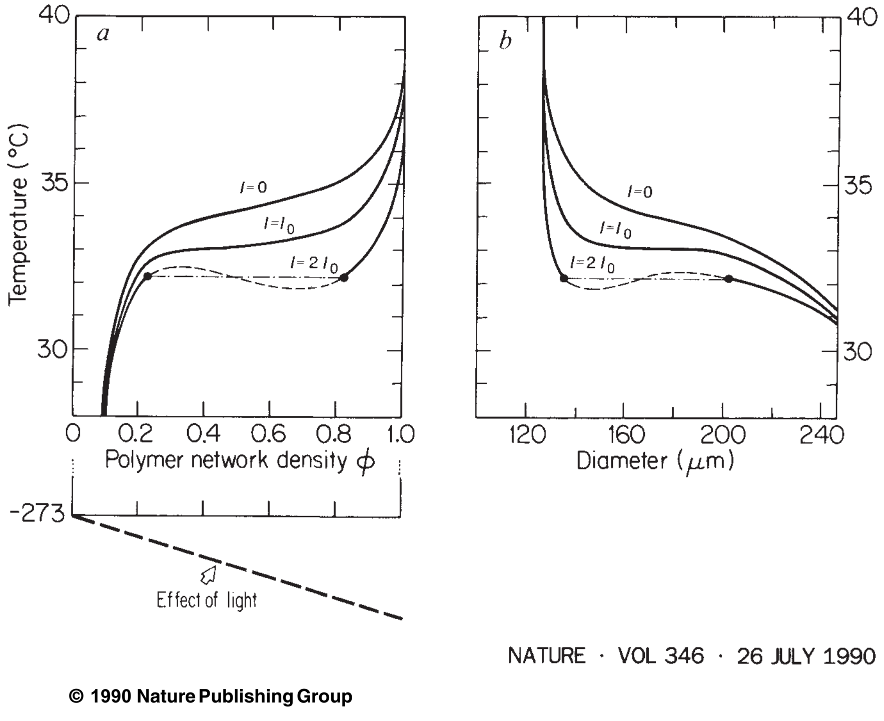

FIG. 4 *a*, Theoretical swelling curves of a gel for various light intensities, constructed using the equations in the text. The effect of illumination is to add a linear distortion of negative slope in proportion to the polymer density, *b*, Theoretical swelling curves as in *a* except that the horizontal axis is reduced diameter $d=d_0(\phi_0/\phi)^{1/3}$.

constant, N is Avogadro's number, v_1 is the molar volume of water, ν_e is the total number of the effective polymer chains in the gel, ϕ is the polymer network density, ϕ_0 is the density when polymers are in the random-walk configuration, and f is the number of counter-ions per chain. For N-isopropylacrylamide gels the interaction parameters ΔS and ΔH are both negative.

For simplicity we rewrite equation (1) as

$$T = T_{\text{gel}}(\phi) \tag{2}$$

This function increases monotonically with network density ϕ for small ionization f of carboxyl groups of chlorophyllin. When the gel is irradiated, the chromophore absorbs the light, which is then dissipated locally as heat by radiationless transitions, increasing the 'local' temperature of the polymer. The temperature increment should be proportional to the light intensity and the chromophore concentration, and therefore to the polymer network density ϕ. Thus

$$T = T_0 + \alpha I \phi \tag{3}$$

where T_0 is the ambient temperature, I is the light intensity, and α is a constant, ~0.6 °C at $I = 100$ mW (Y. Li, personal communication). Combining equations (2) and (3)

$$T_0 = T_{\text{gel}}(\phi) - \alpha I \phi \tag{4}$$

As illustrated in Fig. 4, the effect of the second term in equation (4) is to bring the gel state into the unstable region in the $T_0 - \phi$ space, inducing a discontinuous transition and to lower the transition temperature. Theoretical swelling curves and the contribution by light ($+\alpha I \phi$) to them are shown in Fig. 4. Because thermal diffusion is much faster than collective diffusion of the gel network, the swelling and shrinking process of the gel in response to light is governed only by the motion of the polymer network. For 1-μm-diameter gels the response time[13,14] is expected to be ~5 ms. ☐

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Temperature and rainfall estimates for the past 40,000 years in equatorial Africa

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THERE has been considerable debate about the magnitude of the decrease in temperature[1,2] and the change in precipitation[3] in the African tropics during the last glacial period. With the advent of fossil pollen studies in equatorial regions, it is now generally agreed that the temperature did decrease at this time in tropical regions[4], but the magnitude of the temperature fluctuations and discrepancies between the continental[5] and marine[6] temperature records have yet to be resolved[7]. Here we present new quantitative estimates of temperature and precipitation using a multivariate analysis[8] of pollen time-series data from peat deposits in Burundi for the past 40,000 years[9]. For the last glacial period, our estimate of a temperature decrease of 4 ± 2 °C is less than those (ranging from 5 to 8 °C) derived from snow-line and tree-line records[5,7]. Model simulations[7] indicate that the snow-line and tree-line estimates (from high-elevation sites at ~4,000 m above sea level) are incompatible with the marine temperature record. Our lower estimate from a site of intermediate elevation may help resolve the differences between these records. We also estimate that the mean annual rainfall decreased by 30% during the last glacial period, in agreement with the rainfall history inferred from lake level fluctuations[10].

Pollen data contains climate information which can be extracted using a variety of statistical techniques[11,12]. Although the response of vegetation to climate needs further investigation[13], pollen data have already provided successful quantitative estimates of climate parameters for temperate regions in North America[12], India[14] and Europe[15,16]. Here we focus on a fossil sequence recently obtained in the mountains of the Zaire/Nile divide in Burundi[9], which provides new data for the region south of the Equator[17]. Our statistical procedure has been described in detail elsewhere[18].

The modern data set that we used is from East Central Africa between latitude 4° S and 12° N and longitude 28° and 42° E[19]. It contains pollen samples from 356 sites that cover most plant communities from desert to subalpine grasslands and includes all types of forests[20]. Mean annual rainfalls range from 200 to 2,000 mm (ref. 21). The decreasing temperature gradient is registered by the change with altitude of the vegetation on high mountains[22] (Fig. 1).

For meteorological data, we compiled means of the modern measured values (normals) for about thirty years[23]. To adjust data from the meteorological stations to the modern pollen sampling sites, an interpolation of temperature and precipitation values was carried out when necessary, according to the rules and procedure previously described[8]. Although the seasonal pattern linked to the movements of the Inter Tropical Convergence Zone is important in the tropics[24], we have focused on reconstructing the mean annual climate and have used the mean annual temperature and rainfall. The reconstruction of a palaeoclimate from pollen data relies on the assumption that climate is the main factor forcing changes in the vegetation and therefore pollen frequencies[13]. This is a subject of some debate, but we consider it to be valid for the 100–300 yr resolution of the fossil sequence.

Multiple regression shows that the modern-pollen database contains a significant climate signal: the correlation of estimated values extracted from pollen data to observed meteorological data was 0.90 for temperature and 0.80 for rainfall[19]. Although the regression method has been successfully applied to pollen data from temperate regions[11,12,16], it has gradually been replaced because it does not separate the different components of the climate signal. Best-analogues methods, such as surface response[25] and palaeobioclimate analogues[15] have now been shown to yield plausible palaeoclimate estimates.

The analogue approach consists of looking for modern pollen data similar to the fossil ones and of equating the appropriate modern climate to the palaeoclimate. The statistical distance is a measure of the difference between the modern and the fossil-pollen assemblages[17]. In our palaeobioclimate approach, this