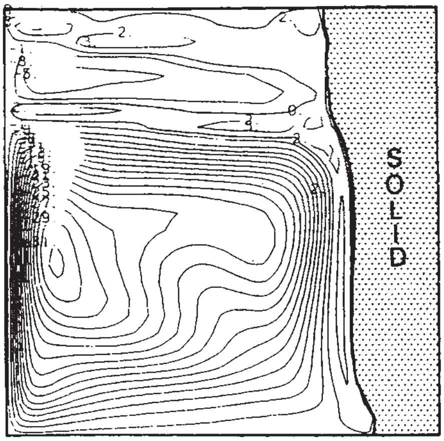
Crystal growth

From multi-branched snowflakes to precious minerals

from Herbert E. Huppert

MULTI-BRANCHED snowflakes, gallium arsenide crystals for use in integrated circuits and the olivine crystals that permeate the Earth's mantle are all formed by solidification. Can the understanding gained from carefully controlled industrial crystallization processes lead to clearer insight into naturally occurring crystallization? Or can industrial solidification be made more efficient by mimicking natural phenomena? These were among the questions considered at a conference* of some 60 crystal growers, geologists, mathematicians and metallurgists.

In many industrial processes, solidification of a one-component product from a multicomponent melt is induced by moving a heat sink at constant velocity along the outside of the receptacle containing the melt. If the velocity is too large, the planar solid/melt interface becomes unstable and leads to a disastrous, irregular form of solidification. In a quiescent melt, the velocity which determines instability to infinitesimal disturbances was evaluated by Mullins and Sekerka in 1964. A recent numerical study by R.A. Brown (Massachusetts Institute of Technology), which allows for large departures from a planar interface, shows that at suitably rapid solidification velocities a cell generated by the initial linear instability can bifurcate into two cells of half the wavelength, each of which can bifurcate again and again, until a field of stable dendrites of sufficiently small wavelength evolves. It appears that parameters for the cooling of large bodies of magma within the Earth's crust are such that an interface dominated by denrities almost always results.



Stream function

Fig. 1 The numerically calculated stream function and solid region produced when an initially uniform, 10 wt per cent aqueous Na_2CO_3 solution is cooled for 20 min at the right wall and warmed at the left (M.E. Thompson). One large cell has developed with most rapid flow at the two vertical edges, and two much weaker cells are evolving near the top of the container.

Evaluations of the paradigm shape of a single, smooth dendrite and its inherent instability are evoking considerable controversy at the moment. A steady-state model by G.P. Ivantsov, which neglected surface tension, does not predict a unique solution, but merely a family of solutions. J.S. Langer determined that dendrites could be unstable to side-branching and suggested that a dendrite propagates at the velocity of marginal stability. This seems to be in good agreement with experiments. But why? This question has vexed many physicists who are developing quite complicated but rather *ad hoc* models that attempt a resolution by appealing to special effects such as the anisotropy of surface tension. A different approach was described by J.J. Xu (Rensselaer Polytechnic Institute). He considered the axisymmetric dendrite as a slender body (an idea first pioneered in the study of flow past airplane fuselages which has now been applied to the study of the motion of ships and the growth of roots of plants). Xu determined the form of solution close to and far from the dendrite and related these two solutions using the technique of matched asymptotic expansions to derive a single integro-differential equation for the growth velocity. For zero surface tension, the original one-parameter family obtained by Ivantsov is retrieved. With the inclusion of surface tension, the equation has a solution only for growth velocities less than a critical value; beyond this critical value no solution exists. The relationship between this critical velocity and the velocity of marginal stability has yet to be determined.

As dendrites grow, they develop secondary, tertiary and higher-order branching. With time, the solid protrusions became more rounded due to the Gibbs–Thomson effect, which states that the local temperature at a curved solid/liquid interface is depressed from the freezing point because of the capillary effects of the curved interface by an amount proportional to $\gamma\Gamma_l$, where γ is the surface tension and Γ_l the total local curvature. Fluxes of heat then occur resulting from the temperature gradients between interfacial regions of differing curvature and these fluxes induce preferential melting and change of shape and size. Generalizing this idea in a statistical sense to a complicated two-phase mixture suggests that the mean undercooling, $<\Delta T>$, is proportional to $\gamma\bar{\Gamma}$, where $\bar{\Gamma}$ is the average curvature. Theoretical analysis indicates that the size of particles evolves with time t resulting from the different fluxes between adjacent interfaces with $<\Delta T> \propto \bar{\Gamma} \propto t^{-1/3}$ for large time. Experiments by M.E. Glicksman (Rensselaer Polytechnic) in several partially molten systems including succinonitrile, ethylene carbonate and ice/water, which solidify with different morphologies, verify this relationship and for the first time allow the surface tension coefficient to be determined simply and directly. The evolution to sphericity of snowflakes in a snow field in the timescale of weeks is an example of this process.

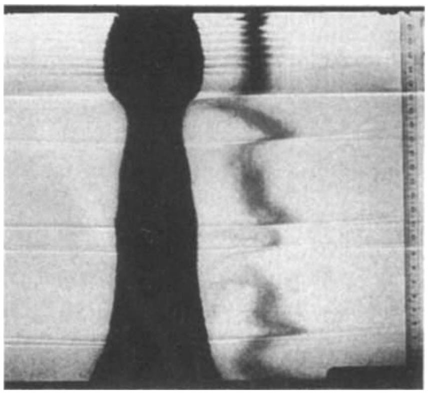


Fig. 2 The result of cooling for 22 h an initially homogeneous, almost saturated, aqueous Na_2CO_3 solution at a thin central rod (J.S. Turner). Five large cells have developed at the base with nine thinner cell above, as seen by the double-diffusive interfaces and the $KMnO_3$ dye trace initiated a few seconds before the photograph was taken.

Solidification of a multicomponent melt is often dominated by fluid effects, in particular convective phenomena, because the solid rejects part of the melt, which is of a different density. Considerable interest has been shown recently in various fluid processes by geologists who wish to apply the concepts to understand the solidification of magma and to predict the formation of precious minerals such as chromium, nickel and platinum. I summarized comparisons between recent laboratory experiments and theoretical calculations predicting the fluid flows and rate of production of the solid. One particular case — cooling and solidfying a multicomponent melt from the side — was considered further by A.M. Leitch (Toronto) and M. Thompson (MIT). Leitch has conducted experiments with different aqueous solutions (of, for example, Na_2CO_3, $FeSO_4$, KNO_3, NH_4Cl). In all cases the buoyancy difference of the released liquid at the solid/liquid interface induces a vertical convective flow. Because of the finite volume of the experi-

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mental container the released liquid pools at the top or the bottom of the container and causes a strong vertical density stratification to be set up. In the experiments the rate of solidification and the vertical mass transfer rate does not vary much, although the crystal habit and roughness of the wall changes considerably. Thompson has numerically calculated the flow fields corresponding to this two-dimensional situation (Fig. 1), which are also in qualitative agreement with laboratory observations of an axisymmetric experiment conducted by J.S. Turner (Australian National University) (Fig. 2). M.G. Worster (Cambridge) analysed the cooling of a subeutectic binary alloy from below, and extended the earlier model that he and I derived based solely on global conservation relationships to predict local variations of the solid fraction; both models yield predictions quite close to those observed in the laboratory.

A.R. McBirney (Oregon) was one of several geologists who described the consequences of crystallization of slowly cooling bodies of molten rock and the interpretation of the final products of this process long after the solidification is complete. He described how differentiation caused by a process akin to metallurgical zone refining could be responsible for strong fractionation in large intrusions, and suggested that residual products of crystallization sweep through the crystal mush, fluxing earlier crystals and collecting the excluded components in a zone of water-rich melt. I.H. Campbell (Australian National University) and J. Peterson (Aarhus) proposed other processes to explain various puzzling features of slowly crystallizing magmas, such as thick sequences of very uniform rocks that have crystallized on the walls and floors of large intrusions. □

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Lectin biochemistry

New way of protein maturation

from Nathan Sharon and Halina Lis

WHEN last year it was claimed that the mature form of the jack bean lectin concanavalin A (Con A) is made by the breakage and rejoining of its precursor peptide[1], some scepticism was voiced in a *News and Views* article[2]. This was not surprising as a novel form of protein maturation had been invoked. Doubts should be quelled, however, by a more recent paper[3] that also suggests transpeptidation is the mechanism involved.

Con A, which consists of four identical subunits of relative molecular mass (M_r) 27,500, is a member of the family of legume lectins (including, for example, lentil lectin, soybean agglutinin and fava bean lectin), all of which show extensive sequence similarities when properly aligned. But a puzzling feature of Con A (and of another lectin recently isolated from *Dioclea grandiflora*) has been that maximum similarity with the other legume lectins only occurs when its amino terminus is positioned near the middle of the polypeptide chains of the other lectins (Fig. 1).

Although it has been suggested that reorganization within a common ancestral gene of the legume lectins is responsible for this unusual feature of the Con A sequence[4,5], the report published last year by Carrington *et al.*[1] shows, surprisingly, that the amino-acid sequence deduced from complementary DNA derived from the messenger RNA encoding Con A compares directly with the other legume lectins. The DNA contained a coding region corresponding to 29 amino-acid residues of a signal sequence, followed by a region corresponding to amino acids 119–237 of Con A, a region encoding 15 amino acids not found in the mature lectin, and finally a region corresponding to amino acids 1–118 of the lectin, followed by a 9-residue carboxy-terminal extension. To explain the sequence found in the mature lectin, Carrington *et al.* suggested that during formation there must be a transposition and ligation (between residues 118 and 119) of two peptides produced from the precursor polypeptide.

Two recent reports by D.J. Bowles and her colleagues[3,6] provide a new look at the

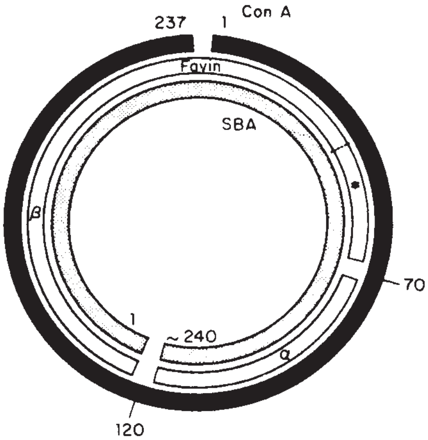

Fig. 1 Alignment of fava bean lectin (favin), soybean agglutinin (SBA) and Con A, showing the circular permutation that gives maximum homology among the sequences of these lectins. (From ref. 9.)

mechanism of Con A biosynthesis. In studies of the formation of the lectin during embryogenesis by ^{125}I-substituted Con A overlays and Western blotting, they obtained evidence that a putative precursor of the lectin (M_r 33,500) was glycosylated[6]. The formation of an N-glycosylated Con A precursor was also observed by Herman *et al.*[7]. Mature Con A is not a glycoprotein and does not contain any potential glycosylation sites. However, as pointed out by Herman *et al.*, there is a potential glycosylation site (Asn-Ser-Thr) in the 15-amino-acid insert mentioned above. These authors suggested the removal of a glycopeptide as the sole processing step between the glycosylated precursor and the final lectin form.

The studies by Bowles *et al.* on the post-translational processing of Con A, using metabolic labelling of immature jack beans and pulse–chase experiments, reveal a more complex series of events[7]. They show that the glycosylated M_r 33,500 precursor is first deglycosylated and then converted into two peptides of M_r 18,800 and 14,200. Surprisingly, after continued chase, there is a gradual disappearance of the low M_r peptides and the appearance of a new entity of M_r 30,400, suggesting ligation between the two fragments of low M_r. Amino-terminal sequence analyses revealed that the alignment of residues 1–118 and 119–237 was reversed in the mature lectin from that of the precursor first label-

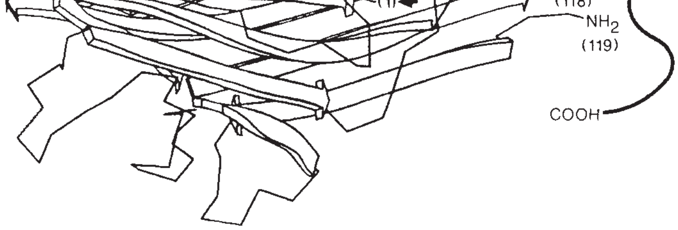

Fig. 2 Hypothetical three-dimensional structure for the M_r 33,500 precursor of Con A fitted with a computer model of the structure of the mature lectin. Numbers correspond to residue positions in mature Con A. Arrows indicate the approximate positions of proteolytic processing. The proposed location of the oligosaccharide side chain is also marked (□). (From ref. 3.)