place more deeply and plastically, involving also the folding of the crystalline basement. Two different pressure and temperature regimes are thought to be responsible for these two different structures. They also show up in the distribution of some metamorphic index minerals: jadeite and lawsonite occur only in the Western Alps and in the uppermost Suretta nappe, and glaucophane is the alternate high pressure phase elsewhere[7].

Essentially paragonite plays a role intermediate between that of lawsonite and glaucophane as an index mineral. It is abundant where the former is present but rare where only the second occurs. And like glaucophane[8], it disappears entirely where a late temperature increase is superimposed on the early high pressure assemblage (Simplon–Ticino culmination[8], Tauern window[9]).

Therefore paragonite is related to the early, high-pressure phase of the Alpine metamorphism (80–110 m.y. (ref. 8)). It is significant for the history of the Alps that the concentration of paragonite in the western range confirms that this was the area where the maximum tensional shear accompanying the bending of the Alpine arch was located.

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in the Permian Berry formation to infer alkaline conditions. The latter occurrence differs from the other two because not only is independent evidence of alkaline conditions lacking, but also the nordstrandite polymorph of Al(OH)₃ is reported to accompany dawsonite.

The authigenic occurrences of dawsonite are not readily interpreted in terms of experimental syntheses recorded in the literature; Bader's synthesis[7], for example, was accomplished by passing CO₂ into a solution of sodium hydroxide and sodium aluminate. The aluminium amalgam technique[8], however, allows the construction of a synthesis diagram which is clearly applicable to authigenic occurrences.

Aluminium amalgam was immersed in a number of media ranging from distilled water to saturated Na₂CO₃ solution. The experiments were carried out at 25° C and 1 atmosphere total pressure, and the resulting assemblages are summarized in Fig. 1. These experimental conditions are a reasonable approximation to the physico-chemical environment at the Earth's surface. The mercury acts solely as a catalyst and enables the aluminium to display its true electropositive character.
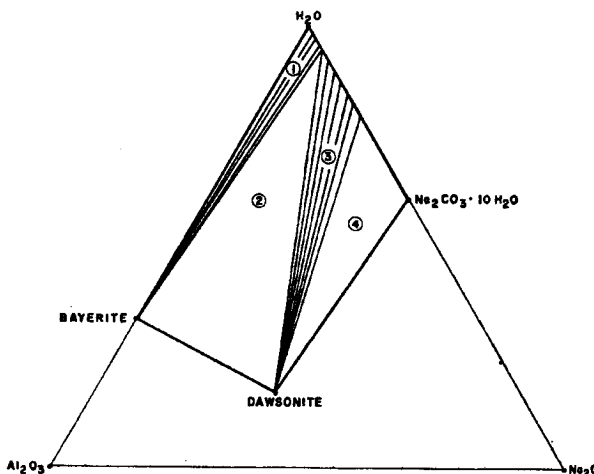


Fig. 1 Isobaric, isothermal section of the system $Na_2O$–$Al_2O_3$–$H_2O$–$CO_2$ projected from the $CO_2$ apex. The phases are plotted in weight percentages. Conditions are 25° C, 1 atmosphere total pressure, $3 \times 10^{-4}$ atmospheres $P_{CO_2}$. Assemblages: 1, bayerite and solution; 2, bayerite and dawsonite and solution; 3, dawsonite and solution; 4, dawsonite and $Na_2CO_3.10H_2O$ and solution.

# Laboratory Synthesis of Dawsonite and its Natural Occurrences

Dawsonite ($NaAlCO_3(OH)_2$) was first discovered in Canada[1] and has since been found at widely scattered localities throughout the world. Most occurrences suggest a hydrothermal origin for the mineral[2] but in at least three places an authigenic origin seems likely. Thus in the Pleistocene deposits of the Olduvai Gorge, in the Green River formation of Colorado, and in the Greta Coal Measures and the Berry formation of the Sydney Basin of New South Wales there is clear field evidence of the formation of dawsonite in Earth surface conditions.

At the African[3] and American[4] localities the presence of zeolites and evaporitic minerals suggests that dawsonite requires a highly alkaline environment in which to form. It is not so apparent that this is true at the Australian locality[5,6], though Goldberry and Loughnan use the presence of dawsonite

Experimental work confirms that a highly alkaline environment is necessary for the formation of dawsonite. The isobaric, isothermal, invariant three phase equilibrium represented by bayerite + dawsonite + solution shows that at least 0.4 M Na₂CO₃ is required—equivalent to a pH ~12. If this is a true equilibrium value, it is not surprising that dawsonite is a rare mineral, in view of the scarcity of natural environments of such alkalinity.

The presence of nordstrandite in the Berry formation of the Sydney Basin allows a further application of the diagram. The experimental work also produced a polymorph of Al(OH)₃ (bayerite). It is not known whether this is the stable form of the hydroxide in these conditions or whether, given enough time, it would age to nordstrandite which has been successfully produced in reactions of aluminium amalgam in the highly alkaline medium NH₄OH. Coexistence of Al(OH)₃ with dawsonite in the presence of aqueous Na₂CO₃ would certainly indicate a closely buffered solution, even if the temperature

was allowed to depart a little from 25° C. Such precise buffering is unlikely in the tidal or supratidal environment deduced for the Berry formation by Goldberry and Loughnan. A more reasonable explanation of the coexistence of dawsonite with a polymorph of $Al(OH)_3$ is that one mineral formed after the other in response to a change in the concentration of $Na_2CO_3$ in natural waters. This could happen in one of two ways: either the solution could become more concentrated (by evaporation, for example), or it could become more dilute, perhaps because of an influx of "fresher" water. If the concentration increased, dawsonite would form after $Al(OH)_3$ and the appearance of evaporites might ultimately be expected. If the concentration decreased, $Al(OH)_2$ would follow dawsonite and evaporites would not be expected; this seems to fit the facts closely. No evaporites are reported from the Berry formation and in some cases nordstrandite has been found in rims around dawsonite, possibly indicating the reaction[5,6]

$$NaAlCO_3(OH)_2 + H_2O = Al(OH)_3 + NaHCO_3$$
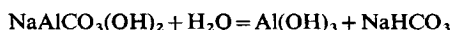
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# Brittleness in Graphite Epoxy Composites

THE response of materials to uniaxial stress can be broadly classified as ductile or brittle according to whether plastic strain or fracture follows the initial elastic behaviour[1]. Obviously, ductile materials are more "forgiving" in structural applications. Brittle failure usually proceeds by the propagation of a crack nucleated at a flaw. Even a little plasticity can mitigate severe flaws by a blunting of the crack tip. An alternative view is that localized deformation at the crack tip is a sink for stored elastic energy which would otherwise be used in spreading the crack across the entire cross-section.

Fibre-reinforced composites are able to absorb the energy of crack propagation by means of localized action at the interface between fibre and matrix; this may be either frictional sliding or matrix deformation (refs. 2, 4, 5, and unpublished work of McCullough and of Kelly). In the case of graphite fibre-reinforced epoxy it is largely frictional sliding as broken fibre ends are pulled out of the matrix. The pullout energy is expected to be greater, the lower the adhesion[4]. Adhesion of high modulus graphite fibres has been a major problem, and it is only recently that relatively high adhesion has been achieved by treatment of the fibre surface. Untreated fibres, therefore, have low adhesion and high resistance to crack propagation. Failed tensile specimens of untreated 0° graphite epoxy have a characteristic splintered and fibrous appearance, but this is not a ductile material as the elastic deformation is terminated abruptly by complete fracture. The fracture of treated

material is very clean, suggestive[3] of the involvement of crack propagation. New and vivid evidence that this is so is given in this article.

A new development of the fibre microstructure and surface condition (which is proprietary but of no relevance to the physics of this discussion) has resulted in very high fibre-matrix adhesion. Two examples of 0° tensile fracture surfaces of this unidirectional graphite-epoxy material are shown in Fig. 1. Classic "river" lines can be seen delineating the course of propagation of the crack away from its source. It is interesting that the source is on the specimen surface in both cases. Although this degree of adhesion is probably excessive for practical application, the observation provides convincing evidence of the reality of crack propagation effects and extreme brittleness in graphite fibre-reinforced epoxy composites.
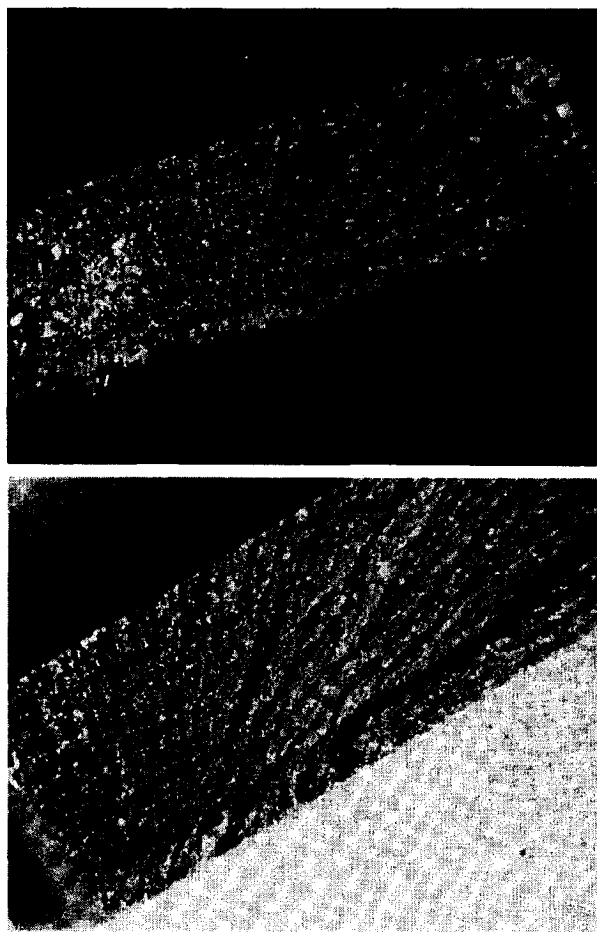


Fig. 1 Tensile fracture surfaces of extremely high adhesion graphite epoxy composite, showing crack propagation.

Crack propagation in a 0° composite is tantamount to individual fibres breaking because of failure of neighbouring fibres. Kelly[6] has suggested that fibre breaks will occur independently of one another if

$$\tau < \sigma_f (G_m/E_f)^{\frac{1}{2}}$$

where $\tau$ is the interfacial shear strength, $\sigma_f$ and $E_f$ are the tensile strength and Young's modulus of the fibre respectively, and $G_m$ is the shear modulus of the matrix. This is based on the hypothesis that fibre breaks are independent when the strain energy stored in the matrix is much less than that stored in the