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Stacking Faults and Polytypism in Opal, $SiO_2 . nH_2O$

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A replication electron microscopy study of etched fracture surfaces of opal revealed four distinctive patterns of packing of the constituent SiO_2 spheres. These patterns could be accounted for by consideration of appropriate stacking faults or modifications in a cubic closest packed structure. These were (1) intrinsic stacking faults (2) extrinsic stacking faults (3) twinning and (4) rhombohedral polytypism. The success in predicting some of the observed packing patterns by assuming stacking modifications of a cubic closest packed structure indicates the existence of a basic, though frequently faulted, f.c.c. opal structure. Screw dislocation-spiral growth is proposed as a possible mechanism for explaining the occurrence of the ordered opal structures.

Introduction

Precious opal has been shown by electron microscopy to be composed of spheres of amorphous silica having a uniform diameter of about $0{\cdot}2\mu$ and sometimes packed in a regular array (Pense, 1963; Jones, Sanders & Segnit, 1964). The iridescence observed when precious opal is viewed in reflected light is attributed to this uniform arrangement of the constituent particles. The ordered packing arrangement is surmised to be that of cubic closest packing since the fracture surfaces examined by electron microscopy commonly display either a surface of hexagonally closest packed spheres or a surface of spheres packed on a square lattice; the fracture is apparently controlled by these two closest packed layers. Optical diffractometry studies of opal (Baier, 1932; Sanders, 1968) have also indicated that some opals have an ordered structure. From optical diffraction, Sanders (1968) reported some opal samples having well-ordered cubic closest packing, some with hexagonally packed layers stacked randomly, and some having both the cubic closest packing and random stacking and, in addition, regions of hexagonal closest packing.

The occurrence of packing imperfections has been observed by replication electron microscopy on the hexagonal and square packed surfaces of opal and has been described as point defects, dislocations, stacking faults and twinning (Sanders, 1964; Cole & Monroe, 1967). The present study examines some of these packing anomalies observed in two-dimensions and attempts to explain their occurrence on the basis of a three-dimensional opal structure.

Procedure

Fractured surfaces of opal, etched for one minute in 10% HF, were replicated by the preshadow carbon technique and viewed in the electron microscope. Observations were made of surfaces showing the silica spheres in hexagonal and in square packed arrangements, and also areas having highly disordered arrangements. These ordered regions of hexagonal and square packing were frequently modified. Four distinctively different packing modifications were observed and recorded photographically. An explanation was then sought for these four different kinds of packing patterns by considering various types of three-dimensional packing arrangements of spheres.

Results

The four observed patterns of packing were accounted for by consideration of appropriate stacking faults or modifications of a cubic closest packed structure. These were (1) intrinsic or single hexagonal triplet stacking fault, (2) extrinsic or double hexagonal triplet stacking fault, (3) twinning and (4) rhombohedral polytypism. The first three types of faults are found in cubic closest packed crystals (Gruber, 1966).

(1) *Intrinsic or single hexagonal triplet stacking fault*

This type of fault arises when the cubic closest packed (hereafter designated f.c.c.) sequence symbolized by $ABCABCABC\ldots$ is altered by a stacking anomaly shown by the sequence $ABCABC\overline{ABA}BCABC\ldots$ The

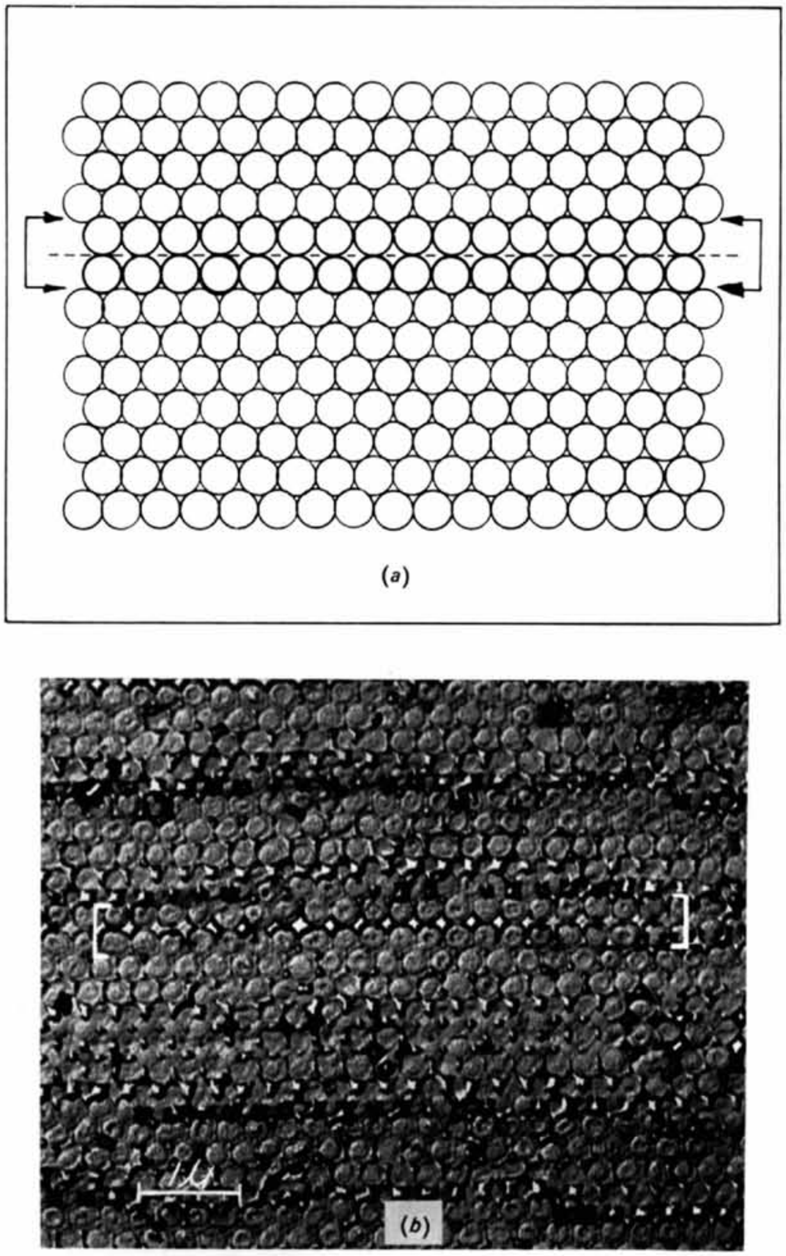

Fig. 1. A (111) surface of an f.c.c. array of spheres showing the hexagonal packing interrupted by two rows of spheres having square packing (indicated by brackets) caused by a stacking fault. The surface of this Figure is not in the same plane since the fault causes a step in the surface indicated by the dashed line in (*a*) .Diagrammatically illustrated in (*a*) and shown in (*b*) on an etched fracture surface of opal by replication electron microscopy.

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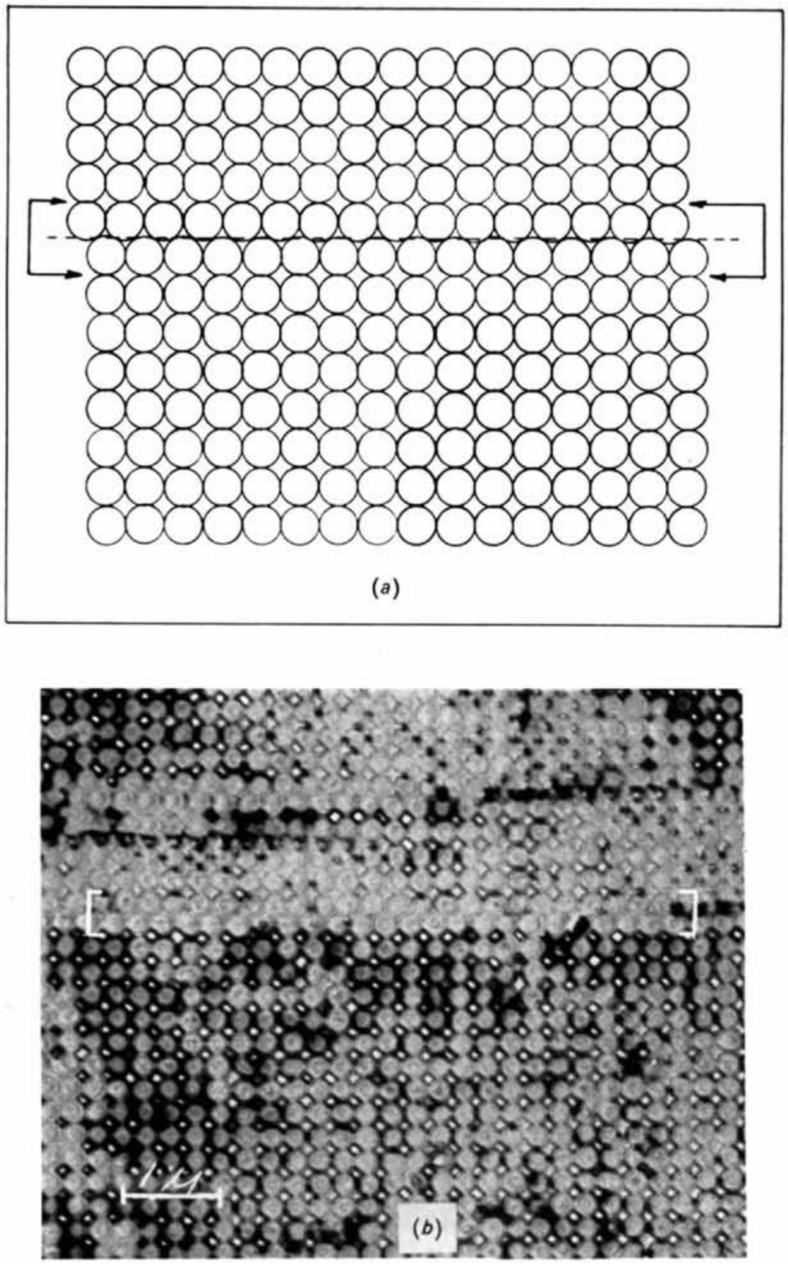


Fig. 2. A (100) surface of a f.c.c. array of spheres showing the square packing interrupted by two rows of spheres having hexagonal packing (indicated by brackets) caused by a stacking fault. A step in the surface occurs along the fault line as indicated by the dashed line in (*a*). Diagrammatically illustrated in (*a*) and shown in (*b*) on an etched surface of opal by electron microscopy.

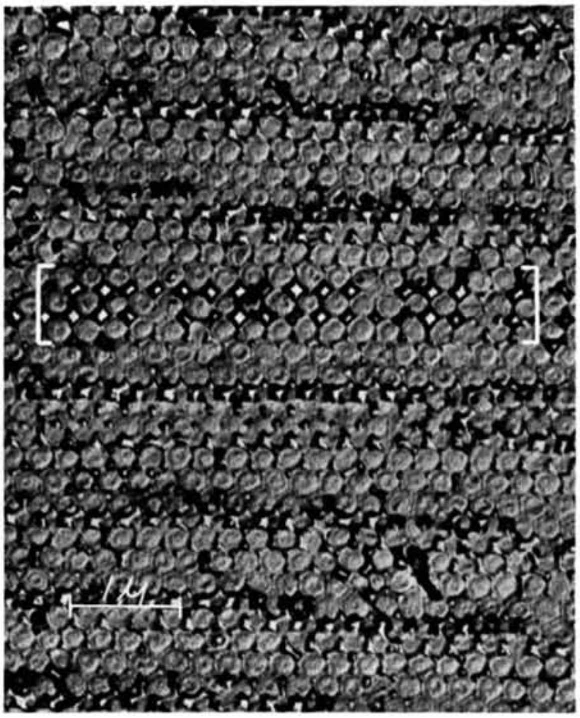


Fig. 3. Etched fracture (111) surface of opal showing three consecutive rows of (100) square packing (indicated by brackets) caused by an extrinsic stacking fault. The surface is not in the same plane but suffers a 15·8° angular deviation between the (111) and (100) plane.

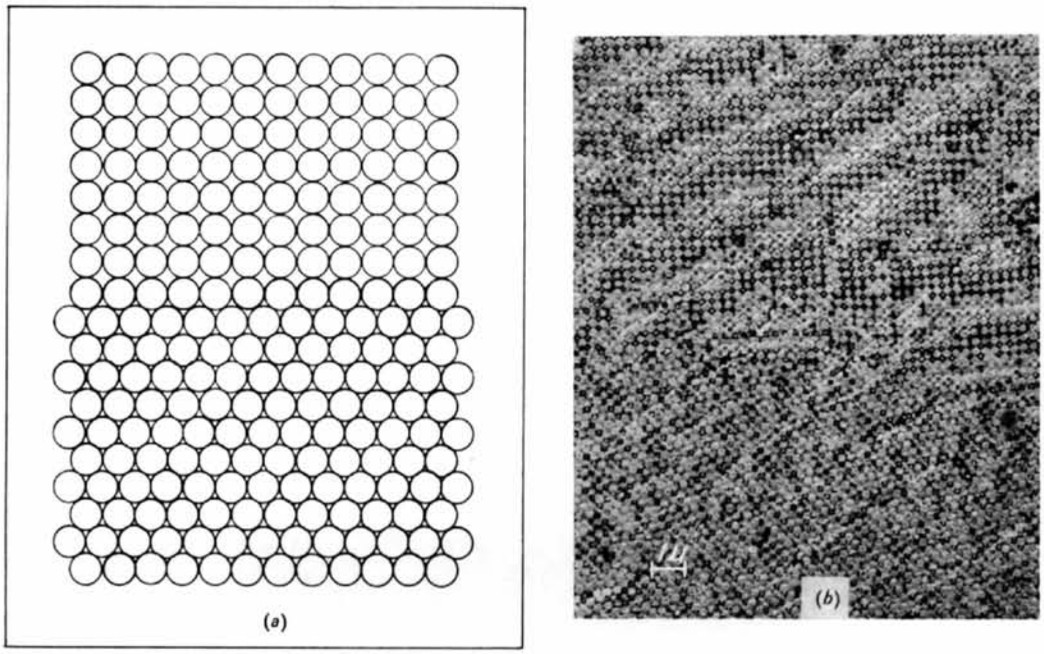
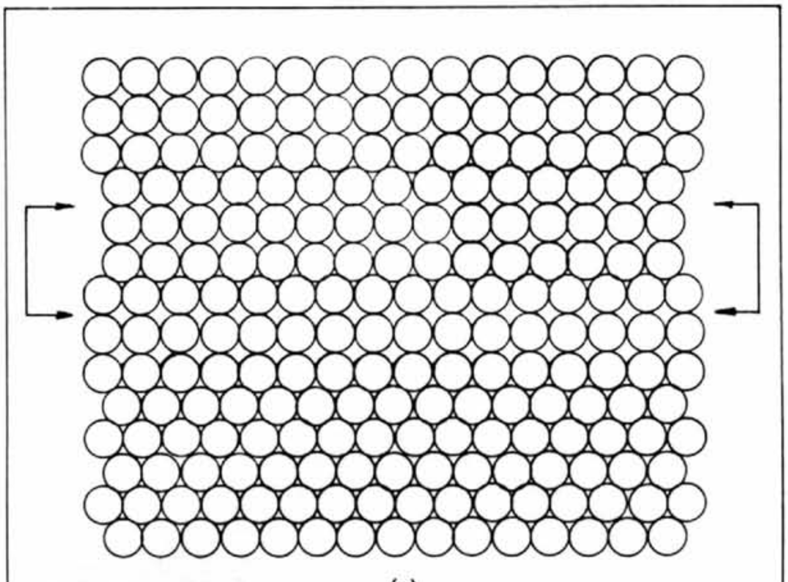
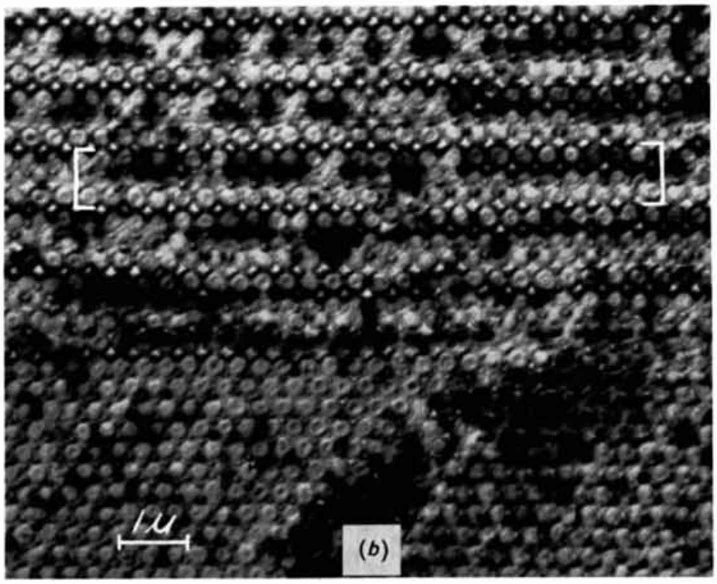


Fig. 4. A (100) and a (111) plane brought into juxtaposition by twin faulting. The two surfaces do not both lie in the plane of the Figure, but have an angular divergence of about 15·8°. Diagrammatically illustrated in (a) and shown in (b) on the opal surface by electron microscopy.



(a)



(b)

Fig. 5. A hexagonally packed (111) surface representing the f.c.c. structure coalesces into an ordered pattern of alternating rows of hexagonal and square packing giving rise to a 9*R* polytypic opal structure. This surface of the polytype is not in the same plane, but has an angular deviation of 15·8° between regions of the square and hexagonal packing. Shown diagramatically in (*a*) and by electron microscopy of the opal in (*b*); brackets indicate one unit of the pattern.

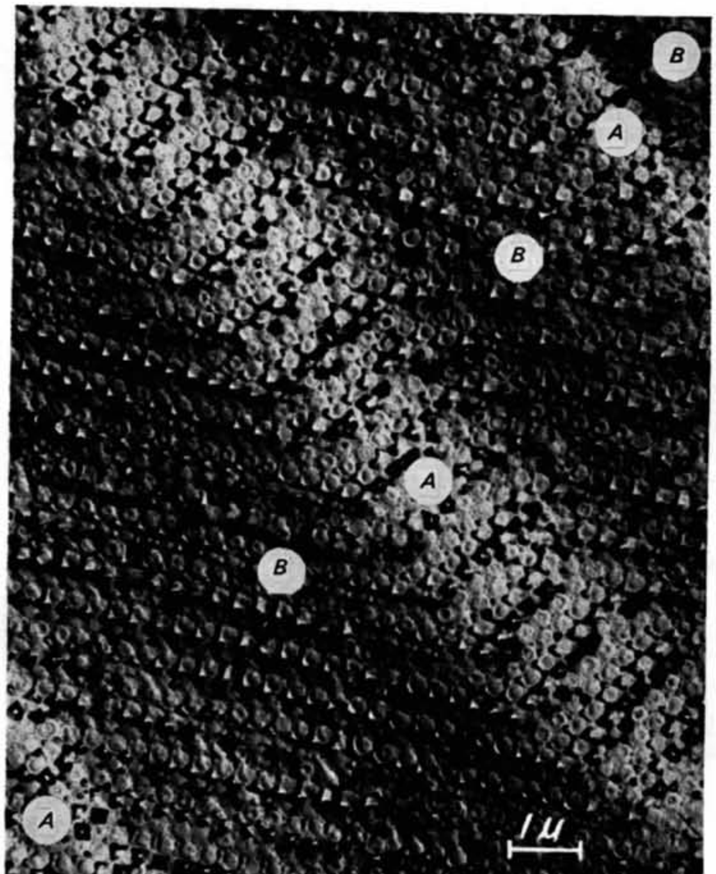


Fig. 6. Fracture surface of the opal showing an alternation between two different {111} planes labeled *A* and *B*. The marked contrast between the two planes is due to the large angular divergence between them. Replication electron microscopy.

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bracket indicates the hexagonal triplet that arises. This fault can be obtained by omitting a *C* layer or by translating the upper part of the structure with respect to the lower so that a *C* layer becomes an *A* layer. The fault was observed in the opal by the packing change it created on the {111} and {100} surfaces. When one of the remaining planes of the {111} form which is inclined to the (111) stacking plane containing the fault is viewed, the fault may appear as two rows of spheres having square packing in the otherwise hexagonally packed surface. A step in this surface amounting to 0·29 of the sphere diameter occurs along the fault line, arising from the shift in the structure across the fault plane of $a/\sqrt{6}\ \langle 211\rangle$. Fig. 1(*a*) and (*b*) illustrates the appearance of this fault observed on a (111) surface.

When viewed on one of the {100} surfaces, this fault may give rise to two rows of hexagonal packing in the otherwise square packed array of spheres with a step in the surface along the fault line [see Fig. 2(*a*) and (*b*)].

(2) *Extrinsic or double hexagonal triplet fault*

This kind of fault is defined by the stacking sequence

ABCABACABCABC... in which the brackets indicate the two hexagonal triplets. This fault is obtained by the addition of an extra *A* layer between the layer *B* and the layer *C*. The fault may create three rows of square packed spheres on {111} planes as was observed on the opal in Fig. 3. In addition the fault may appear as other arrangements of packing depending upon the exact path taken by the fracture plane at the intersection with the fault. The pattern of packing described above is unequivocal for an extrinsic fault and is believed to be the favored pattern since the (111) fracture plane would suffer the least angular deviation (15·8°) in following this path.

(3) *Twinning*

A third type of fault involved the stacking sequence *ABCABC,BACBAC*... where the stacking modification after the comma creates a twin relationship in which the *C* layer preceding the comma is the twin plane. This corresponds to spinel twinning found in f.c.c. crystals where two crystals join at a (111) twin plane and are related in orientation to one another by a 180° rotation about the [111] normal to the twin plane. The effect of this twin fault upon the packing arrangement of the {100} surfaces and the remaining surfaces of the form {111} is to change the arrangement at the faulting line. The square packing arrangement of spheres on a (100) surface becomes a hexagonally arranged surface across the fault line with an angular divergence between these two surfaces of about 15·8°. Similarly, a (111) hexagonal arrangement of spheres becomes a (100) square pattern across the twin boundary with an angular divergence of about 15·8° between them. Fig. 4(*a*) diagrammatically shows this effect of the twinning upon the packing and Fig. 4(*b*) shows this effect observed on the opal.

(4) *Rhombohedral polytypism*

This modification of the opal structure is illustrated in Fig. 5 where a coalescence of the f.c.c. opal with a rhombohedral structure occurs. The Figure shows the f.c.c. (111) hexagonal array of spheres to change abruptly into a different packing pattern composed of a basic repetitive unit of two rows of hexagonal packing and two rows of square packing. A stacking sequence which will result in this packing pattern is *ABACACBCB,ABACACBCB*..., where the commas indicate the repeat unit composed of nine layers. Each of these stacking units will result in three units of the basic pattern observed on a (111) surface. Fourteen pattern units corresponding to $4\frac{2}{3}$ stacking units were recorded on the photo plate for study. This stacking sequence creates a rhombohedral structure with the *c* axis of the hexagonal cell parallel to the stacking direction and the periodicity consisting of nine layers. This new structure may be considered a polytype of the opal in analogy to crystals such as SiC that have polytypic modifications.

Discussion

An alternate explanation for these various changes in the packing arrangements as observed from electron microscopy might be merely in the mode of fracture of the opal. Since the surfaces used for observation were fracture surfaces, it is possible that the opal may preferentially cleave along the closest packed planes, alternating from a hexagonally packed (111) surface to the square packed (100) surface and so forth, resulting in the observed changes in the packing arrangement from hexagonal to square to hexagonal, *etc.* This explanation was ruled out since the angle between a (111) and a (100) plane in f.c.c. packing of spheres is 54·7°. Such a large angle would produce noticeable contrast differences between these surfaces when observed in the microscope as a result of variations in the metal shadowing used in the preparation of the replicas. Such contrast differences were not observed. On the other hand, the change in the packing arrangement resulting from faulting results in the much smaller angular divergence of about 15·8° between these two surfaces and hence, high contrast differences would not be expected. However, fracture alternation between different {111} surfaces was observed as shown in Fig. 6. Here the interplanar angle between the different {111} planes is 70·5° and this results in the marked variation in the shadowing contrast seen in the micrograph.

The success in predicting some of the observed packing patterns by considering stacking modifications of an f.c.c. structure indicates the existence of a basic, though frequently faulted, f.c.c. opal structure. The formation of ordered closest packed structures, such as the f.c.c. and the rhombohedral polytypes observed in this study and the h.c.p. structure reported by Sanders (1968), by concentration of colloidal silica particles from aqueous suspension, is surprising in view of the infinite number of closest packed arrangements which spheres of equal size could assume. A possible mechanism for explaining the occurrence of these ordered structures is screw dislocation-spiral growth, in analogy with the theory for crystals (Frank, 1951, 1952).

This theory states that steps or ledges may be raised on the surface of the crystal if the crystal, subjected to stress, undergoes shear. If the shear is by a uniform amount and terminates abruptly, a screw dislocation will be created with a ledge exposed on the surface. The spiral growth mechanism would repeat the structure of the ledge periodically with the repeat period equal to that of the ledge. Thus, screw dislocations differing in their Burgers vector strength may create different polytypic structures.

In this case of the formation of the cubic closest packed opal structure, if, during the concentration of silica spheres, shearing exposed a dislocation ledge composed of an integral number of cubic closest packed layers, *ABC* or *CBA*, the packing arrangement of this exposed ledge and the adjacent surface could serve as a template for subsequent addition of spheres and the f.c.c. packing sequence of the step would be perpetuated thereby.

In the case of a rhombohedral structure, the Burgers vector or exposed ledge need consist of only $\frac{1}{3}$ the height of the hexagonal cell with the first and last layers in the same orientation, *A*, *B* or *C* (Verma, 1957; Krishna & Verma, 1962; Verma & Krishna, 1966). With the first and last layer in the same orientation, the first layer cannot grow over the last without horizontal slip since closest packing cannot have consecutive layers in the same orientation. Thus, every time the structure growth completes one pitch there must be a horizontal shift of the layers in the same direction each time. Three such shifts would bring the structure back to its original position and complete one repeat period corresponding to the *c* dimension of the hexagonal cell.

For the 9*R* opal polytype, the Burgers vector would consist of only three layers with any of the following arrangements satisfactorily producing this structure: *ABA*, *ACA*, *CAC*, *CBC*, *BCB* or *BAB*. These packing sequences are recognized as hexagonal triplets and, therefore, could arise from an intrinsic fault in the exposed ledge that was producing the f.c.c. structure. The fault would be perpetuated by the spiral growth process to produce the 9*R* structure. This explanation is in agreement with the observation of the 9*R* arrangement arising directly from the f.c.c. arrangement (Fig. 5). Vand (1951*a*,*b*) has proposed this explanation of a stacking fault in the dislocation ledge for polytypism of crystals.

The occurrence of the faulted rows of packing parallel to one another on the opal surfaces as seen in Figs. 1(*b*), 2(*b*), 3 and 5(*b*) indicates that the stacking anomalies have occurred along only one of the three possible ⟨111⟩ stacking directions, which is in agreement with this one-dimensional growth theory.

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