Diffraction Lattices in Precious Opal
An Example of Crystallization from Supra-molecular Elements

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There has never been any doubt for the critical observer about the peculiarities in the display of colours of precious opal. Since trivial disturbances often conceal the genuine phenomenon, the conventional classification as colours of thin laminae (Newtonian colours) or even as Tyndall-phenomena seems – in spite of its insufficiency – relatively excusable.

Perfect specimens of precious opal from Australia or Hungary do not permit explanation of the vari-coloured phenomena as a result of iridescent tiny cracks or of turbidness. The reflected colours are much too intense and – as it may be proved by any simple spectrometric test – of remarkable spectral purity. With the naked eye alone, one can clearly perceive that the multicoloured flash with incident white light originates in distinctly separated fields. They only become fully visible, however, on a polished surface and then determine to a high degree the aesthetic effect ('Harlequin opal'). If this remarkable tesselated fabric had been taken into consideration in former investigations, the conventional theory of tiny cracks would never have arisen.

With moderate magnification and vertical illumination the real situation becomes obvious under the microscope: we observe a polyhedral granular fabric very similar to that of marble (Figure 1). Almost all grains are more or less dark; the polygonal course of their mutual boundaries, however, is perceptible. Some grains flash up in colours (in the upper left corner of Figure 1). When the angle of incidence is changed, their flashing instantly disappears and some other grains light up in a pure spectral colour depending on the respective angle of incidence.

The similarity of the pavement-like fabric in precious opal to a *crystalline* granular one is intensified by the fact that the individual grains frequently show thin lamellae of diverging luminous position, sometimes in parallel systems crossing each other. They resemble exactly twinned lamellae as caused by strain in marble and many metals. It is most remarkable that the mosaic of bright colours cannot be explained by obvious peculiarities in material: we have no reason to

doubt that the whole sample is *homogeneous* SiO_2-gel. Thus, there is a strange discrepancy between material on one hand and *optical* phenomenon on the other. These facts require the separate measuring of each single 'luminous grain'[1].

A Fedoroff universal-stage proved to be an appropriate goniometric apparatus for the registration of the different positions of reflection. It was set on the microscope together with a small spectrometer and a special illuminating device. To describe the results we supposed that the coloured light was reflected by a respective plane in the luminous grain. The normals to these planes were plotted on a stereographic projection[2] (Figure 2).

The 'reflectograms' resulting from this procedure are practically identical for each granule of the same specimen, except for the orientation, of course. In addition the angles between two 'equivalent' poles coincide within the accuracy of measurement. The general pattern is – without any exception – of hexagonal syngony. There are, however, characteristic distinctions between different occurrences; in particular,
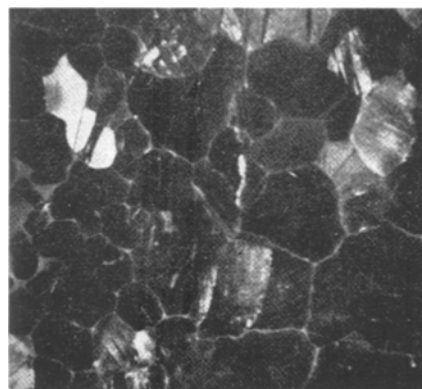

Fig. 1. Pavement-like pattern of an opal from White Cliffs. × 35.

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[1] We are using this working term for the optically homogeneous regions of opal.
[2] There is an example in Figure 2.

we can distinguish between rhombohedral and hexagonal types of diagrams. We may also add that the diagrams of lamellar partners are most regularly oriented one to the other; in a crystallographic interpretation they are to be regarded as *twins*. Obviously these reflectograms correspond in the visible wavelength range very closely to X-ray diagrams of crystals. Sometimes a certain 'pauperization' is indicated by a restriction to the zones of the hexagonal secondary axes. The highly symmetric coloured reflectograms allow the conclusion that here we are dealing with diffraction on a rather exact three-dimensional periodic system. Of whatever kind this diffraction lattice may be, it must become effective in the visible range of optics, i.e. there must exist a periodic change of the optical density.

The determination of the D-values[3] from the reflectograms permits an interpretation of the effective diffraction system. Further information can be drawn from the previously-mentioned deviations from X-ray diagrams of perfect crystals. The result is a model of three equivalent and periodically stratified sets of lamellae crossing each other in space. These sets can be almost plane or also remarkably undulated.

On the whole, the result is a three-dimensional periodic system similar to a (spatial) lattice.

These were the results of my observations in 1932[4]: precious opal, a gel nearly amorphous to X-rays, 'pretends' or 'feigns' to the last detail crystallinity; in particular, it gives – with light of the visible spectral range – Laue-diagrams of remarkable exactitude. If this astonishing fact gained little mention in manuals, monographs and other publications in the field of exact knowledge, the reason may be that precious opal – as an aesthetically attractive curiosity – was and still is not in the centre of scientific interest. Moreover, some statements, e.g. that of occurrences of twins (following several laws), were admittedly unprecedented and a certain reserve seemed to be quite understandable. What is more, the examination of most of the data was not practicable without any special apparatus. Finally, the results were obtained from choice material; when studying less characteristic samples, the sceptic will not find all data proved at first sight.

The possibility of rendering visible the optically effective spatial lattice remained unattainable for decades, until the electron microscope gave unexpected new hope. By application of the replica method the examination of compact substances also became feasible. From the behaviour in the visible light range one could definitely conclude resolvable periodic structures of precious opal; therefore I encouraged Dr. PENSE, who had already been very successful in testing this new apparatus on minerals to study, this promising new apparatus on minerals[5-8], to study this promising subject.

On the occasion of the joint congress of the 'Deutsche Mineralogische Gesellschaft' and the 'Österreichische Mineralogische Gesellschaft' in Vienna (September 1963) PENSE[9] reported his investigation, showing the results of his numerous photographs taken with an electron microscope (Figures 3 and 4). Even in a reproduction the periodicity which is responsible for the diffraction can clearly be seen (Figure 3). These photographs – and many others – taken by PENSE agree surprisingly well in their general structure with the predictions from the optical behaviour with a quite unexpected accuracy. In addition, the photographs taken with the electron microscope exhibit details of the fabric that could simply not be detected before.

Figure 3 shows a kind of lattice-plane formed by strung-out, small, bright (occasionally also dark) marks running from WNW to ESE; we find dots, little three-pronged stars, triangles, squares etc. forming what one might call pronged streaks while keeping rather strictly equal distances from one another. As other prints (of etched fracture surfaces) show, these striking blebs are nothing else than voids – little
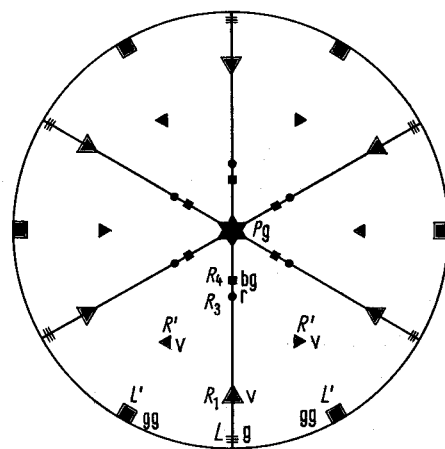

Fig. 2. Precious opal from Bulla Creek. Reflectogram in stereographic projection taken with an angle of incidence of 40°. Colour of the reflexes: g = green, gg = yellowish green, bg = bluish green, r = red, v = violet.

[3] D-values: The vertical distances between the planes.
[4] E. BAIER, Z. Krist. A, *81*, 183 (1932).
[5] E. BAIER and J. PENSE, Naturwiss. *44*, 110 (1957).
[6] E. BAIER and J. PENSE, Naturwiss. *44*, 110 (1957).
[7] J. PENSE, Z. dt. Ges. Edelsteink. *38*, 12 (1961/62).
[8] J. PENSE, *Zur sublichtmikroskopischen Morphologie des Chalcedons*, Jahrestagung der Deutschen und Österreichischen Mineralogischen Gesellschaft, Wien (1963), Kurzreferat in: Fortschr. Min. *41*, 166 (1963).
[9] J. PENSE, *Elektronenmikroskopischer Beitrag zur Optik der Edelopale*, Jahrestagung der Deutschen und Österreichischen Mineralogischen Gesellschaft, Wien (1963). Kurzreferat in: Fortschr. Min. *41*, 166 (1963).

'gussets' – between adjoining spheres (Figure 4). These spheres evidently represent the 'real' opal substance. Their diameters vary within narrow limits only. One sees them with varying clarity in all photographs. Thus, we are bound to look upon precious opal as a package of equally sized spheres, slightly deformed when touching each other: presumably SiO_2-spherulites.

In December 1964 SANDERS published a detailed article[10]; he also examined precious opal under the electron microscope. SANDERS has the privilege of living in the country famous for its occurrences of precious opal. Hence, the quality and variety of his figures is remarkable. In all fundamental characteristics his figures are to a high degree in agreement with those presented by PENSE.

If Sanders, however, should be of the opinion that my former deduction of the diffraction phenomena from sets of lamellae crossing each other was in error on the basis of the photographs, I must disagree. In the last analysis the diffraction depends on the *periodic change of the optical density in space*. It is commonplace that this three-dimensional periodicity can be exhibited in different ways.

The spherical form as such is of no importance whatsoever for the optical aspect of the phenomenon[11]. On the other hand it can possibly be the real cause of the periodic pattern. We know that equally sized spheres packed closely together form certain patterns. Two of these patterns, which are all ruled by the principle of the most economical use of space, stand out because they correspond to cases in pure crystallography: cubic and hexagonal sphere packing of highest density. These two patterns thus comply with crystal lattices including all consequences; they should also diffract light of commensurable wavelengths.

It is a reasonable assumption to explain precious opal also *genetically* by some process of crystallization, i.e. by a subsequent packing of highly complex elements. We could suppose the fact (and SANDERS does so apparently without reservations) that uniform spherulites emerged from a SiO_2-colloid, which was

[10] J. V. SANDERS, Nature *204*, 1151 (1964).
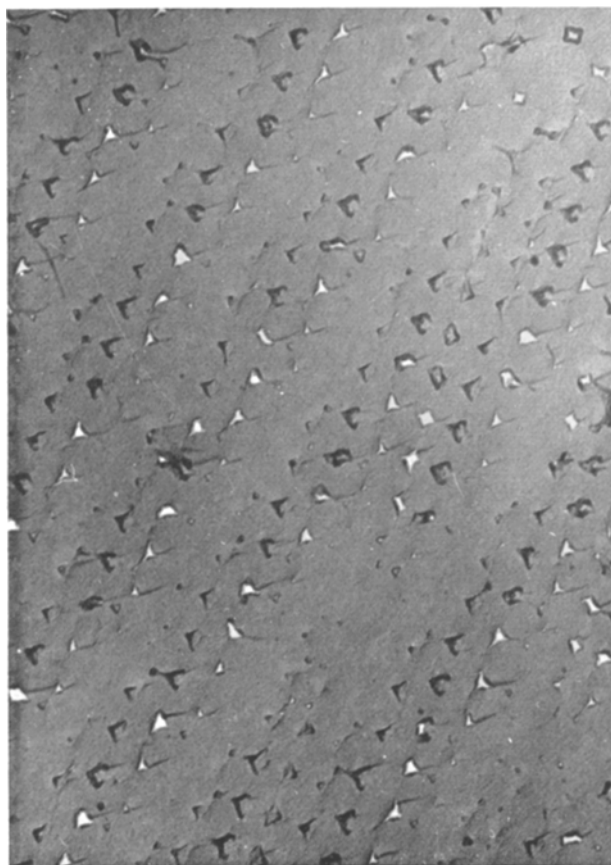[11] Except for the proportional intensity of the reflections.

Fig. 3. Fracture surface of precious opal [Aufdampfabdruck . Evaporation replica taken with an electron microscope, × 33,000; PENSE (1963).
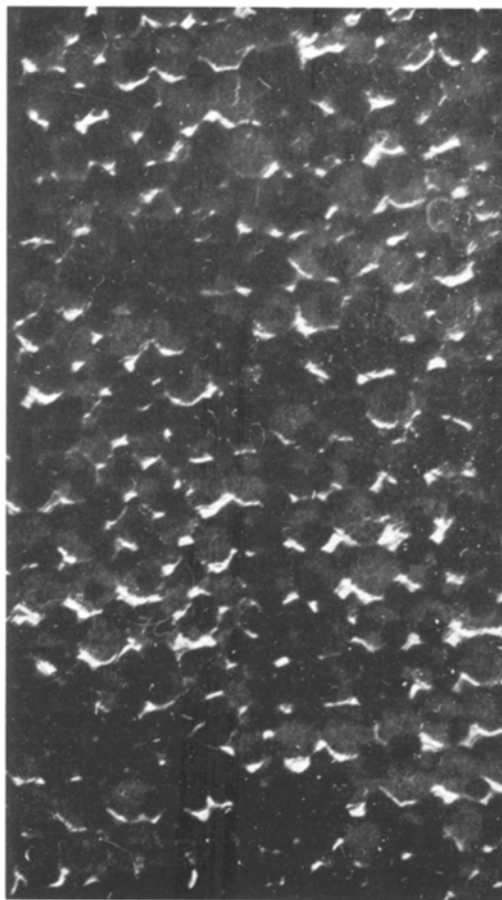

Fig. 4. Fracture surface of precious opal, etched. Evaporation replica showing distinctly the *fabric* of spheres, × 30,000; taken by PENSE (1963).

still sufficiently mobile, and formed a lattice pattern either by sedimentation or by squeezing out the residual soil.

This genetic explanation – reasonable and obvious in itself – is supported by some spectacular analogous cases: Luck, Klier, and Wesslau[12] reported on their experiences with spherical particles obtained by emulsion polymerization (synthetic latex). Under favourable conditions these particles assemble in patterns of space lattices[13]. At an adequate lattice period (respectively radius of the spheres) diffraction with visible light is obtained from such 'crystals' as well.

Returning to the previously mentioned fabric of a polished section of precious opal (Figure 1), the most striking observation was that the SiO_2-gel, apparently homogeneous in material, seemed to be divided into polygons (a three-dimensional granular fabric), i.e. into fields that obviously differed only in the orientation of their reflections. According to the description of Luck et al.[12] the latex precipitates with multicoloured reflections show granular fabrics of great similarity. This similarity holds true even to some of the above-mentioned details: the individual 'luminous grains' of opal often contained lamellae of different luminous positions or even lamellar systems crossing each other. According to the figures such lamellae are found in latex crystals too, and the authors emphasize their twin character.

In the case of opal the spherical elements cannot be considered as 'amorphous' in the strictest sense. Under adequate conditions opal substance shows – for the most part rather faded – Debye rings. Among others, Raman et al.[14,15] attempted a crystallographic interpretation of these rings. We are, however, of the opinion that the question of the particular SiO_2-modification of our spheres can be omitted as the very problem is restricted to the range of *visible* light.

Luck, Klier, and Wesslau[12] call the systematically assembled accumulations of latex spheres simply 'crystals' without any restriction. They cannot be blamed for such an extension of the concept of 'crystal' to really homogeneous structures of any optional 'elements'. From this point of view the sphere packages producing the coloured flash in precious opal can also be called 'crystals'.

Whereas mineralogists tend to emphasize the *peculiarity* of precious opal, Luck et al.[12] are obviously interested in pointing out the *general* and compulsory aspect of the phenomenon. In this connection they come up with further impressive examples, i.e. some types of crystallized virus. If their lattice period remains within the wavelengths of visible light, a more or less distinct iridescence occurs here too, as has been proved by many observations, e.g. [16-19].

The number of examples of 'crystal lattices' formed by polymolecular elements is thus augmented by precious opal as an *inorganic* case. Because of the far-

reaching analogy in structure and behaviour one is inclined to suppose also an analogous *genesis*. Nevertheless, we must remember that coloured diffraction phenomena can originate from 'genuine' crystals, as described in the literature[20,21]. The cause may be rhythmic inhomogeneities (unmixing, translations, twins, inclusions etc.). In these cases the lattice of the host dictates the orientation of the diffraction system for visible light. These examples show that such diffraction systems may originate from causes other than subsequent crowding of pre-existent mobile spheres. So, from the beginning, we must consider the possibility of convergences.

In the particular case of precious opal, the free mobility of the spheres, which is a prerequisite for the realization of the lattice, can hardly be assumed. It is true that opals may originate in several ways, a few of them allowing a subsequent packing of those spherulites, for instance in geyser deposits or during weathering of silicates or inside agate-like geodes. In all these cases, as far as I know, a display of colours was never observed.

On the other hand, *metasomatic replacement* is frequently reported from occurrences of precious opal, with calcite being replaced by opal substance. During this process the finest structural details of fossils, oolites etc. were preserved. How should we explain that, under these circumstances, the SiO_2 spheres gained the exact lattice structure?

With reference to the often evident *pseudomorphous* character of precious opal, I hinted[5] at the possibility that a slight rhythmic pattern in the replaced calcite had regulated the diffraction system in the opal. The structure, as now proved by Pense and Sanders, is at least not in contradiction to my old hypothesis. Supposing the intersections of the sets of glide-lamellae had served – during the replacement of the calcite by SiO_2 gel – as starting points for the growth of the spheres, then the adjustment of the entire 'lattice of higher order' to the former calcite structure would be clear.

[12] W. Luck, M. Klier, and H. Wesslau, Naturwiss. *50*, 485 (1963).
[13] E. W. Fischer, Kolloid-Z. *160*, 120 (1958).
[14] C. V. Raman and A. Jayaraman, Proc. Ind. Acad. Sci. *38 A*, 101 (1953).
[15] C. V. Raman and A. Jayaraman, Proc. Ind. Acad. Sci. *38 A*, 343 (1953).
[16] M. H. F. Wilkins, A. R. Stokes, W. E. Seeds, and G. Oster, Nature *166*, 127 (1950).
[17] N. Xeros, Nature *174*, 562 (1954).
[18] R. C. Williams and K. M. Smith, Nature *179*, 119 (1957).
[19] A. Klug, R. E. Franklin, and S. P. F. Humphreys-Owen, Biochim. biophys. Acta *32*, 203 (1959).
[20] C. V. Raman and A. Jayaraman, Proc. Ind. Acad. Sci. *32 A*, 1 (1950); *38 A*, 199 (1953). – C. V. Raman and D. Krishnamurti, Current Sci. *21*, 327 (1952); Proc. Ind. Acad. Sci. *38 A*, 261 (1953); *391*, 1 (1954). – C. V. Raman, A. Jayaraman, and T. K. Srinivasan, Proc. Ind. Acad. Sci. *32 A*, 123 (1950).
[21] E. Baier, Z. Krist. *A, 83*, 141 (1932).

Prior to the publications of PENSE and SANDERS such 'remembrance' of former lattices offered me the only explanation for the crystal behaviour of precious opal. Admittedly this behaviour is now easily explained by the effect of packed spheres. In the particular case of opal gel, however, the mutual adjustability for the 'deliberate' arrangement is not granted. Therefore, for the present time, I think that the hypothesis of the spherulites growing according to a pre-existent pattern is indispensable and quite compatible with experience as well. We do hope that the systematic review of the extensive former literature on opal in the light of recent findings by means of the electron microscope will soon lead to a decision on the *genetic* question and therewith to a definite solution of precious opal's 'last' secret.

Zusammenfassung. Im Jahre 1933 konnte der Verfasser anhand umfangreicher goniometrischer Messungen nachweisen, dass im Edelopal – einem nahezu röntgenamorphen Gel – irgendwelche dreidimensionalen, lichtoptisch wirksamen, periodischen Systeme (Beugungsgitter) wirksam sind. Über die Geometrie, insbesondere über die Symmetrie dieser Systeme, konnten genaue und verbindliche Angaben gemacht werden; über ihre materielle Natur hingegen war beim damaligen Stand der Untersuchungsmethoden nichts zu ermitteln.

Vor einigen Jahren ist es nunmehr PENSE (Mainz, Institut für Mineralogie) gelungen, im Abdruckver-

fahren diese Beugungsgitter elektronenmikroskopisch sichtbar zu machen. Sie bestehen aus regelmässig im Raum verteilten kleinen Höhlen, die sich zwanglos als Zwickel zwischen dichtgepackten, gleich grossen Kügelchen – vermutlich Chalcedon-Sphärolithen – ausdeuten lassen. Der Edelopal ist damit nach Kunststofflatices und gewissen Viren ein weiteres Beispiel für «Kristalle aus übermolekularen Bausteinen».

Es liegt nahe, den Edelopal auch genetisch gleich zu erklären wie die entsprechenden Produkte des Lebens bzw. der organischen Chemie, nämlich aus dem einfachen Packungseffekt ursprünglich im Dispersionsmittel gegeneinander beweglicher Kügelchen im Verlauf eines Sedimentations- oder Abquetschungsvorgangs. Gewisse Beobachtungen scheinen mir aber diese an sich gewiss plausible Erklärung hier zu verbieten: Edelopal pflegt nämlich in ausgesprochenen Pseudomorphosen nach Fossilien, Oolithen u.ä. Bildungen aus kristallinem Calcit aufzutreten, und zwar bei oft bester Erhaltung feinster morphologischer Details. Dieser Befund verträgt sich schlecht mit der Annahme von erst nachträglich sich ordnenden, vorgebildeten Sphärolithen. Eher könnte man daran denken, dass ein schon in den nachher verdrängten Kristallen bestehender Überrhytmus lichtoptisch wirksamer Periode (verschränkte Gleitlamellen, Entmischungen u. dgl.) den Verteilungsplan der Sphärolithzentren bestimmt hat. Dabei sei daran erinnert, dass lichtoptisch wirksame Systeme bei einigen Kristallarten beschrieben sind.

SPECIALIA

Über einige Reaktionen des Selentrioxids

In einer früheren Arbeit[1] berichteten wir über die Reaktion des Selentrioxids mit wasserfreiem Fluorwasserstoff, die nach der Gleichung $SeO_3 + HF = HSeO_3F$ zur noch unbekannten Fluoroselensäure führte. Inzwischen haben M. SCHMIDT und I. WILHELM[2] auch die Chloroselensäure auf analogem Wege hergestellt. Da über Eigenschaften und Reaktionen von Selentrioxid bisher nur wenig bekannt ist, interessierten wir uns für weitere Umsetzungen dieser Verbindung und suchten daher nach geeigneten Lösungsmitteln. M. SCHMIDT benützt flüssiges SO_2[3]. Dieses Lösungsmittel bedingt jedoch eine tiefe Arbeitstemperatur, ausserdem löst es SeO_3 nur in begrenztem Masse. Wir fanden nunmehr, dass sich SO_2Cl_2 und $POCl_3$ gut als Lösungsmittel für SeO_3 eignen. Beim

Eindampfen der Lösungen erhält man SeO_3 unverändert zurück. Wir haben die Lösung von SeO_3 in SO_2Cl_2 durch ihr IR-Spektrum charakterisiert (Figur) und dieses mit dem bekannten Spektrum von SeO_3 in festem Zustand[4] verglichen. Die dort auftretenden Banden finden sich auch im Lösungsspektrum (Tabelle), daneben erscheinen im letzteren eine Reihe von zusätzlichen Banden.

Mit solchen SeO_3-Lösungen lassen sich die folgenden neuen Umsetzungen durchführen. So konnten wir zeigen,

[1] H. BARTELS und E. CLASS, Helv. chim. Acta 45, 179 (1961).
[2] M. SCHMIDT und I. WILHELM, Chem. Ber. 97, 876 (1964).
[3] M. SCHMIDT und I. WILHELM, Chem. Ber. 97, 872 (1964).
[4] R. PAETZOLD und H. AMOULONG, Z. anorg. Chem. 337, 225 (1965).