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The Structure and Si,Al Distribution of the Ultramarines

BY S. E. TARLING AND P. BARNES

Industrial Materials Group, Department of Crystallography, Birkbeck College, Malet Street, London WC1E 7HX, England

AND J. KLINOWSKI

*Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, England*

Abstract

The structure and Si,Al distributions of various ultramarine pigments have been investigated using X-ray and neutron powder diffraction with Rietveld refinement, and magic-angle-spinning NMR (MAS NMR). The basic structures of the ultramarines studied are found to be very similar: refinement proceeds far better in space group $I\bar{4}3m$ than in $P\bar{4}3n$ which indicates that Si and Al in the framework of ultramarines are disordered. This conclusion is supported by ^{29}Si MAS NMR spectra which contain five signals, rather than a single signal which would be present if Al–O–Al linkages were forbidden. The intensities of the five peaks are consistent with the presence of Si–O–Si, Si–O–Al *and* Al–O–Al linkages in the structure. Such disordered Si,Al distributions in pyrolytically formed ultramarines are in striking contrast to the ordered distributions found in both the naturally formed counterpart lazurite and in hydrothermally synthesized zeolites.

Introduction

The ultramarines are a family of closely related pigments, the best example of which is Reckitt's blue with the ideal formula

$$Na_{7.5}Al_6Si_6O_{24}S_{4.5}.$$
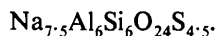
The framework structure is that of sodalite, and the pigments may be obtained synthetically by furnacing a mixture of the appropriate amounts of kaolin, sulfur, sodium carbonate and minor ingredients (Beardsley & Whiting, 1948; Prener & Ward, 1950; van Order & Hill, 1950).

Historical records trace the knowledge of ultramarines to ancient times when natives of the Badaskan district of Afghanistan used pieces of an intensely blue rock as an ornament for making crude pigment. The rock formed in a calcite and dolomite matrix with small flakes of iron pyrites and became known as lapis lazuli or lazurite. Ancient legend believed it to be pieces of the night sky fallen to earth. By the Middle Ages, the material had assumed considerable importance as an expensive blue pigment.

The high cost of extracting and shipping lapis lazuli from Afghanistan led in the 1800's to chemical analyses (Desormes & Clement, 1806) and various attempts (Guimet, 1828; Gmelin, 1828) to make the pigment synthetically culminating with commercial production (in the UK by James Reckitt and Sons during the mid-1880's). From that time the rare natural pigment has been referred to as lazurite while the synthetic counterparts have adopted the name ultramarine.

The basic structure of the ultramarines was first studied by Jaeger (1929), and later by Leschewski (1935), who concluded that it is based on sodalite (Pauling, 1930; Barth, 1932). However, until the mid-1980's, there had been no substantial crystallographic analyses of this structure and no successful dynamic study of the intermediates formed during the production of ultramarines (Tarling, Barnes & Mackay, 1984) though a number of spectroscopic techniques (see below) had been brought to bear on the problem of identifying the colour groups in the various ultramarine products.

We have refined the structure of ultramarine using X-ray and neutron diffraction methods, and have probed the Si,Al distribution using magic-angle-spinning nuclear magnetic resonance. These analyses are also supported by the current literature results from other spectroscopic techniques.

Previous studies on the structure of ultramarines

Jaeger (1929) identified the three main structural components of ultramarine: the aluminosilicate cage;

the colour group located inside the cage; and exchangeable cations. He also narrowed down the space group to a few possibilities including body centred and primitive cubic.

There followed many early chemical modifications to the basic structure (e.g. Jaeger & van Melle, 1929; Podschus, Hofmann & Leschewski, 1936; Gruner, 1935) though the chemistry of these processes was not well understood. These studies led to the suggestion (see Fig. 1) that (i) the cations are located near the centre of the six-membered rings of the sodalite cage; (ii) colouring is caused by a clathrate group located inside the cage; and (iii) the stoichiometric formula is:

$$Na_8Al_6Si_6O_{24} + (colour\ group)^{2-}$$
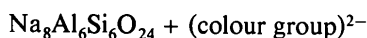
which is electrically neutral and in reasonable agreement with the measured composition.

The search for the precise nature of the intensely blue colour group continued in the 1960's and 1970's, and involved extensive spectroscopic studies of the various ultramarines and sulfur-containing systems (doped alkali halides, sodalites etc.). S_2^-, S_2^{2-}, S_3^-, S_4^- were considered to be likely contenders. Opinions in favour of S_3^- gradually hardened (Morton, 1969), and a quantum-mechanical calculation (Cotton, Harmon & Hedges, 1976) on the S_3^- radical identified an anti-bonding $2b_2$ to non-bonding $1a_2$ transition at $13\ 190\ cm^{-1}$ which compared well with the spectroscopic observation ($13\ 500\ cm^{-1}$) for a C_{2v} S–S–S configuration with S–S distances between $2·0$ and $2·1$ Å and an S–S–S angle of about $110°$. Thus the current picture of the ultramarine blue chromophore is that of an (S–S–S)⁻ group trapped in the sodalite cage and isotropically disordered at room temperature.
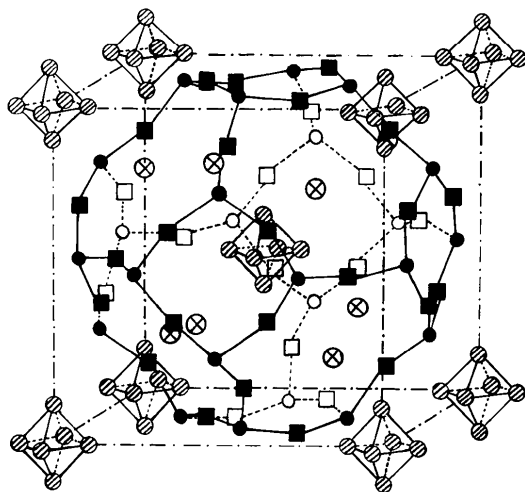

Fig. 1. Schematic drawing of the basic structure of standard ultramarine, showing the available sites for sulfur and sodium: □ = oxygen, ○ = silicon or aluminium, ⊗ = sodium, ⊘ = sulfur.

Background and strategy

Although the sodalite cage is the most likely candidate for the basic framework structure of the ultramarines, it would have been desirable to have confirmed this directly by solving the structure from single-crystal data. Therefore the structure analysis inevitably started with attempts to produce or find single crystals. These were as follows.

(a) Furnacing and melting

When an ultramarine is made in the conventional manner the crystallite size is small, typically below a few micrometres. Several potential improvements have therefore been considered such as using a fluxing agent, and changing the heating conditions. All these techniques were tried without success, the volatility of sulfur (boiling point 718 K) and the high melting point of the framework proving to be the main obstacles.
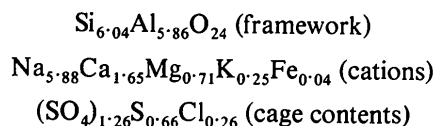
(b) Hydrothermal and solvent methods

Large single crystals of some zeolites can be grown by hydrothermal techniques but the products have a substantially higher water content than ultramarine. Recently, Bye & White (1970) succeeded in hydrothermally growing single sodalite crystals in the presence of NaCl. However, in the case of standard ultramarines the hydrothermal method cannot be used as the S_3^- anion does not form in aqueous media. Isomorphous substitution of single crystals of sodalite in the solid state is one of the avenues that remain to be explored.

(c) Search for natural crystals

We have examined a sample of natural lazurite from the 1971 French expedition (Wyart, Bariand & Filippi, 1972). Although it was described as a single crystal, synchrotron-radiation transmission topographs (Tarling, 1986) of sections (0·5 to 1·0 mm thick) revealed that it was in fact composed of a large number of randomly oriented microcrystallites with some regions displaying longer-range order. Even the most uniform blue parts have been shown by powder diffraction (Evans, 1984) to contain substantial amounts of a dolomite matrix.

Hassan, Peterson & Grundy (1985) were able to obtain crystals of lazurite to enable collection of single-crystal data. Their analysis however showed very little S_3^-, but rather SO_4 in the cage, and a substantial substitution of sodium by calcium (and other cations) yielding an approximate formula:

$$Si_{6·04}Al_{5·86}O_{24}\ (framework)$$

$$Na_{5·88}Ca_{1·65}Mg_{0·71}K_{0·25}Fe_{0·04}\ (cations)$$

$$(SO_4)_{1·26}S_{0·66}Cl_{0·26}\ (cage\ contents)$$

plus some water and/or hydroxyl groups. Their data included reflections which were consistent with space group $P\bar{4}3n$. In what follows, we shall see how surprisingly different are pure ultramarine and natural lazurite, their respective space groups indicating that the Si,Al-site occupancies are quite different.

In the absence of suitable single crystals, powder diffraction is the obvious route towards a structure solution since the sodalite cell can serve as a realistic trial structure. While powder X-ray diffraction was used for the preliminary structure refinement, it is not sufficiently effective in differentiating between neighbouring elements in the Periodic Table, and is insufficiently sensitive to Al,Si ordering. Ultramarines are particularly unfortunate in possessing four ten-electron species (O_2^-, Na^+, Al^{3+}, Si^{4+}) as well as other features (e.g. the disordered S_3^- group) which make structure refinement particularly difficult. All these factors point to the need for neutron powder diffraction studies.

Because of the importance of accurate determination of the distribution of Si and Al atoms in the framework of ultramarines, we have also resorted to ^{29}Si and ^{27}Al magic-angle-spinning NMR which is sensitive to the local environment of the respective nuclei.

Sample preparation

There are many different ultramarines. From an idealized formula

$$Na_{7\cdot5}Al_6Si_6O_{24}S_{4\cdot5}$$
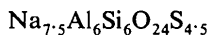
there are three directions in which the structure can be modified.

Firstly, we can perform conventional ion exchange where a substitution of the Na cation would indeed be desirable for replacing one of the ten-electron species and thus create improved X-ray (or electron) contrast. A number of such ion exchanges were attempted (see Table 1) and, while the results agreed closely with those of Barrer & Raitt (1954), the end products were unfortunately always less ideally crystalline than the starting material.

Secondly, modifications of the clathrate group are now carried out as standard industrial practice (Cork & Cattle, 1982), producing a range of colours from mauve to pink. Powder diffraction (Tarling, 1986; Table 1) indicates that the structural changes are confined mainly to the contents of the sodalite cage. Since the S_3^- group is paramagnetic, there are good reasons for considering its substitution when using methods which probe the atomic nucleus (neutron diffraction and MAS NMR). Also the diffraction backgrounds of the ultramarines are inherently high and so there are additional reasons for wanting to minimize disordered paramagnetic scattering. The so-called 'pink ultra-

Table 1. *The various ultramarines studied*

The Si/Al ratios were derived from the bulk formulations with a correction for the unreacted silica source where required. The neutron data were collected over 24 h for pink and standard ultramarines and over 42 h for pure ultramarine. The instrument D1A (ILL, Grenoble) was used in Debye–Scherrer geometry with a monochromator, the step-scan increment was 0·05° in 2θ, and the specimens were contained in standard vanadium cans. The X-ray data were collected on a Guinier–de Wolff camera using Cu $K\alpha$ radiation at room temperature but with no humidity control.

Ultramarine: type and formulation		Mean Al/Si (range)	Colour	Data: $\lambda(\text{Å})$ T (K)	Unit cell, a (Å)
Standard:	standard with high Si/Al	1·11 (1·05–1·20)	Red-shade blue	Neutron: 1·384 ~4	9·034
Pure:	purest raw mix	1·04 (1·01–1·10)	Green-shade blue	Neutron: 1·384 ~4	8·039
Pink:	standard + colour group exchange	1·11 (1·05–1·20)	Pink	Neutron: 1·909 ~4	9·090
Ag:	Na→Ag cation exchange	1·11 (1·05–1·20)	Olive green	X-ray: 1·542 293	9·036
Li:	Na→Li cation exchange	1·11 (1·05–1·20)	Deep blue	X-ray: 1·542 293	8·828
Ca:	synthesis from a Ca zeolite	1·11 (1·05–1·20)	Blue	X-ray: 1·542 293	9·070

marine' is less paramagnetic (Hofmann, Herzenstiel, Schoenemann & Schwarz, 1969), the colour group being thought (Clark & Cobbold, 1978; Seel & Guettler, 1973; Seel, Guettler, Simon & Wieckowski, 1977; Seel, Guettler, Wieckowski & Wolf, 1979; Tarling, 1986) to be S_3Cl or S_4 in addition to S_3. Accordingly the pink ultramarine was chosen as one of the samples for this project.

Thirdly, there is a standard 'red shade' preparation (Cork, 1978) with an Si/Al ratio greater than unity. Since this is the standard commercial ultramarine (as manufactured by Reckitt's Colours Ltd), it was also chosen.

After washing and grinding, the pigment is classified into a range of particle sizes. Powder X-ray diffraction (Tarling, 1986; Table 1) shows that there are no substantial changes in unit-cell dimensions, though the coarsest grade contains the largest fraction of impurities. For this reason samples were always taken from the fine end of the range prior to further purification. The purest ultramarine is obtained by using the highest quality ingredients which yield a product with less siliceous impurities and little substitution of the sodium cations. A sample of 'pure ultramarine' was therefore also included. The three ultramarines chosen for the neutron diffraction studies are listed in Table 1.

The major impurities in ultramarine are silicaceous (metakaolinite, kaolinite, mica, quartz, feldspars) and sulfurous (free sulfur and sodium sulfate). There are

standard procedures (*e.g.* Barrer & Raitt, 1954; Thompson, 1933; Gettens, 1950) for the removal of these components, and the standard 'bromine insolubles' purity test shows that these purification processes are effective in removing sulfurous impurities and quartz but less effective for removing kaolinite (and presumably metakaolinite). The purest ultramarine had less than 1% bromine-insoluble material, while the pink and standard ultramarines had less than 2%.

static disorder. This required some specialized treatment of the data sets.

The runs were originally planned to span *ca* 40 peaks at 1·384 Å to give a reasonable ratio for the number of observational to refinement parameters in space group *I*$\bar{4}$*3m*. In practice the signal-to-noise ratio became significantly poorer beyond $S = h^2+k^2+l^2 = 104$, though with the pure ultramarine the data was extended to $S = 114$.

Data collection

Neutron diffraction experiments were carried out at the Institut Laue–Langevin on instrument D1A (Barnes, Mackay & Tarling, 1984). Prior to this a preliminary neutron data collection had been carried out on the Harwell Dido reactor 10H diffractometer ($\lambda = 0\cdot9977$ Å), the data extending to ~1·2 Å. The Harwell data however were not of sufficient quality for structure refinement, but this trial run did highlight the problems of static and dynamic disorder at room temperature. Thus all the experiments at ILL were performed at liquid-helium temperature.

Altogether three neutron data collections were successfully completed as detailed in Table 1. A typical diffraction data set is given in Fig. 2(*a*). It is apparent that even with the usual precautions (D_2O/H_2O exchange and drying) and at liquid-helium temperature the background is high and modulated by the effects of

Structure refinement

The trial structure model used for the neutron refinements was based on our X-ray data: this involved the sodalite structure with partial occupancy of the octahedral sites by sulfur atoms (see Fig. 1) to represent the S_3^- colour group.

All refinements were performed at least twice, that is in space groups *P*$\bar{4}$*3n* and *I*$\bar{4}$*3m*, these space groups representing respectively the two extreme cases of perfect Loewensteinian (Loewenstein, 1953) and of completely random Si,Al ordering. The standard ILL-D1A data reduction and Rietveld refinement programs (Hewat, 1973; Heathman, 1981) were used. No preferred orientation parameters were included and no constraints were placed on the refinement of the unit-cell parameters. Peak-related parameters were refined only at later stages under the influence of heavy relaxation factors.
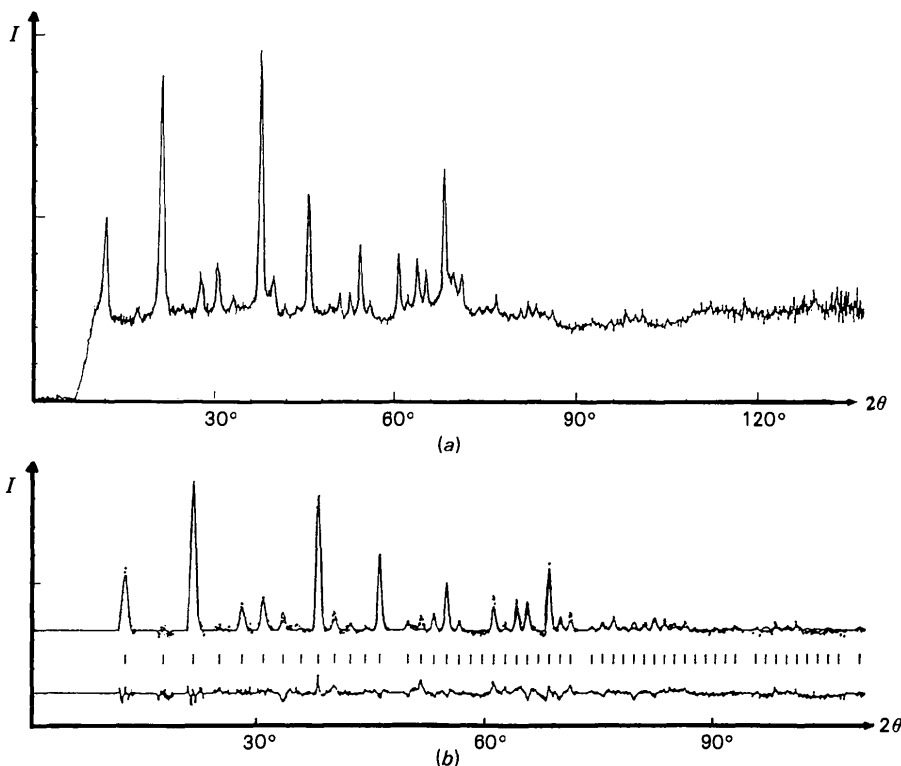

Fig. 2. (*a*) Raw powder neutron diffraction data obtained from the D1A instrument at ILL, Grenoble for pure ultramarine. Further details are given in Table 1. (*b*) Standard Rietveld refinement plot showing observed pattern (points), calculated pattern (line) and difference (lower line) for pure ultramarine refined in *I*$\bar{4}$*3m*. There are no signs of peak doubling at positions corresponding to space group *P*$\bar{4}$*3n*.

Initial Rietveld refinements (Rietveld, 1966, 1967, 1969) yielded only slow improvements in the R factor from around 40 down to 30% in either $I\bar{4}3m$ or $P\bar{4}3n$. At this point several changes were made to the refinement strategy:

(1) The high-angle data were omitted in the early stages, and introduced as refinement proceeded.

(2) It was found more advantageous during early stages of refinement to release refinement parameters gradually, particularly the thermal and occupancy parameters.

(3) Initial attempts to fix backgrounds at a few points were much too crude because the backgrounds were not only high but also modulated (see, for example, Fig. 2). The backgrounds were therefore defined interactively using a larger number (~50) of points which were chosen and displayed on an enlarged scale. Application of this procedure dramatically improved the refinement.

(4) In some runs the model was modified by introduction of a 0·5 occupancy of a D_2O molecule inserted into the (effective) partial vacant site resulting from having only 7·5 Na ions filling the eight available cation sites. Again, to accommodate the indications emerging from the difference maps, the octahedral model of sulfur occupancy was modified to reproduce a more even density inside the cage by adding a further sulfur to the hollow octahedral shell, with sulfur occupancies rescaled accordingly to maintain S_3 overall.

An example of a conventional Rietveld plot is given in Fig. 2(b).* The conclusions regarding the Si,Al ordering became quite decisive since it was found that refinements (for all three ultramarines) in space group $P\bar{4}3n$ always led to R factors greater than 20%, whereas refinements of the same data sets in $I\bar{4}3m$ yielded R factors consistently between 12 and 17%. Thus the distribution of Si and Al for all the ultramarine frameworks is effectively random, and this conclusion is strikingly confirmed by the NMR results discussed in the next section.

Though the eventual structure and R factors in $I\bar{4}3m$ were similar for each type of ultramarine, the best R factors of 14·7 and 16·99% were obtained with the standard high-silicon and pure ultramarine respectively. The lower paramagnetism of the pink ultramarine was presumably offset by the greater uncertainty concerning its cage contents, although the R factor was improved by adding a small occupancy of Cl to the centre of the cage. The refined structure of

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* The numbered intensity of each measured point on the profile has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44552 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Structure and refinement parameters for the best cases of pure and standard ultramarines refined in* $I\bar{4}3m$

Thermal and Rietveld half-width parameters are in the standard form and program units of Hewat (1973). No absorption corrections were necessary. The ranges over which contributions were considered were determined by the preprofile (3 FWHM). Weights were calculated as being proportional to $(y_i)^{-1/2}$, where y_i is the observation. Refinements were terminated when shifts were within 0·3 e.s.d.'s. E.s.d.'s for coordinates (not fixed by special equivalent positions) are given in parentheses according to differences found between the various ultramarines. R factors are in the form defined as R_{wp} by Young, Prince & Sparks (1982). The neutron scattering (b) lengths are those given by Koester & Yelon (1982).

Structure parameters					Thermal
	x	y	z	Occupancy	parameter
Si/Al	0·25	0·50	0·0	0·25	0·5
O(0·003)	0·350	0·350	0·018	0·5	4·2
Na(0·04)	0·182	0·182	0·182	0·1458	19·7
S(0·03)	0·079	0·0	0·0	0·09375	24·5
D_2O (0·04)	0·182	0·182	0·182	0·02	11·6

Refinement parameters
Relaxation factors: coordinates 0·80
                    temperature 0·60
                    scaling 0·80
Rietveld half-width parameters: $u = 3500$
                                   $v = -6123$
                                   $w = 5897$
            zero point $= -9·223$

Structural parameters: unit cell, $a = 9·0338$ (0·0012) Å
                       volume $= 737·25$ (0·29) Å^3
                R factor $= 14·73\%$ (standard)
                          $= 16·99\%$ (pure)

standard ultramarine is now considered to be the best available, and this is the structure detailed in Table 2.

Magic-angle-spinning nuclear magnetic resonance (MAS NMR)

In magic-angle-spinning NMR the powdered sample is rapidly spun (at *ca* 4 kHz) about an axis inclined at an angle $\theta = 54° \, 44' \, 8''$ to the direction of the magnetic field, so that $3\cos^2\theta - 1 = 0$. MAS averages chemical shift to its isotropic value, heteronuclear dipolar interactions to zero and reduces the quadrupolar interaction of nucei with spin $> \frac{1}{2}$ with the electric field gradients. The technique enables high-resolution NMR spectra of many solids to be readily obtained.

^{29}Si MAS NMR spectra of aluminosilicates are normally composed of up to five Si(nAl) signals where n, which can be 0,1,2,3 and 4, is the number of Al atoms tetrahedrally linked (*via* bridging O atoms) to the central Si atom. The ^{29}Si MAS NMR spectrum of pink ultramarine given in Fig. 3(a) contains five signals at $-87·8$ (shoulder), $-92·5$, $-97·6$, $-103·4$ and $-108·2$ (shoulder) p.p.m. from tetramethylsilane (TMS). The chemical shift of the lowest field signal is close to that of

the single Si(4Al) signal (−86·5 p.p.m.) in synthetic sodalite (Klinowski, Carr, Tarling & Barnes, 1987) which supports our assignment. However, the spectrum of the strongly paramagnetic standard blue ultramarine (Fig. 3c) is much less well resolved: there is a broad line centred at ca −100 p.p.m. with some indication of fine structure. This is clearly a case of paramagnetic broadening: by applying 260 Hz line broadening to the spectrum of pink ultramarine we obtain the spectrum given in Fig. 3(b) which then becomes virtually identical to that for blue ultramarine (Fig. 3c) but lies ca 5 p.p.m. to low field. It is clear that the Si,Al distribution in both samples is the same even though the resolution of the spectrum for pink ultramarine is much higher. A computer deconvolution of this spectrum using Gaussian line shapes is shown in Fig. 4. This gives the intensities of the individual Si(nAl) lines as:

$$Si(4Al) : Si(3Al) : Si(2Al) : Si(1Al) : Si(0Al)$$
$$7·3 \quad : \quad 28·6 \quad : \quad 30·2 \quad : \quad 20·1 \quad : \quad 13·8.$$

It is of interest to consider the implication of this result in relation to the Si,Al distribution in the ultramarine frameworks. If Loewenstein's (1953) rule, which forbids the presence of Al—O—Al linkages, is observed the probability of occurrence of an Si—O—Al linkage is $p = 1/R$ where R is the Si/Al ratio. For the ideal composition of ultramarine, $R = p = 1$ and this means that all bonds in the framework are Si—O—Al bonds, i.e. only Si(4Al) units can be present and so the ^{29}Si spectrum will contain only one signal. For R slightly greater than unity, some Si(3Al) and an even smaller number of Si(2Al) units will be present. But the presence of five Si(nAl) signals in the intensity ratio corresponding to Fig. 4(b) must indicate that the Loewenstein rule is disobeyed. If the rule does not hold, $p = 1/(R+1)$ and the probabilities of the five possible (nAl) configurations are thus given by the binomial formula as p^4 for Si(4Al), $4(1-p)p^3$ for Si(3Al), $6(1-p)^2p^2$ for Si(2Al), $4(1-p)^3p$ for Si(1Al) and $(1-p)^4$ for Si(0Al). For 'ideal' ultramarine with $R = 1$ and $p = \frac{1}{2}$, the expected populations of the five structural units are in the ratio of 6·25:25:37·5:25:6·25. In our samples $R = 1·11$ and the calculated populations are 5·0:22·4:37·3:27·6:7·7 which is in good agreement with the results of deconvolution shown in Fig. 4 and summarized in Table 3. We conclude that ^{29}Si MAS NMR results indicate random distribution of Si and Al atoms in the ultramarine frameworks. This is in striking agreement with the results of Rietveld refinement described earlier.
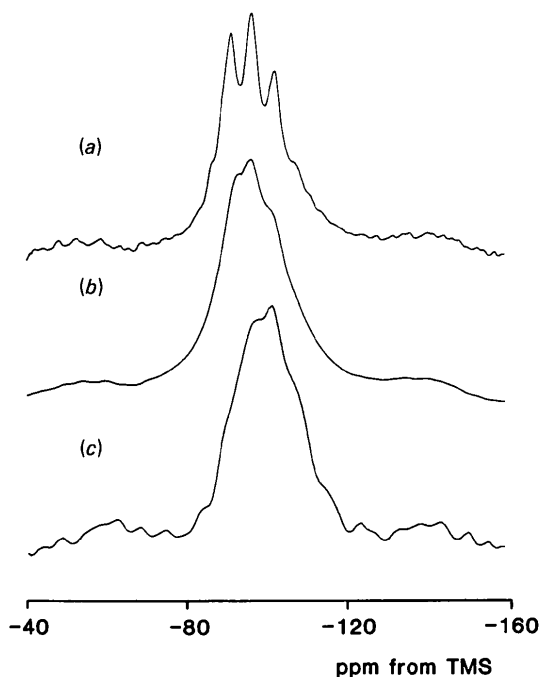

Fig. 3. ^{29}Si MAS NMR spectra of ultramarines: (a) pink ultramarine with no line broadening; (b) spectrum in (a) with 260 Hz line broadening; (c) standard blue ultramarine with no line broadening. The spectra were obtained at 79·5 MHz using 45° resonant pulses with 15 s recycle delay. Samples were spun in air at 4 kHz. Reproduced by permission of Nature (Klinowski et al., 1987).
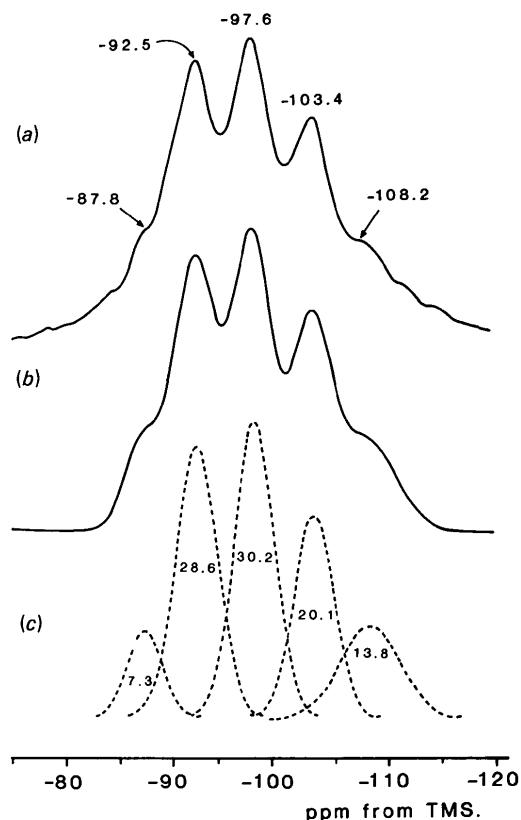

Fig. 4. The ^{29}Si MAS NMR spectrum of pink ultramarine: the original spectrum, (a), as given in Fig. 3(a), can be simulated, (b), using five Gaussian peaks, (c), with intensity ratios of 7·3:28·6:30·2:20·1:13·8. Reproduced by permission of Nature (Klinowski et al., 1987).

Table 3. *Experimental and calculated intensities (normalized to a total of* 100) *of the* Si(nAl) *signals in* ^{29}Si *MAS NMR spectra of pink ultramarine*

(a) Assuming a perfectly random Si,Al distribution.
(b) Assuming a random distribution of Si and Al, but in which Al—O—Al bonds are forbidden.

| Building block | Experimental intensity | Calculated intensity for $R = 1 \cdot 11$ | |
		(a) Non-Loewenstein	(b) Loewenstein
Si(4Al)	7·3	5·0	65·9
Si(3Al)	28·6	22·4	29·0
Si(2Al)	30·2	37·3	4·8
Si(1Al)	20·1	27·6	0·3
Si(0Al)	13·8	7·7	—

Al—O—Al bonds are not excluded on theoretical grounds (Barrer & Klinowski, 1977) and are indeed found in the entire family of silicon-free sodalites with frameworks composed exclusively of AlO$_5^{4-}$ tetrahedra (Saalfeld & Depmeier, 1972; Depmeier, 1979; Kondo, 1965). These, like the ultramarines, are prepared pyrolytically. Hydrothermally synthesized aluminosilicates, notably zeolites, are invariably Loewen-steinian. Indeed, it has been claimed that Al—O—Al linkages are forbidden even in aluminosilicate anions in solution (Muller, Hoebbel & Gessner, 1981).

^{27}Al MAS NMR spectra of two ultramarines are given in Fig. 5. Both consist of a single signal typical of tetrahedrally coordinated Al. The linewidth of the spectrum of pink ultramarine (840 Hz) is considerably smaller than that of the standard strongly paramagnetic blue ultramarine (1800 Hz). However, the linewidth of the spectrum of pink ultramarine is still greater than that of synthetic aluminosilicate sodalite (480 Hz) with identical framework topology (Klinowski *et al.*, 1987). This is partly due to the residual paramagnetism in pink ultramarine and partly to the disordered environment of Al in synthetic ultramarines. In all hydrothermally prepared zeolites, including sodalite, *all* tetrahedral Al atoms are in an identical Al(4Si) environment. However, in synthetic ultramarine all five Al(nSi) environments are present ($n = 0,1,2,3,4$).
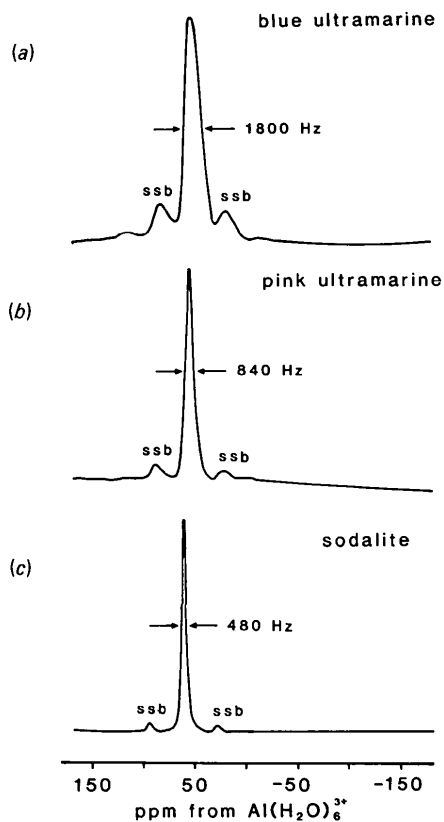
Fig. 5. ^{27}Al MAS NMR spectra obtained at 104·26 MHz: (a) standard blue ultramarine; (b) pink ultramarine; (c) synthetic sodalite.

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Microstructure of Chain Silicates Investigated by HRTEM

BY M. A. GRIBELYUK AND N. D. ZAKHAROV

Institute of Crystallography, Academy of Sciences of the USSR, Leninski prospekt 59, 117333 Moscow, USSR

R. HILLEBRAND

Institute of Solid State Physics and Electron Microscopy, Academy of Sciences of the GDR, Weinberg 2, 4010 Halle (Saale), German Democratic Republic

AND T. A. MAKAROVA

Institute of Silicate Chemistry, Academy of Sciences of the USSR, Makarova 2, 199034 Leningrad, USSR

Abstract

A number of sodium chain silicates have been studied by high-resolution transmission electron microscopy, where the second cation, cobalt, has been partially or fully substituted by nickel. Optimum conditions for electron microscope observation of (100) and (101) structure projections as well as of chain-width disorder regions were determined on the basis of computer simulation. The vacancies in the octahedral sites were detected in all samples and their types determined. It has been shown that tetrahedral sites may be occupied in the structure, the cation valence changing correspondingly. Several kinds of ordering of these interstitials were observed in a sample with cobalt partially substituted by nickel. Inclusions of sheet silicates of talc type as well as formation of a 3×1 cation vacancy superlattice in a sheet silicate structure were found in Ni-containing samples.

1. Introduction

Wide-chain pyriboles cover all members of a homologous series with the general stoichiometric formula $M_{n-1}P$. Here M and P indicate mica- and pyroxene-type slabs, having structure formulae $AM_3T_4O_{10}(OH)_2$ and $M_4T_4O_{12}$, where $A = A$ site, $T =$ tetrahedral sites, M = octahedral sites, $n =$ the width of the chain. The progress in their structure determination, particularly