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Accuracy in structure analysis of layer silicates. By A. MCL. MATHIESON,* E. W. RADOSLOVICH† and G. F. WALKER*, *Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia.*

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In several of the analyses of layer silicates reported during recent years, it is claimed that small departures from the high symmetry of the 'ideal' structures have been demonstrated. In addition to displacements of atoms, variations in the filling of, or substitution in, tetrahedral and octahedral sites have been inferred.

In order to justify these claims, diffraction data which are sufficiently accurate and extensive both in angular

(θ) and amplitude (F) range are an essential prerequisite, for minor details of the final stage of the refinement can hardly be considered significant unless the number of structure amplitudes measured is considerably in excess of the number of parameters deduced.* Extensive overlap

* Because it is implicit in the Fourier technique of structure refinement using data of the normal measured accuracy e.g. by eye-estimation, this condition should be self-evident; however, its significance appears to be frequently overlooked or under-estimated.

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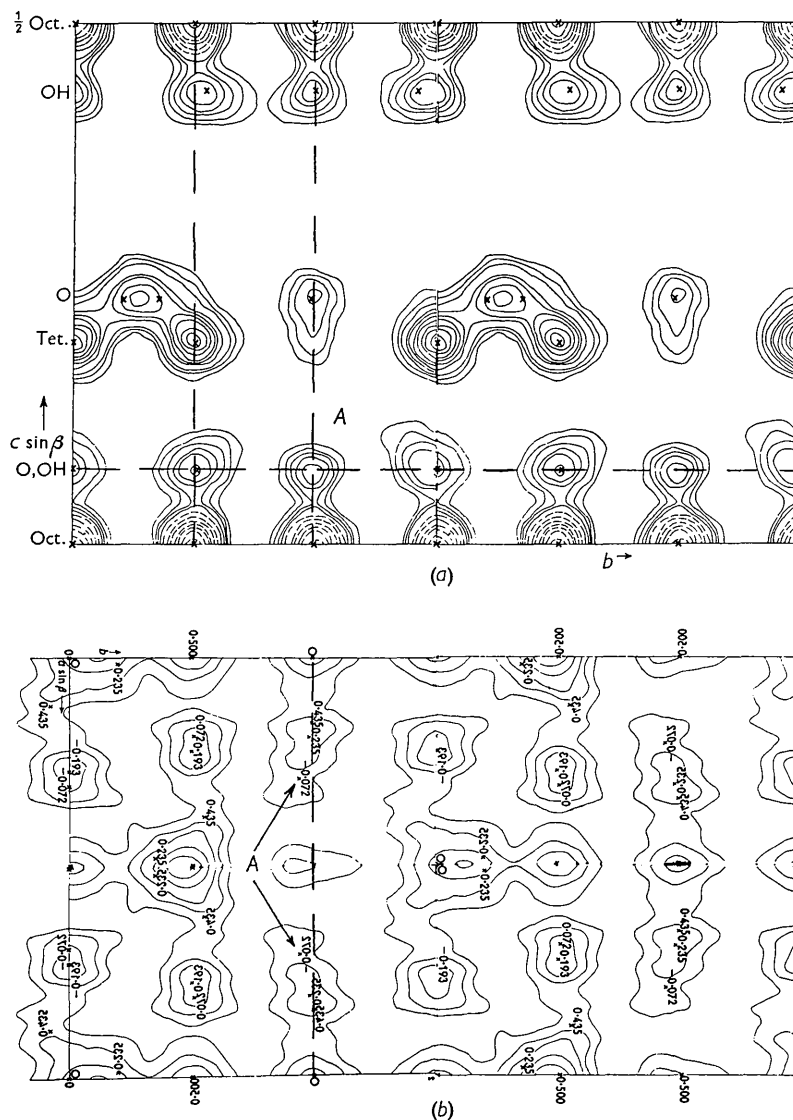


Fig. 1. (a) An extended reproduction of the $(0kl)$ projection of Steinfink's paper with dashed lines superimposed at $y = \frac{1}{8}, \frac{1}{4}$ and $z = 0.072$. A refers to atom OH_1 . (b) An extended reproduction of the $(hk0)$ projection of Steinfink's paper, adjusted so that the b axis is on the same scale as Fig. 1(a).

of atoms in the two-dimensional projections generally used and the high symmetry of the 'ideal' structures require that deviations from special positions be supported by unambiguous evidence. The methods currently employed for assessing the accuracy of the electron-density distributions, atomic parameters and the significance of differences in bond lengths at each stage of the refinement (Lipson & Cochran, 1953; Jeffrey & Cruickshank, 1953) are hence of particular importance in the analysis of layer silicates. Where no recourse to these criteria has been made, plausible but unwarranted structural features have been proposed.

As an obvious example of the effects of inadequate data, the recent analysis of a chlorite by Steinfink (1958) may be cited. In this analysis, 51 positional parameters, as well as hidden parameters involved in loading the atomic scattering curves, are claimed to have been derived from 28 $hk0$ and 50 $0kl$ structure amplitudes, with an accuracy, implied by the later discussion, of considerably better than ± 0.05 Å, although no actual limits are quoted. The suspect nature of the atomic parameters and inter-atomic distances derived from these data is immediately apparent from a comparison of the tabulated atomic parameters (Table 2 of the paper) with the contoured electron-density maps (Figs. 1 and 2 of the paper). In our Fig. 1, we have placed in juxtaposition extended reproductions of Steinfink's $(0kl)$ and $(hk0)$ electron-density projections. Inspection reveals the following, more obvious, points of criticism:

(i) The displacement of atoms OH_2 and OH_4 (Fig. 1(a)) from 'ideal' positions is justified by Steinfink on the basis of the asymmetry of their peak distributions. Atom O_2 , however, which shows equally marked asymmetry of distribution, is assigned an 'ideal' position.

(ii) No account is taken of the ridge extending from O_3 in the z -direction, while a displacement of the y -parameter of this atom is held to be significant. The latter displacement involves a shift of $\Delta y = 0.333 - 0.328 = 0.046$ Å.

(iii) The selected y parameter of atom OH_1 , as indicated in the $(hk0)$ projection at A (Fig. 1(b)) is clearly inconsistent with the observed peak distribution in the more reliable $(0kl)$ projection* (Fig. 1(a)). In this connection, it should be pointed out that the projection corresponding to the $(hk0)$ contour map is inherently extremely complex due to overlap. With typical peak heights of individual octahedral, tetrahedral and oxygen sites of the order of 46, 50 and 20 e.Å⁻² respectively (derived from Mathieson, 1958), it is evident that this projection is so crowded by the heavier scattering units that exact deductions regarding oxygen positions cannot be expected from 28 structure amplitudes.

These considerations lead us to the conclusion that the probable errors in this analysis are much greater than would be required to substantiate a real deviation from the 'ideal' structure and hence, to support the subsequent detailed argument put forward by Steinfink.

In view of the increasing interest presently being shown in the analysis of layer silicates, we are of the opinion that a general plea for caution in the interpretation of minor details in such analyses is called for, more particularly in the interests of those not fully conversant with the methods of structure analysis and hence unable to judge the strength of the evidence presented.

References

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* Although neither projection is based on adequate data, y parameters derived from the $(0kl)$ projection with 50 terms will be more trustworthy than those from the $(hk0)$ projection with 28 terms.

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Anhydrous bis-salicylaldehydato-nickel. By F. K. C. LYLE, B. MOROSIN and E. C. LINGAFELTER, *Department of Chemistry, University of Washington, Seattle 5, Washington, U.S.A.*

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We have previously reported the isomorphism of anhydrous bis-salicylaldehydato-nickel and -zinc as possible evidence for a tetrahedral configuration for 4-coordinated nickel (II) (Curtiss, Lyle, Lingafelter, 1952). Because of the considerable likelihood of the existence of a 'polymerized' octahedral coordination, it would be desirable to have a complete determination of the crystal structure. We have succeeded in obtaining a few very small single crystals of the nickel compound and report at this time the cell dimensions and space group.

Crystals were obtained by two different techniques. The first batch was prepared by the slow evaporation at about 60 °C. of a saturated solution of nickel stearate in benzene to which stearic acid and salicylaldehyde had been added. The second batch was prepared by the slow

evaporation of a chloroform solution formed by refluxing a mixture of dry chloroform and bis-salicylaldehydato-nickel. Neither batch was large enough to allow chemical analyses to be made. However, powder patterns of both batches are identical with that from a dehydrated sample of bis-salicylaldehydato-nickel (Curtiss, Lyle & Lingafelter, 1952).

The crystals are monoclinic, with 12 molecules in a cell of dimensions:

$$a_0 = 15.34, b_0 = 12.46, c_0 = 19.44 \text{ \AA}; \beta = 97^\circ 8'.$$

Density, observed 1.61 g.cm.⁻³; calculated 1.63 g.cm.⁻³.

The data were collected from rotation and equi-inclination Weissenberg photographs, using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å).