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STRUCTURAL VARIATIONS IN IDOCRASE

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ABSTRACT

Idocrase from several localities crystallizes with space groups not previously reported for this mineral. Violations of glide-plane extinction criteria in the commonly-found space group, *P*4/*nnc*, appear on single-crystal photographs, but are not observable on high-resolution Guinier-type powder photographs. Cell dimensions of the various modifications are all similar. Structural differences indicated by these symmetry variations are not controlled by gross changes in chemical composition.

Single-crystal X-ray photographs of idocrase from various localities reveal that this mineral crystallizes in any of several tetragonal space groups rather than only in the one previously known. Attempts to refine the crystal structure, based on diffractometer data, indicate that the previously-established structure model is at least partially incorrect.

The structure of idocrase (vesuvianite) was originally determined by Warren and Modell (1931), using only 41 ionization spectrometer measurements on a crystal from the Wilui River, U.S.S.R. ("wiluite"). The space group was determined with crystals from Sanford, Maine, and Franklin, New Jersey. Both crystals showed diffraction effects of *P*4/*nnc*, and it was assumed that the "wiluite" also possessed this space group. The authors calculated that one unit cell of idocrase contains 4 formula units, with an "ideal" composition: $Ca_{10}(Fe,Mg)_2Al_4Si_9O_{34}(OH)_4$.

Warren and Modell (1931) proposed a structural model based largely on the close similarity, in both cell dimensions and chemical composition, between idocrase and grossular garnet. They obtained fairly good agreement between observed and calculated structure factors by postulating the presence of garnet-like columns within the idocrase cell, parallel to the *c*-axis. In all subsequent literature, *P*4/*nnc* is the only space group reported for idocrase, and a reexamination of the Sanford material has confirmed the original determination.

Idocrase crystals from a number of localities, however, exhibit space groups previously unrecognized for the mineral. Precession photographs along the *a*, *c*, and [110] axes reveal violation of one or more of the glide-plane extinction criteria in *P*4/*nnc*, leading to the assignment of several other space groups. Although the single-crystal photographs clearly show the additional spots, powder photographs of the various samples appear

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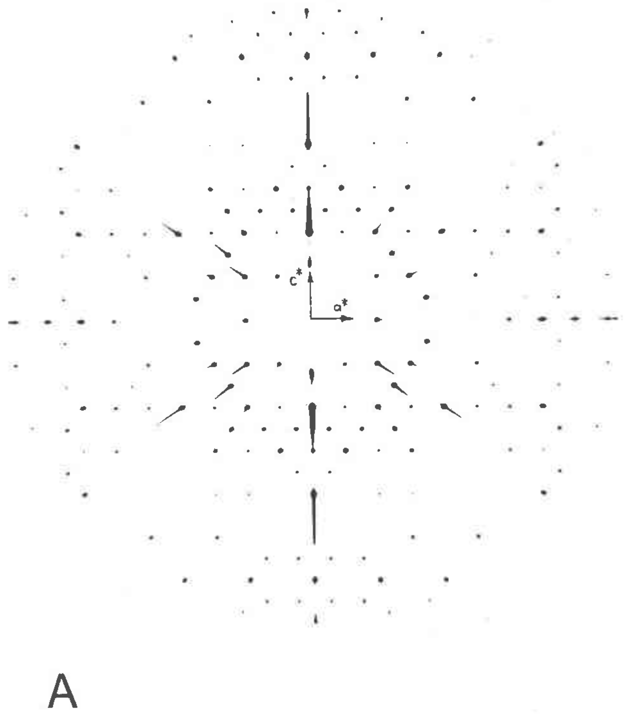
identical. No additional lines could be detected, even using a high-resolution Guinier camera. This is due to the coincidence of strong lines with some of the violation-reflections (resulting merely in line-broadening), and to the low intensity of the latter. Figure 1A shows an *a*-axis precession photograph of idocrase from Sanford, Maine, with space group *P*4/*nnc*. An *n*-glide plane is present in this orientation. Fig. 1B shows the equivalent photograph of a crystal from Asbestos, Quebec, in which many violations of the glide-plane extinction criteria can be seen.

The first new space group to be noted was *P*4/*nmm*. However, a sensitive piezoelectric test showed one specimen, from Asbestos, Quebec, to be non-centrosymmetric, hence precluding *P*4/*nmm* as the correct space group. Very long exposures, some more than 120 hours, revealed the presence of weak violations of the *n*-glide perpendicular to the *c*-axis. This produces the diffraction symbol 4/*mmmP*-/---, which allows the following space groups as possibilities; $P\bar{4}2m$, $P\bar{4}m2$, *P*4*mm*, *P*42 and *P*4/*mmm*. The piezoelectricity eliminates only *P*4/*mmm*. Idocrase from Hindubagh, Pakistan, also shows violations of the *n*-glide perpendicular to *c*, but without a test for centricity all 5 space groups remain possibilities.

Table 1 summarizes space group determinations made on idocrase from several localities. The precession photographs used in these determinations were taken with Zr-filtered Mo radiation. Spots violating glide-plane extinction restrictions are not due to double diffraction, since many of the more intense violations show white radiation streaks; unfiltered photographs show this effect more clearly. Furthermore, the additional spots appear on Weissenberg photographs, taken with Ni-filtered Cu radiation.

No correlation has been observed between space group and crystal coloration. All the idocrase from Asbestos, Quebec, for example, display diffraction symbol 4/*mmmP*-/---, although crystal color ranges from pale apple-green to deep emerald-green, colorless, brown and lilac.

To determine unit-cell dimensions of idocrase crystals exhibiting different space groups, precision back-reflection Weissenberg photographs were taken. Samples from Asbestos, Quebec, and Sanford, Maine, each provided approximately 100 independent reflections on photographs taken with Ni-filtered Cu radiation, utilizing both $K\alpha_1$ and $K\alpha_2$ spots. The data were refined using a least-squares program that corrects for specimen absorption, film shrinkage, and camera eccentricity (Burnham, 1962). Convergence occurred, after 2 cycles, to the values summarized in Table 2. The internal precision, approximately one part in 100,000, obtained in the Sanford refinement is extremely high for this type of mathematical analysis. It should be emphasized that the quoted errors



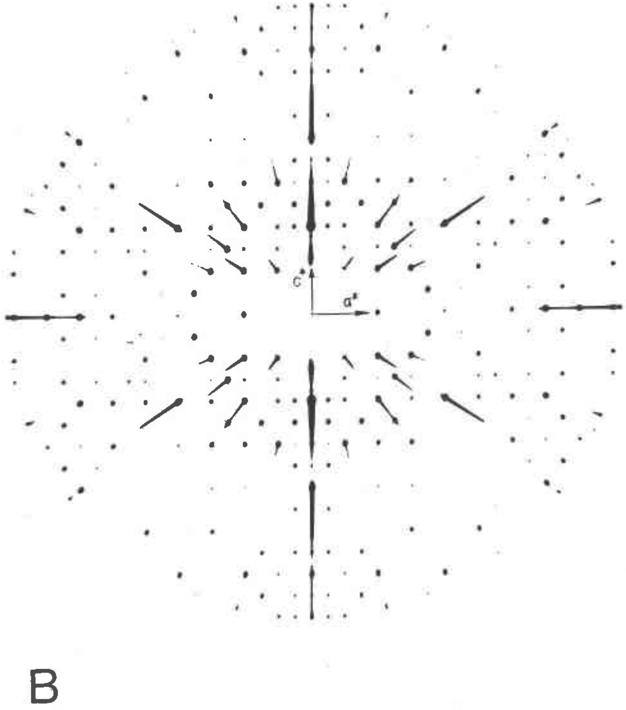


FIG. 1A. *a*-axis zero-level precession photograph of idocrase from Sanford, Maine. Reflections are absent in accordance with the restrictions of an *n*-glide plane. Exposure time: 50 hours; $\mu=25°$.

FIG. 1B. *a*-axis zero-level precession photograph of idocrase from Asbestos, Quebec. Many violations of the *n*-glide restrictions are evident. Exposure time: 57 hours; $\mu=25°$.

TABLE 1. IDOCRASE: SPACE GROUPS DETERMINED FOR CRYSTALS FROM VARIOUS LOCALITIES[a]

*P*4/*nnc*	*P*4/*nmm*—"strong"[b]
Sanford, Maine	Black Lake, Quebec
Ural Mtns., USSR	Coleraine, Quebec
Crestmore, Calif.	Eden Mills, Vermont
Franklin, N.J. (Be-rich)	Laurel, Quebec
Wilui R., USSR	
Antamina, Peru	
Lake Jaco, Mexico	
4/*mmm*P-/---	*P*4/*nmm*—"weak"[c]
Hindubagh, Pakistan	Franklin, N.J. (Cu-rich)
San Benito County, Calif. (Ce-rich)	Telemark, Ny. (Cu-rich)
Asbestos, Quebec (*P*4/*mmm* eliminated)	Monte Somma, Vesuvius, Italy

[a] Diffraction symbol is listed if space group is ambiguous.

[b] "strong"—many intense violations of glide planes observed.

[c] "weak"—few weak violations of glide planes observed.

relate only to the internal consistency of the least-squares system, and are not measurements of accuracy.

To assess the validity of Warren and Modell's structure model, 3-dimensional intensity data were obtained from crystals from Asbestos, Quebec, and Sanford, Maine. A Picker automated 4-circle diffractometer, utilizing Nb-filtered Mo radiation, provided intensity measurements, which were corrected for absorption using numerical integration techniques (Burnham, 1966). Data from the Quebec idocrase were refined in space group *P*4/*nnc* by excluding the observed reflections which violate glide-plane restrictions in this space group. The reliability index, *R*, was 22 percent after 4 least-squares cycles. Data from the Sanford material refined to an *R* value of 25 percent.

TABLE 2. LEAST-SQUARES REFINEMENTS OF UNIT-CELL PARAMETERS OF IDOCRASE FROM ASBESTOS, QUEBEC, AND SANFORD, MAINE[a]

Specimen	Asbestos, Quebec	Sanford, Maine
No. of observations	109	91
a	15.5232(4)	15.5333(2)
c	11.8167(4)	11.7778(2)
Cell volume (Å^3)	2847.44(19)	2841.81(8)

[a] Parameters are given in Ångstrom units. Standard errors are in parentheses.
CuKα_1 = 1.54051 CuKα_2 = 1.54433

These *R* values indicate that the model is only partially correct. Unfortunately, three-dimensional difference-Fourier syntheses did not clearly indicate errors in the model, probably because, at this level of refinement, a substantial number of structure-factor signs are incorrect. Examination of interatomic distances reveals major discrepancies, such as a distance of 2.8 Å between two Ca atoms. We are now in the process of determining a correct model for *P*4/*nnc* idocrase, as well as a structural scheme for the other modifications.

Recent synthesis data (J. Arem and J. Ito, in progress) suggest that the idocrase stability field is restricted in size primarily by composition. Coupled substitutions involve Mg, Si and Al; and the chemical formula cannot be firmly established until structural studies are completed. We anticipate that the results of these studies will shed some light on the factors influencing the formation of idocrase in various geological settings and on the crystal-chemical idiosyncrasies of large-cation silicates.

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