

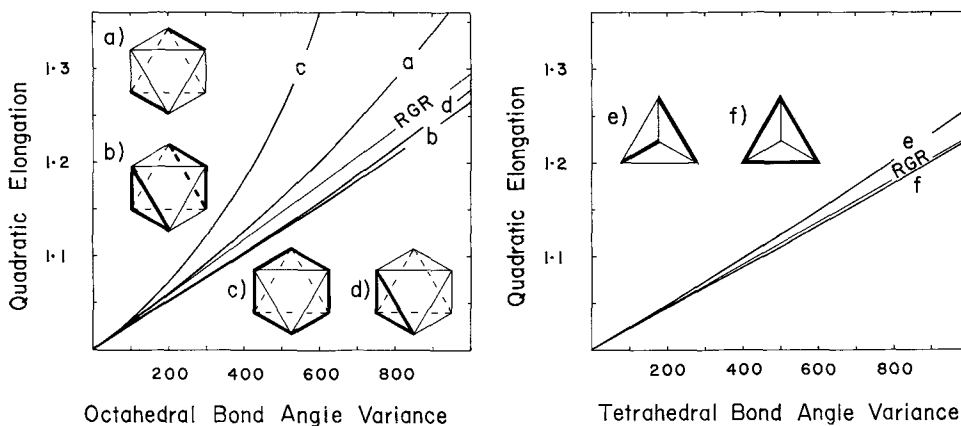
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Distortion parameters for coordination polyhedra

ROBINSON, Gibbs, and Ribbe (1971) have introduced the parameters bond angle variance (σ^2) and mean quadratic elongation (λ) as measurements of distortion in coordination polyhedra. For a coordination octahedron

$$\sigma_{\text{oct}}^2 = \frac{1}{11} \sum_{i=1}^{12} (\theta_i - 90^\circ)^2 \quad \text{and} \quad \lambda_{\text{oct}} = \frac{1}{6} \sum_{i=1}^6 (l_i/l_0)^2,$$

where θ_i are the bond angles, l_i are the bond lengths and l_0 is the bond length for the ideal, undistorted octahedron equal in volume to the one in question; the expressions



FIGS. 1 and 2: FIG. 1 (left). Calculated mean quadratic elongation (λ)–bond angle variance (σ^2) distributions for four ideal types of distortion in coordination octahedra arising from the progressive shortening of the octahedral edges emphasized in insets a, b, c, and d; RGR, trend line for observed data (Robinson *et al.*, 1971). FIG. 2 (right). Calculated mean quadratic elongation (λ)–bond angle variance (σ^2) distributions for two ideal types of distortion in coordination tetrahedra.

for a coordination tetrahedron are analogous. They have shown that there is a remarkably strong linear correlation between λ_{oct} and σ_{oct}^2 for five rock-forming mineral groups and that a similar but less marked correlation exists between λ_{tet} and σ_{tet}^2 for a wide variety of minerals and compounds. An explanation for the proposed linear dependence of λ on σ^2 was not given.

Robinson *et al.* suggest that λ is independent of polyhedron size. However, λ should tend exponentially to infinity as the polyhedron volume (and hence l_0) decreases toward zero and for invariant, equal bond distances there will exist a separate λ vs. σ^2 relation for each point symmetry. Thus, in general, there cannot be a single linear

relation between λ and σ^2 for each polyhedron type. This is demonstrated in figs. 1 and 2 in which several ideal types of octahedral and tetrahedral distortion have been documented for reference purposes. The distortion types arise from the progressive shortening of the various polyhedral edges emphasized in figs. 1, inset, a, b, c, and d, and 2, inset e and f, and approximately correspond, respectively, to the distortion association with shared edges in (a) M site octahedron in the rutile structure, (b) $M(1)$ site octahedron in the olivine structure, (c) $M(1)$ and $M(3)$ site octahedra in the amphibole structure (Fleet, 1974), (d) $M(2)$ site octahedron in the olivine structure, (e) T site tetrahedron in the garnet structure, and (f) T site tetrahedron in the olivine structure. Distortion type c also corresponds, very approximately, to the distortion of the $M(2)$ site octahedron in the amphibole structure and the $M(1)$ site octahedron in the pyroxene structure.

For the two tetrahedral distortion types investigated (fig. 2) there is actually a close correspondence of the λ_{tet} vs. σ_{tet}^2 distributions with the trend line for the observed data (Robinson *et al.*, 1971, fig. 1B) in the range of distortion expected for most minerals (0 to 100 σ_{tet}^2). However, the λ_{oct} vs. σ_{oct}^2 distributions vary quite markedly from each other, even within the range of distortion expected for most minerals (0 to 250 σ_{oct}^2). The greatest variation is between the stretched distortion types (b and d) and the compressed distortion type (c) since the latter causes a more abrupt decrease in octahedral volume. In fact, this is reflected in the observed data of Robinson *et al.* (1971, fig. 1A), in that the amphibole and pyroxene plots do tend to fall above the trend line. It appears that the linear correlation obtained with the natural data is the result of compensating factors, for example, the increase in λ_{oct} through bond length variation,

and the rather restricted number of mineral groups investigated. Clearly λ is not a simple function of σ^2 .

Bond angle and bond length distortions in coordination polyhedra are not necessarily correlated and their crystal chemical significances may be quite separate. Hence, in discussing polyhedral distortions the use of σ^2 alone and of combined distortion parameters (for example, λ) should be discouraged. When an independent measure of bond length distortion, for example, mean-square relative deviation from average bond length, $\Delta_{oct} = \frac{1}{6} \sum_{i=1}^6 [(l_i - \bar{l})/\bar{l}]^2$,

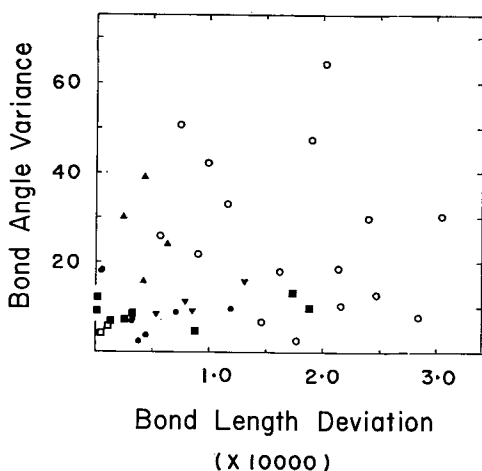


FIG. 3. Comparison of bond angle variance (σ^2) and mean-square relative deviation from average bond length (Δ) for T site tetrahedra in various feldspars. ■ K-feldspar; □ Rb-feldspar; ● Low- and high-albite; ○ Anorthite; ▲ Celsian; ▼ Reedmergnerite.

where \bar{l} is the mean bond length (Brown and Shannon, 1973) is used in conjunction with a bond angle distortion parameter more information is obtained and, if necessary, the correlation of bond

angle and bond length distortions may be tested by established statistical procedures. Two examples are given below:

For $M(1)$ and $M(2)$ site coordination octahedra in $\alpha\text{-Co}_2\text{SiO}_4$ (olivine structure type), σ^2 (Morimoto, Tokonami, Watanabe, and Koto, 1974) is 114.5 and 97.7 respectively, and Δ is 0.000277 and 0.001076 respectively. Thus, the $M(1)$ site has a slightly greater bond angle distortion but a markedly less bond length distortion.

Δ parameters for a variety of T site tetrahedra in feldspars have been calculated from the data organized by Smith (1974, Table 4-2) and are compared in fig. 3 with σ^2 parameters calculated from Smith's data (Table 4-5). Using all of the data as one population, Δ is essentially independent of σ^2 . However, distinct and characteristic fields are evident for many of the minerals and mineral groups recognized, for example, for celsian and anorthite. Thus, although the Δ values are numerically small compared to data for polyhedra showing pronounced bond length variations, as in Jahn-Teller distorted CuII salts, they are nevertheless quite significant.

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An occurrence of vesigniéite in Leicestershire

IN 1968 an inclined road was driven on the north-eastern face of Newhurst Quarry, near Shepshed (SK 488179), to provide access to new lower working levels.

Towards the top of this incline a number of hypogene copper-rich quartz-carbonate veins were cut. These veins, confined to one of three large north-westerly-trending shear zones, connected with late movements in the so-called Long Cliff Reversed Fault System (Watts, 1947), were here seen cutting intrusive granophyric diorite