

Nevada. [Again we emphasize an earlier conclusion (5): Peralkaline silicic rocks—until recently often considered to be little more than petrologic curiosities—are not uncommon in the western United States.] Other chemically unusual, and presumably highly differentiated, late-Tertiary silicic rocks, such as the Sr-poor rhyolites of Glass Mountain in Mono County, California (12), the F-rich and Be-rich rhyolites of western Utah (13) and southwestern Idaho (14), and the Sn-rich and topaz- and fluorite-bearing rhyolites of northernmost Lander County, Nevada (15), also appear to be restricted to or more prevalent in the marginal parts of the Great Basin area. Silicic volcanic rocks in the center of the Great Basin, on the other hand, appear to be almost exclusively relatively primitive quartz latites rich in strontium and potash.

Silicic volcanic rocks younger than about 20 million years are abundant only toward the margins of the Great Basin, being absent or rare toward the center (16). The significance of this annular distribution pattern is not fully understood, but it may be genetically related to the apparent restriction to the margins of the Great Basin area of peralkaline and other chemically unusual types of silicic rock.

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- Lacroix [*Acad. Sci. Paris Compt. Rend.* **185**, 1410 (1927); *Mem. Acad. Sci. Paris* **61**, 169 (1934)], recognizing the continuity of the comendite-pantellerite series, proposed that rocks containing more than 12.5 percent of total normative feric constituents be termed pantellerite; those with less than 12.5 percent, comendite. Of 55 silica-rich, nonhydrated peralkaline glasses so classified by Noble, all the comendites have less than 4.0 percent by weight of total iron (as FeO) plus MnO, whereas all the pantellerites but one contain more than 4.0 percent by weight. Iron-plus-manganese content thus provides a simple and internally consistent method for classification of the silica-rich peralkaline rocks, one that is especially useful when the rocks have undergone various changes in oxidation and alkali content subsequent to deposition.
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Zinnwaldite: Octahedral Ordering in Lithium-Iron Micas

Abstract. Ordering of the octahedral sheet of some lithium-iron micas is proposed on the basis of chemical compositions and crystallographic properties. The model of the ordered sheet has large and small sites in the ratio 2:1 and explains all observed properties—the small layer thickness, the “dioctahedral reflections,” and the $n(120\text{ deg})$ motif in polytypism.

Zinnwaldites are lithium-iron micas on the siderophyllite $[\text{K}_2\text{Fe}_4^{2+}\text{Al}_2\text{Al}_4\text{Si}_4\text{O}_{20}(\text{F},\text{OH})_4]$ -polyolithionite $[\text{K}_2\text{Li}_4\text{Al}_2\text{Si}_8\text{O}_{20}(\text{F},\text{OH})_4]$ join. They are the characteristic micas of greisens (hydrothermally altered granitic rocks) and the veins associated with them. During geochemical study of these micas I measured the lattice parameters of several chemically analyzed specimens. The data suggest that the octahedral sheet of zinnwaldites differs from those of muscovite, annite, and phlogopite (1, 2) and resembles that of xanthophyllite (3).

Crystallographic parameters of micas have previously been related to composition. Mikheev (4) obtained a roughly linear plot of d_{060} (5) against the “average size of octahedral cations”; regression analysis by Radoslovich and Norrish (6) gave good linear correlation between b and octahedral composition. On the other hand, Munoz (7) found that b varied continuously with respect to composition, but distinct gaps appeared in plots of a and c for the system muscovite-polyolithionite-trilithionite. Polytypism also appears to be a function of composition (8); lepidolites close to trilithionite crystallize usually as $2M_2$; muscovites, mostly as $2M_1$. The $1M$ polytype is found commonly in the “trioctahedral” micas but rarely in muscovites.

Additional structural differences are suggested by the presence or absence of the “dioctahedral reflections” $[0l]$ and $h0l$ where $l \neq nN$ (9); because of pseudotrigonal symmetry, the same applies to $33l$, $3\bar{3}l$, $h3hl$, and $h3\bar{h}l$. These reflections always appear in photographs of muscovite, but have not been reported for “trioctahedral” micas other than zinnwaldites (10, 11).

In this study, zinnwaldites from greisens and veins of the tin-tungsten-lithium formation in the Krušné Hory Mountains (Czechoslovakia) and the Erzgebirge (Germany) were chemically analyzed and examined with the precession camera; three pegmatite lepidolites and a skarn biotite were included.

The compositions of zinnwaldites lie close to the siderophyllite-polyolithionite join in accordance with Foster's (12) findings. Among the octahedral cations (apart from the irregular number of vacancies), there are always close to two small ions (Al^{3+} , Fe^{3+}), as was noted (12). The sum of large ions (Li^+ , Fe^{2+} , Mg^{2+} , Mn^{2+}) (13) is variable but never exceeds four. This finding is not true of the octahedral compositions of the pegmatite lepidolites [composition close to trilithionite: $\text{K}_2\text{Li}_3\text{Al}_3\text{Al}_2\text{Si}_6\text{O}_{20}(\text{F},\text{OH})_4$] and the skarn biotite [composition close to annite: $\text{K}_2\text{Fe}_6^{2+}\text{Al}_2\text{Si}_6\text{O}_{20}(\text{F},\text{OH})_4$].

Dimensions a and b of the studied micas are continuous functions of octahedral composition, but gaps appear in the d_{00N} (9) plot (Fig. 1); included in the plot are data from the literature. Values for siderophyllite (D), zinnwaldites, and polyolithionite (F) lie distinctly below those for synthetic annite (A and B), synthetic aluminous biotite (C), trilithionite (E), and synthetic Li-Fe

micas (open circles) buffered with respect to fluorine (14).

Several different polytypes were found in the zinnwaldites, but all are based on rotations of 120 deg and its multiples; all having more than one layer [including $1M_{r-n}(120)$ (15)] exhibit weak "dioctahedral reflections."

All the features described above can be explained by an ordered octahedral sheet with four large and two small cation sites per cell, as was found in xanthophyllite (3) and the brucite sheet of a Cr-chlorite (16). Sites of different sizes are produced by distortion of two-thirds of the octahedra (as, for example, in annite) into trigonal trapezohedra with pinacoid (17). For such an ordered mica we can predict the following:

1) Its octahedral layer will be notably thinner than a disordered one (the same applies to the unit layer).

2) a and b will differ only slightly if at all from those of micas with disordered octahedral sheets; this is because the increase in size of an octahedron upon flattening (18) is partly compensated by counterrotation of top and bottom anionic triads.

3) Ordering of the octahedral cations lowers the symmetry in the plane of anions, thus causing nonideality of the tetrahedral arrangement. If the model is correct, the "dioctahedral reflections" (11) must appear on patterns of these micas.

4) Its polytypes have to be based on rotations of 0, 120, and 240 deg because the symmetry in the plane of octahedral anions is $3m$ (Fig. 2c), so that trigonal arrangement of the tetrahedra is necessitated.

There is complete agreement between observations and predictions on the basis of this ordering (19).

If the layer thickness of zinnwaldite-type micas is indeed a function of octahedral ordering, heating to high temperatures may produce disorder and consequently increase thickness. Prolonged heating of a natural ordered $1M$ zinnwaldite (2 kb, 701° to 712°C, 604.5 hours; 2 kb, ~ 526°C, 957 hours; 2 kb, ~ 715°C, 62 hours) produced no significant increase in d_{001} (J, K, L in Fig. 1). However, a synthetic zinnwaldite (Fig. 1, H), grown from the fluorine-rich composition $K_2Li_2Fe_2^{2+}Al_2Al_2Si_6O_{20}F_4$ (2 kb, 682.5° to 685°C, 163 hours), plots close to the ordered micas. Synthetic micas grown in equilibrium with a buffer of low fluorine fugacity (14) show much greater layer thickness (Fig.

1, open circles); they plot close to a line joining the values for annite and trilithionite. I believe that these micas are disordered. Hence the ordering in zinnwaldites appears to be a function of fluorine content.

Trilithionite is a fluorine-rich mica, yet its properties separate it from the zinnwaldites. The analyses of trilithionite indicate more than two small octahedral cations, so that octahedral ordering is precluded. The diffraction symbol of the $1M$ trilithionite is $C^*/*$.

The space groups compatible with this symbol require that the six octahedral sites with $z = .5$ be distributed between one twofold and one fourfold position. Thus the idealized composition Li_3Al_3 must be distributed as $(Li)_2(Al, Li)_4$, $(Al)_2(Li, Al)_4$, or most likely as $(Li, Al)_2(Li, Al)_4$ with all sites equal in size. This fact suggests that the octahedral sheet of trilithionite is disordered.

If this ordering holds for the zinnwaldites (20), three arrangements in the octahedral sheet of the micas can

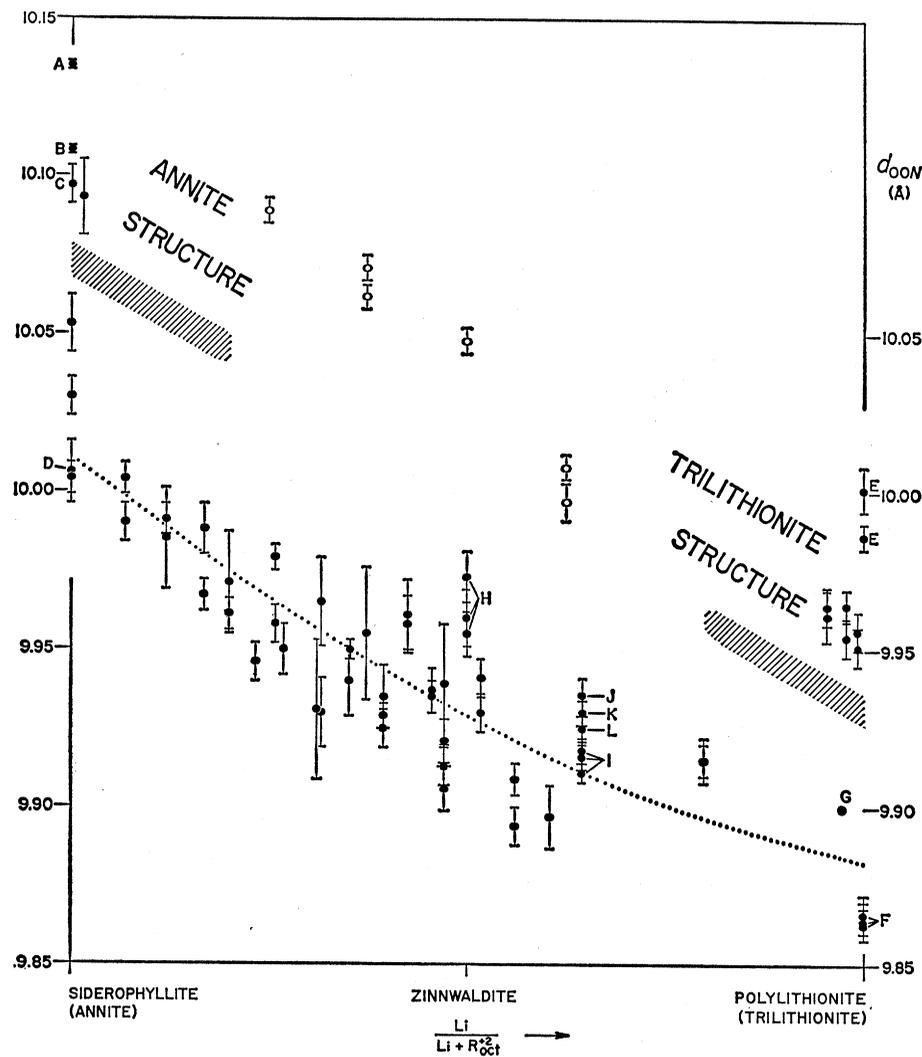


Fig. 1. A plot of d_{001} (9) versus octahedral composition (projected onto the siderophyllite-polyolithionite join) for lithium-iron micas. Tentative boundaries separating annite and trilithionite structures from the ordered micas are dashed. The dotted line is a least-squares approximation ($y = .071x^2 - .199x + 10.011$) of data for the ordered Li-Fe micas. Open circles denote refined powder data for synthetic micas, along the siderophyllite-polyolithionite join, that were grown in equilibrium with fluorine buffer (14). A, Synthetic annite buffered by the wüstite-magnetite assemblage (refined powder data) (22); B, synthetic annite buffered by the hematite-magnetite assemblage (refined powder data) (22); C, synthetic aluminous biotite, approximately $K_2Fe_{4.5}^{2+}Al_{1.5}Al_{3.5}Si_{4.5}O_{20}(OH)_4$ (refined powder data) (23); D, 3Tc [022] siderophyllite [analysis (24), single-crystal value (25)]; E, synthetic trilithionite (refined powder data) (26); F, synthetic polyolithionite (refined powder data) (26); G, "grey lepidolite," Kangerdluarsuk, Greenland [analysis (27), single-crystal data (in 7)]; H, synthetic zinnwaldite $K_2Fe_2^{2+}Li_2Al_2Al_2Si_6O_{20}F_4$; I, $1M$ natural mica, the d_{001} of which increased upon heating to values J (2 kb, 701° to 712°C for 604.5 hours), K (2 kb, ~526°C for 957 hours), and L (2 kb, ~715°C for 62 hours).

be distinguished: (i) muscovite with two small cations for each vacancy capable of accommodating a large ion (21) (Fig. 2a); (ii) xanthophyllite with two large cations for each small (Fig. 2c); and (iii) annite with all cations of the same size, or with large and small in a disordered arrangement (Fig. 2b). The xanthophyllite ordering should occur in siderophyllite, zinnwaldite,

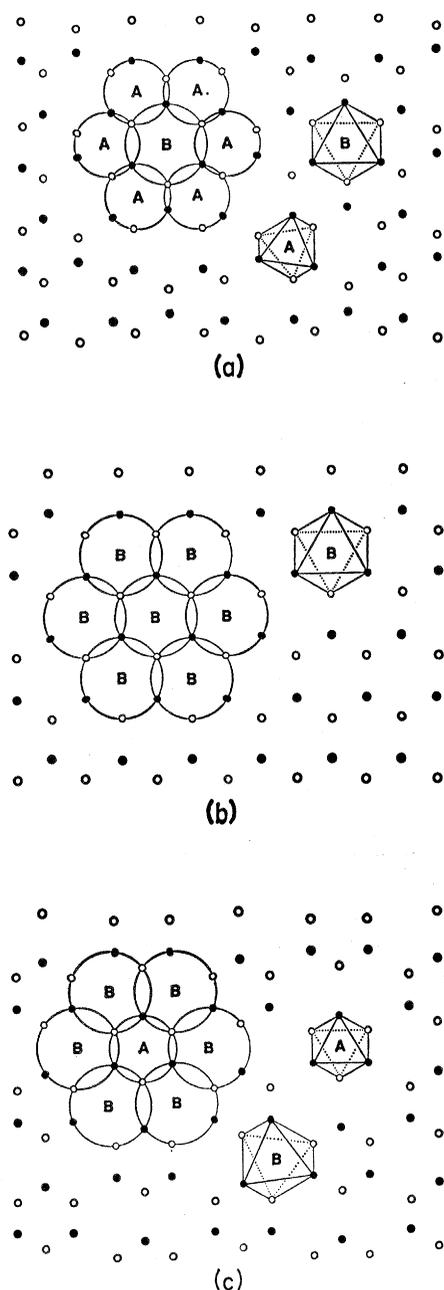


Fig. 2. Idealized octahedral anionic arrangements in the micas projected on (001) (along c^*). Octahedral cations are not shown, small (A) and large (B) sites being shown instead. The upper anion layer is shown by solid circles; open circles represent the lower layer. (a) Muscovite [modified from Veitch and Radoslovich (28)]. (b) Annite [modified from Donnay *et al.* (2)]. (c) Zinnwaldite (geometrical construction; this report).

polyolithionite, and possibly in a mica with an octahedral formula $Al_2Li_2Mg_2$. The annite arrangement applies to phlogopite, biotites, and trilithionite.

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Mode of Chemical Degradation of *s*-Triazines by Montmorillonite

Abstract. *Chemical hydrolysis of the s-triazines after interaction with less than 2-micron (equivalent spherical diameter) montmorillonite clay occurs as a result of protonation at the colloidal surface; protonation occurs even when the exchange sites are occupied by metallic cations. The adsorbed hydrolytic degradation product is not the hydroxy analog, but it is predominantly the keto form of the protonated hydroxy species. This cationic form is held tightly by the clay which may restrict vertical movement and entrance into groundwater. Protonation of the hydroxy analog occurs on the heterocyclic ring nitrogen.*

The *s*-triazines are widely used herbicides, yet their fate in soil and water has not been clearly defined. Metabolism of simazine (1, 2), atrazine (3), and ipazine (4) by soil microorganisms has been clearly shown. Recent work (2, 4) calls into question the assumption that microbial degradation is a major factor in the detoxification and loss of *s*-triazine herbicides from soil. These authors measured the evolution of CO_2 containing labeled C^{14} and concluded that very little degradation of the 2-chloro *s*-triazine derivatives occurred within a period of 4 to 16 weeks.

Chemical hydrolysis of atrazine produces hydroxyatrazine in strongly acid or basic solutions (5). The hydroxy analogs of simazine (6, 7), atrazine (8), and propazine (7) have been recovered from soils treated with the 2-chloro *s*-triazine derivatives. Thus the hydroxy analog has been proposed as the major degradation product of non-biological degradation processes. The importance of the inorganic soil constituents in nonbiological degradation has been illustrated by Harris (7), who found that formation of the hydroxy analogs of simazine, atrazine, and propazine in five soils was not inhibited by 200 parts per million (ppm) of sodium azide. Atrazine was rapidly detoxified at 95°C in soil, but only slowly detoxified in aqueous solution at the same temperature in the absence of soil.

Direct evidence is not available on whether the degradation product of the *s*-triazine herbicides exists in the adsorbed state and whether the alkyl-amino functional group significantly affects the degradation reaction. Arm-