Further discussion of framework structures built from four- and eight-membered rings

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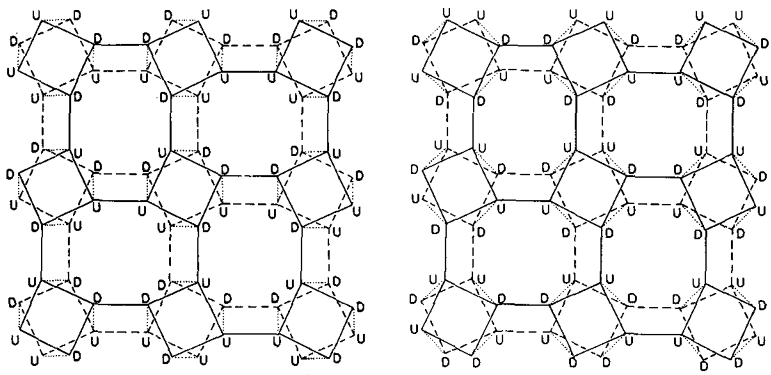
Summary. The classification of framework structures built from chains of four-membered rings of type UUDD is incomplete: there are two basic ways in which the chains can be cross-linked to form eight-membered rings. The first type of framework (already described) is extremely flexible, permitting the cavities to be either large or small; the second type is inflexible and the cavities are small. Feldspar belongs to the second type and had been incorrectly ascribed to the first type: paracelsian, harmotome, and gismondine had been correctly placed in the first group.

Smith and Rinaldi (1962), following earlier workers who had noted resemblances between the sheets of tetrahedra in frameworks of feldspar, paracelsian, and harmotome, determined the ways in which frameworks could be formed from near-parallel four- and eight-membered rings; one of the predicted frameworks was later found to occur in gismondine. Unfortunately, the analysis is incomplete, and the description of the structure of feldspar is incorrect. There are actually two types of frameworks based on double crankshaft chains built from UUDD rings (see fig. 1 of Smith and Rinaldi (1962) for explanation of symbolism); the distinction may be seen by comparing the frameworks in figs. 1*a* and *b* of the present paper. Each sheet of tetrahedra in each structure consists of alternating four- and eight-membered rings; the eight-rings are alternately of type UUUUDDDD and UUDUDDUD. The distinction lies in the linkage between the sheets: in *a*, the projections of the linkages between the four-rings are parallel to the edges of the printed page, while in *b*, the projections are approximately at 45° to the edges. An important distinction between the two frameworks is the different reaction to compression. The *a* structure can expand or contract very easily by opposite rotations of alternate UUDD rings of each crankshaft chain. The eight-rings can be circular with superposition in projection of the UUDD rings, or near-elliptical as in fig. 1*a*.

The *b* structure can expand or contract only with difficulty. Twisting of one chain is hindered by twisting of adjacent chains, unlike the movements in the *a* structure, which can be cooperative. The eight-rings in the *b* structure cannot be circular; they must be near-elliptical. The two structure types based on the same sequences of U and D tetrahedra in the eight-rings will be distinguished by the adjectives *flexible* and *inflexible*.



Flexible Analogue of Feldspar (a) Actual Structure of Feldspar (b)

FIG. 1 (*a*) Flexible analogue of feldspar; (*b*) actual structure of feldspar. Tetrahedral atoms lie at the intersections and oxygen atoms near to the centres of the lines. U represents a tetrahedron with its base nearly horizontal and its opposing vertex pointing upwards. D represents a tetrahedron with its vertex pointing downwards. The frameworks may be considered to be formed by linking together chains of four-rings or by joining layers of four- and eight-rings. The layers are distinguished by the solid and broken lines, while the links between tetrahedra of adjacent layers are shown by dotted lines. Each chain is represented by nearly-superimposed UUDD and DDUU four-rings.

The scheme given by Smith and Rinaldi is for the *flexible* type. Re-examination of the mineral structures shows that feldspar has the *inflexible* type of structure (fig. 1*b*) not the *flexible* type given in fig. 1*a* of this paper and in fig. 3 of Smith and Rinaldi. Paracelsian, harmotome, and gismondine were correctly ascribed to the *flexible* type; in paracelsian, the eight-rings are near-elliptical, while in the two zeolites the eight-rings are nearly circular to accommodate the water molecules.

Smith and Rinaldi showed that there were seventeen simple ways of linking UUDD chains in the *flexible* structure type. There are only thirteen simple ways of linking UUDD chains in the *inflexible* structure type. Unlike the *flexible* type for which alternate layers perpendicular to the chain must contain the same sequences of U and D tetrahedra (though with U and D reversed, of course, in absolute orientation), the *inflexible* type may have different patterns for the alternate layers. The sequences in feldspar, UUUUDDDD and UUDUDDUD, occur in both layers of both the *flexible* and *inflexible* types, but the UUDUDDUD sequence of the paracelsian type of *flexible* structure alternates in the *inflexible* equivalent with the UUUUDDDD sequence found in the gismondine type of *flexible* structure. Similarly the eight-rings of the harmotome and *J flexible* structures combine to give one *inflexible* structure; so do *C* and *L*, and *E* and *M*. All other *flexible* structures have a one-to-one correspondence with an *inflexible* structure. It is possible to combine *flexible* and *inflexible* pieces of structure in the same framework to give further structural patterns.

Smith and Rinaldi suggested that there may be zeolitic equivalents of feldspar and paracelsian. The equivalent of the latter could result merely from bond-angle changes of the actual *flexible* structure. Since the feldspar structure is inflexible, a zeolitic equivalent of feldspar would be based on the *flexible* analogue.

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Reference

SMITH (J. V.) and RINALDI (F.), 1962. Min. Mag., vol. 33, p. 202.

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