

CRYSTAL STRUCTURE OF YOSHIOKAITE BASED ON SYNTHETIC SAMPLE - RELATION TO NEPHELINE. Ian M. Steele, Dept. of Geophysical Sciences, The University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637.

Yoshiokaite is a phase recently described by Vaniman et al. (1) which occurs as rare grains in Apollo 14076,5 breccia. Its composition based on analyses of some tens of grains can be described as  $\text{Ca}_{8-0.5x}[\ ]_{0.5x}\text{Al}_{16-x}\text{Si}_x\text{O}_{32}$  where  $x$  ranges from 2.8 to 6.0 and  $[ ]$  = vacancy for the lunar analyses (2). The cell parameters were reported as  $a_0=9.939$  and  $c_0=8.245\text{\AA}$  (2). A similar phase was originally described by Sugiura and Yoshioka (3) and Yoshioka (4) from experiments in the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  system with cell parameters  $a_0=9.9961$ ,  $c_0=8.2195\text{\AA}$ . They suggested a similarity to the nepheline structure based on the cell dimensions and optical properties. Another synthetic phase was synthesized by Kirkpatrick (5) with a composition  $\text{CaAl}_2\text{SiO}_6$ , and an x-ray study (6) showed a hexagonal structure, space group  $\overline{\text{P3c1}}$  or  $\text{P3c1}$ , with  $a_0=9.943$  and  $c_0=8.228\text{\AA}$ . The composition of this phase can also be described as  $\text{Ca}_{5.3}[\ ]_{2.7}\text{Al}_{10.7}\text{Si}_{5.3}\text{O}_{32}$ . The powder diffraction patterns of all three materials are very similar which suggests that all have the same structure. All occurrences show a crystalline phase associated with glass and the synthetic crystals are grown by crystallization of glass near  $1000^\circ\text{C}$ . Using the synthetic sample described in (6) a single crystal x-ray structure determination was made and the results described below.

The structure as previously deduced from cell parameters is closely related to nepheline and hence can also be described as a stuffed tridymite structure. The basis of the structure is a single nepheline layer where ever other 6-ring within one layer is rotated in the same direction forming a layer of near-hexagonal 6-rings alternating with elongated 6-rings. Cations are present above and below the elongated 6-ring. The tridymite layer and the derived nepheline layer are shown in Fig.1. The nepheline structure is formed by stacking two of these layers such that similar 6-rings nearly superpose (Fig. 3a). In the case of yoshiokaite, one layer is similar to that of nepheline while the second layer has the opposite sense of rotation relative to the first (Fig. 2). Layers are stacked along  $c$  such that the two types of layers alternate and the elongated 6-rings lie above one another but show opposite directions of elongation when the structure is viewed parallel to the  $c$ -axis. For the synthetic composition, calcium is located between these layers in the cavities formed by the elongated 6-rings (the Na site of nepheline) but with 8% vacancy, and the larger cavities (K site of nepheline) are vacant. The two-layer yoshiokaite structure is illustrated in Fig. 3b. Depending on the Al/Si ratio, the observed yoshiokaite composition range can accommodate about 15% vacancy to full occupancy in the Na-site and up to about 33% occupancy in the K-site. The Si and Al are disordered based on average tetrahedral bond-lengths.

While the structure was reported (6) to have space group  $\overline{\text{P3c1}}$  or  $\text{P3c1}$ , the structure refinement showed that this is not possible. The structure in fact has  $\overline{\text{P3}}$  symmetry but submicroscopic twinning (twin axis  $[110]$ ) gives the observed diffraction symmetry of  $\overline{\text{P3c1}}$ . Except for tetrahedra located along the 3-fold axis, the structure has in fact  $\overline{\text{P3c1}}$  symmetry. With the addition of Ca into the K-site and the consequent increase in the Al/Si ratio, the structure probably reverts to the monoclinic  $\text{CaAl}_2\text{O}_4$  structure. Decreased vacancies and increase in Si/Al apparently makes yoshiokaite unstable and the omega structure forms (2). The addition of Na and K into the system would create competition among the nepheline, kalsilite and yoshiokaite structures with the potential for complex ordering of both tetrahedral and cation/vacancies and complex subsolidus reactions.

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**References:** (1) Vaniman, D.T. et al. (1989), LPS XX,1150-1151; (2) Vaniman and Bish (1990), Am. Mineral., in press; (3) Sugiura, K. and Yoshioka, T. (1968) Proc. 5<sup>th</sup> Inter. Sympos. on Cement Chem., 1, 370-377; (4) Yoshioka, T. (1970) Bull Chem. Soc. Jap., 43, 1981-1987; (5) Kirkpatrick, R.J. (1972) Ph.D. Thesis, U. Ill., Urbana; (6) Kirkpatrick, R.J. and Steele, I.M. (1973) Am. Mineral., 58, 945-946.

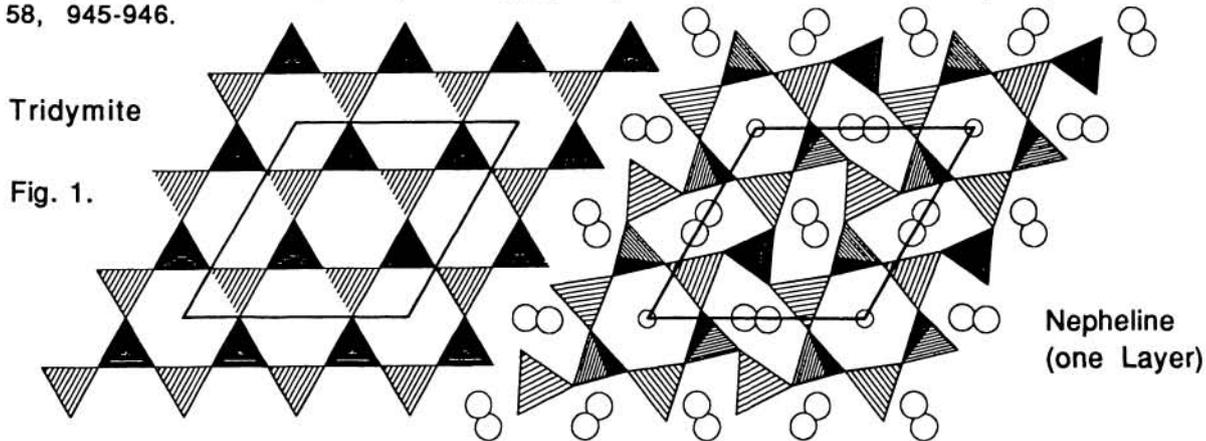


Fig.1. Comparison of tridymite layer and nepheline single layer in c-axis polyhedral projection. The 8.2Å cell is shown and circles show cations above and below nepheline layer.

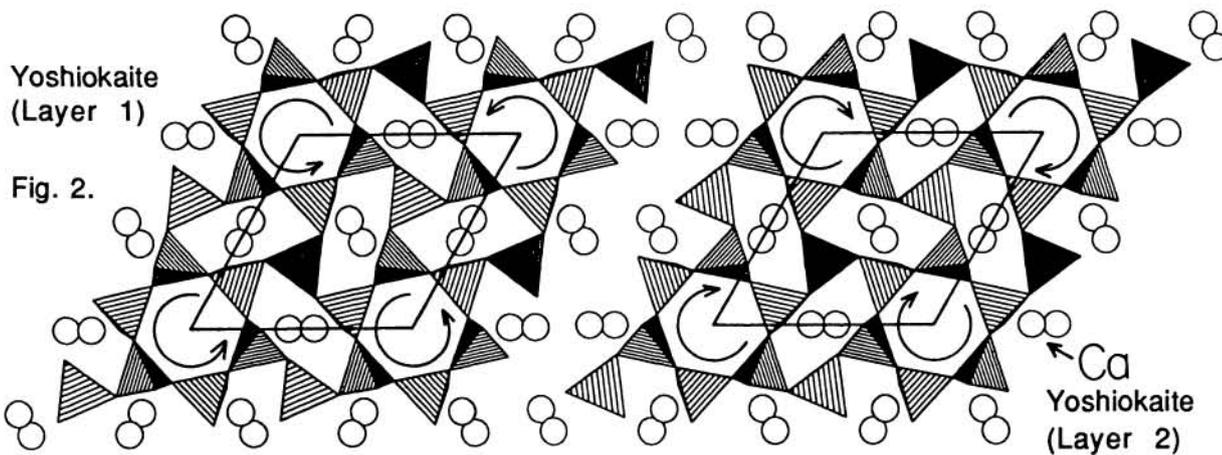


Fig. 2. Two layers of yoshiokaite structure illustrating opposite sense of rotation.

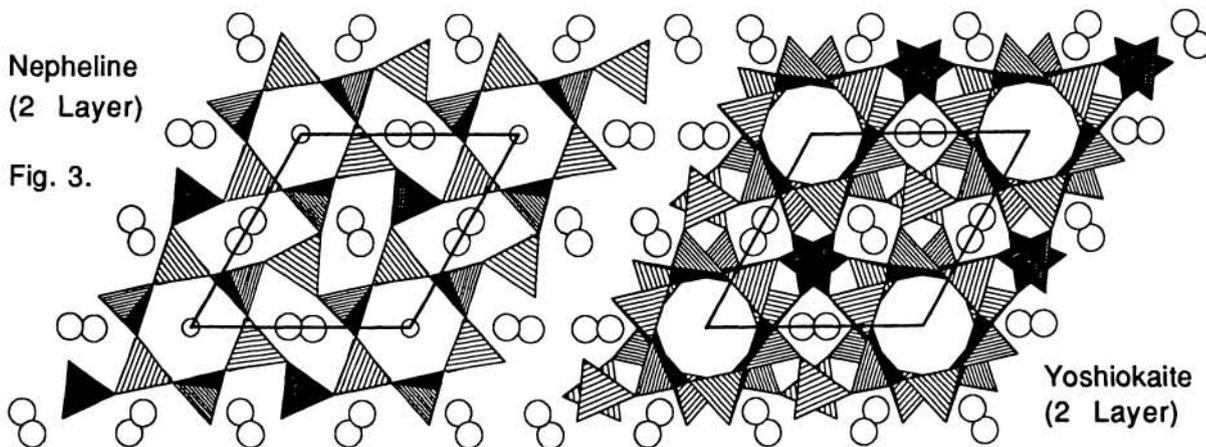


Fig. 3. Two layer structures of nepheline compared to yoshiokaite.