

Truscottite: composition and ionic substitutions

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SUMMARY. Eleven specimens of natural or synthetic truscottite or gyrolite-truscottite intergrowth were studied by analytical electron microscopy and X-ray powder diffraction. The results suggest that, in absence of substitution, the formula of truscottite is $\text{Ca}_{14}(\text{Si}_{24}\text{O}_{58})(\text{OH})_8 \cdot \sim 2\text{H}_2\text{O}$. Truscottite can accommodate Al and K in absence of each other to the extents of 1.4 atoms of Al or 0.5 atoms of K in the above formula. Substitution of Al causes a small increase in cell dimensions, which can approach those of reyerite, but substitution of K has negligible effect.

TRUSCOTTITE is a calcium silicate mineral structurally related to gyrolite and reyerite. There has been some doubt about its composition, because known natural specimens are intimately mixed with quartz and it is difficult to be certain that synthetic preparations are free from other phases. Ca:Si ratios ranging from 0.5 to 0.75 have been proposed from studies on natural specimens (Hövig, 1914; Grutterink, 1925; Mackay and Taylor, 1954; Strunz and Micheelsen, 1958; Minato and Kato, 1967) and synthetic preparations (Meyer and Jaunarajs, 1961; Funk, 1961; Harker, 1964). The $\text{H}_2\text{O}:\text{Si}$ ratio is about 0.25. Truscottite is especially similar to reyerite, which is known from chemical analysis and X-ray structure determination to be $(\text{Na},\text{K})_2\text{Ca}_{14}(\text{Si}_{22}\text{Al}_2\text{O}_{58})(\text{OH})_8 \cdot \sim 6\text{H}_2\text{O}$ (Merlino, 1972). Gard *et al.* (1975) suggested that it was related to reyerite by replacing the latter's Al by Si and omitting its alkali cations, but recognized some uncertainty in view of the experimental evidence.

Truscottite and reyerite are of interest not only as natural minerals, but also because of their potential formation in cements hydrated at elevated temperatures and pressures, as in the casings of deep geothermal wells. Current studies by Dr G. L. Kalousek and collaborators at the Colorado School of Mines, sponsored by the [US] Brookhaven National Laboratory and Department of Energy, have the aim of relating the technical properties of such cements to the nature of the binder. These studies suggested that formation of Al-substituted truscottite or reyerite was possibly

associated with low mechanical strength. They led to the present work, which was carried out partly on natural minerals and partly on synthetic materials kindly supplied by Dr Kalousek.

We have studied these natural and synthetic truscottites by analytical electron microscopy and X-ray powder diffraction. Our aims were to establish the Ca:Si ratio and to find whether the structure can accommodate Al and K separately, and if it can, whether the cell parameters are significantly altered.

Specimens. We have studied the following specimens: truscottite from Redjang Lebong Mine, Benkulen, Sumatra (type locality; BM 1925, 1044); truscottite from Biriya vein, Toi Mine, Tagatagun, Shizuoka, Japan; synthetic preparations, made hydrothermally at saturated steam pressures, as listed in Table I.

The silicic acid was a finely divided, amorphous powder containing about 85% SiO_2 . The cement was a commercial product consisting of $\beta\text{-Ca}_2\text{SiO}_4$ and quartz with about 5% of calcite and containing under 1% each of Al_2O_3 , Fe_2O_3 , SO_3 , and alkalis. X-ray patterns of the first six preparations showed only truscottite, apart from traces of $\text{Ca}_5\text{Si}_6\text{O}_{17}$ (the '3.15 Å phase' of Bezjak *et al.*, 1974) in K355, and of hexagonal $\text{CaAl}_2\text{Si}_2\text{O}_8$ in K108, and a little quartz and possible traces of calcite and scawite in K342. Those of the last three, marked * in Table I, showed them to consist essentially of gyrolite-truscottite intergrowth (Meyer and Jaunarajs, 1961; Harker, 1964), which was mainly truscottite in K356 and K373 and mainly gyrolite in K357. We also examined, for comparison, natural reyerite from the type locality (Niakornak, Greenland; USNM 4016) and natural gyrolite from Bombay, India (BM 93504).

In the absence of alkali, truscottite can readily be synthesized from CaO and silicic acid (Buckner *et al.*, 1960; Meyer and Jaunarajs, 1961) but not from CaO and quartz (Kalousek, 1978). The present results show that, if alkali is present, it can also be made from quartz. When truscottite is made using silicic acid, gyrolite-truscottite intergrowth is

TABLE I. Synthetic preparations of truscottite

Specimen	Starting materials	Composition of mix				T (°C)	Time (d)
		Ca	Si	Al	K		
K355	CaO + silicic acid	0.60	1.00	—	—	325°	7
K353	Synthetic truscottite + trace quartz	0.60	1.00	—	—	340°	7
K108	CaO + silicic acid + Al(OH) ₃	0.60	0.91	0.09	—	345°	7
K349	CaO + quartz + KOH	0.60	1.00	—	0.03	300°	30
K347	Cement + quartz + KOH	0.60	1.00	—	0.03	300°	30
K342	Cement + quartz + K ₂ Si ₂ O ₅	0.60	1.00	—	0.03	300°	7
K356*	CaO + silicic acid + Al(OH) ₃	0.57	0.96	0.04	—	325°	7
K357*	CaO + silicic acid + Al(OH) ₃	0.54	0.93	0.07	—	325°	7
K373*	Cement + silicic acid + Al(OH) ₃	0.54	0.93	0.07	—	325°	7

* Gyrolite-truscottite intergrowth: see text.

formed as an intermediate product. The present results suggest that Al³⁺ retards the conversion of this intergrowth into truscottite.

Analytical electron microscopy. A Kratos CORA instrument was used; this is a transmission microscope fitted with a KEVEX energy-dispersive X-ray detector. The procedures were similar to those described by Cliff *et al.* (1975). Correction factors for losses in the detector were made using α -CaSiO₃, kaolinite, and orthoclase as standards. To render absorption and fluorescence errors negligible, sufficiently thin crystals (probably always under 300 Å) were analysed. Table II gives the

results. The Ca:Si, Al:Si, and K:Si ratios are means for the stated number of analyses, which were on separate crystals; the standard errors relate to these means. Limits of detection for Al:Si and K:Si were about 0.01; for most of the other elements listed as being detected, the limits, expressed as ratios relative to Si, were probably also around 0.01 (0.05 for Na).

A few of the truscottite samples in all the specimens showed signs of beam damage; this was especially true of the Japanese specimen. Such crystals are excluded from the results. All the synthetic preparations contained small propor-

TABLE II. Analytical electron microscopy: results

Specimen	Ca:Si		Al:Si		K:Si		Other elements detected	No. of analyses	Notes
	Mean	SE	Mean	SE	Mean	SE			
Natural truscottites									
Sumatra	0.56	0.01	nil	—	tr.	—	Mn, Mg, Fe, Ni, Zn	10	
Japan	0.57	0.01	nil	—	tr.	—	Mn, S, Cl, Ni, Zn	10	a
Synthetic truscottites									
K355	0.55	0.01	nil	—	nil	—	—	15	
K108	0.60	0.01	0.062	0.002	nil	—	—	15	
K349	0.56	0.01	nil	—	0.018	<0.001	S	10	
Gyrolite-truscottite intergrowths									
K356 (mainly truscottite)	0.59	0.01	0.038	0.002	nil	—	S, Fe	10	
K357 (mainly gyrolite)	0.59	0.01	0.057	0.006	nil	—	S, Fe	7	b
Related minerals									
Reyerite (Greenland)	0.63	0.01	0.073	0.005	<0.01	—	Fe, Na(?)	5	c
Gyrolite (Bombay)	0.66	—	~0.03	—	nil	—	—	1	d

a. Bulk analysis gave 2.41% MnO.

b. Analyses are for seven crystals from a sample evacuated for 2 days before exposure to beam, and which then appeared not to lose Ca. Many other crystals lost Ca in the beam, but had Ca:Si initially < 0.6.

c. Of the five crystals analysed, only one showed any K (K:Si = 0.012) and Na was doubtful or undetected in all of them. Bulk analyses give 1.6% K₂O, 2.2% Na₂O. The sample contained a second hexagonal plate phase, with Ca:Si 0.52 ± 0.06, Al:Si 0.078 ± 0.06, K not detected (mean for five crystals).

d. Highest Ca:Si ratio from ten analyses. Other crystals showed marked Ca loss in the beam and gave results consistent with Ca:Si 0.60-0.75.

tions of thicker platy crystals, or stubby laths, or both. These were not definitely identified, though the laths had Ca:Si \approx 0.8 and could have been either tobermorite or the '3.15 Å phase' of Bezjak *et al.* (1974). One crystal of hexagonal $\text{CaAl}_2\text{Si}_2\text{O}_8$ was identified in K108. The gyrolite-truscottite intergrowths K357 and K373 lost Ca on exposure to the beam. This effect was reduced by leaving the sample in the high vacuum of the instrument for 2 days before putting it in the beam. We attributed the effect to the gyrolite constituent, because it was also shown markedly by the natural gyrolite specimen.

X-ray powder diffraction. A Hägg Guinier camera was used with monochromatized Cu radiation and quartz (a 4.913, c 5.405 Å) as internal standard. Films were measured using a Cooksley microdensitometer capable of measuring peak positions with a standard error equivalent to about $0.02^\circ 2\theta$. The truscottite pattern was unequivocally indexed by comparing spacings and intensities with those observed on single-crystal patterns of the closely similar reyerite, and cell parameters refined by least squares using 10–18 reflections. That of the Sumatra mineral has been accepted for inclusion in the JCPDS file. Table III gives the results.

TABLE III. Unit-cell parameters*

Specimen	Major substituent(s) (bulk analysis)	a (Å)	c (Å)
Natural truscottites			
Sumatra	—	9.731 (2)	18.84 (1)
Japan	—	9.735 (1)	18.85 (1)
Synthetic truscottites			
K355	—	9.740 (4)	18.81 (1)
K108	Al	9.747 (2)	18.89 (1)
K373†	Al	9.751 (4)	18.88 (2)
K349	K	9.740 (1)	18.84 (1)
K347	K	9.743 (4)	18.84 (1)
K342	K	9.738 (2)	18.85 (1)
Reyerite			
Greenland	Na, K, Al	9.751 (2)	18.96 (2)

* Hexagonal unit cell; estimated standard deviations on last significant digits in parentheses.

† Values of lower reliability, for truscottite component of gyrolite-truscottite intergrowth.

Discussion. The results support the view that, in the absence of substituents, the formula is $\text{Ca}_{14}(\text{Si}_{24}\text{O}_{58})(\text{OH})_8 \cdot x\text{H}_2\text{O}$, and that the structure is related to that of reyerite as suggested by Gard *et al.* (1975). The value of x is somewhat indefinite, but for specimens dried at about 100°C in air is around 2. This is probably similar to the corresponding value for reyerite dried under similar conditions.

From careful synthetic work, Harker (1964) proposed the formula $3\text{CaO} \cdot 5\text{SiO}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$, which is close to that suggested here. The formula $\text{Ca}_{14}(\text{Si}_{24}\text{O}_{58})(\text{OH})_8 \cdot x\text{H}_2\text{O}$ is preferred because of the close structural similarity to reyerite.

The results show that truscottite can accommodate Al in absence of other substituents. The limiting Al content is about 1.4 atoms per formula unit or 3.2% Al_2O_3 on the dry weight. If one tries to incorporate more Al_2O_3 under the conditions of synthesis used, hexagonal CAS_2 is formed as a second phase. It is uncertain how the replacement is balanced. The most likely hypothesis is probably that Al replaces Si, with incorporation of additional Ca in otherwise vacant sites, which in reyerite are occupied by alkali cations; if this is correct, the limiting composition is about $\text{Ca}_{14.7}(\text{Si}_{22.6}\text{Al}_{1.4}\text{O}_{58})(\text{OH})_8 \cdot x\text{H}_2\text{O}$, with a structure approaching that of reyerite. Agreement with the analytical evidence is, however, not wholly satisfactory, as this formula corresponds to a Ca:Si ratio of 0.65, which is above the observed value.

The results show that truscottite can also accommodate a little K in absence of other substituents; the limiting K content is about 0.5 atoms per formula unit, or 1% K_2O on the dry weight. It is again not certain how the substitution is balanced; possibly one-half of the K replaces Ca, with the remainder in the otherwise vacant sites.

The X-ray results are consistent with these conclusions. In absence of appreciable substitution, a is 9.735 ± 0.005 Å and c is 18.83 ± 0.02 Å. With maximum Al-substitution, a increases to 9.747 Å and c to 18.89 Å; these values approach those of reyerite (a 9.751, c 18.96 Å). K-substitution has little or no effect on the cell dimensions (a 9.738–9.743, c 18.84–18.85 Å).

The results for gyrolite-truscottite intergrowths are difficult to interpret because of the problem of separating the effects of Al-substitution from those of the intergrowth with gyrolite, which has formula $\text{Ca}_{16}(\text{Si}_{24}\text{O}_{60})(\text{OH})_8 \cdot 14\text{H}_2\text{O}$, a 9.73 Å, and c a multiple of 22.1 Å. The analytical results in Table II could well relate to the truscottite constituent, as they agree closely with those for specimen K108.

The ready loss on exposure to the electron beam of Ca from gyrolite and the gyrolite constituent of the intergrowths is perhaps due to the presence of additional Ca in the structure of this mineral. Gard *et al.* (1975) suggested that the additional Ca occupied interlayer sites, and Ca in such sites might well be vulnerable.

The reyerite sample seemed to contain two hexagonal plate phases with slightly different compositions. One gave Ca:Si and Al:Si ratios near to the theoretical values (0.64 and 0.09 respectively) but appeared to contain little or no K or Na. This

may have been due to very rapid loss of these elements in the beam, with crystal-to-crystal variation and relatively low instrumental sensitivity to Na as contributing factors. The second phase was of lower Ca:Si ratio and deserves further study.

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REFERENCES

- Bezjak (A.), Jelenić (I.), and Jernečić (J.), 1974. *Nature*, **248**, 581.
- Buckner (D. A.), Roy (D. M.), and Roy (R.), 1960. *Am. J. Sci.* **258**, 132.
- Cliff (G.), Gard (J. A.), Lorimer (G. W.), and Taylor (H. F. W.), 1975. *Mineral. Mag.* **40**, 113.
- Funk (H.), 1961. *Z. anorg. allg. Chemie*, **313**, 1.
- Gard (J. A.), Mitsuda (T.), and Taylor (H. F. W.), 1975. *Mineral. Mag.* **40**, 325.
- Grutterink (J. A.), 1925. *Verh. Geol.-Mijnb. Genootschap Nederland, Geol. Ser.* **8**, 197 [MA **3**, 271].
- Harker (R. I.), 1964. *J. Am. Ceram. Soc.* **47**, 521.
- Hövig (P.), 1914. *Jaarb. Mijnwezen Ned. Oost-Indie (Batavia)*, **41** (for 1912), 202 [*Mineral. Mag.* **20**, 466].
- Kalousek (G. L.), 1978. Paper presented at Symposium on Relations between Properties of Lime-Sand Products and Formation of Cementing Material, Karlsruhe.
- Mackay (A. L.) and Taylor (H. F. W.), 1954. *Mineral. Mag.* **30**, 450.
- Merlino (S.), 1972. *Nature*, **238**, 124.
- Meyer (J. W.) and Jaunarajs (J. L.), 1961. *Am. Mineral.* **46**, 913.
- Minato (H.) and Kato (K.), 1967. *Mineral. J. (Japan)*, **5**, 144.
- Strunz (H.) and Micheelsen (H.), 1958. *Naturwiss.* **45**, 515.

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