

Scawtite and its synthesis

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Summary. Since its discovery by Tilley in 1930, scawtite has been recognized in several locations in regions of metamorphosed siliceous limestones. Scawtite is believed to be the same as CSH(A) and, as such, has been synthesized sporadically many times during runs in the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system where slight contamination from CO_2 has occurred. Attempts to synthesize scawtite were successfully carried out at low partial pressures of CO_2 in an excess of water. The stability of selected scawtite compositions lies between 140 and 300° C, and above saturated steam pressures is not pressure-dependent, at least up to 50 000 psi. The scawtite facies (2) lies between the tobermorite-calcite facies (3) and the xonotlite-calcite facies (1). A hydration series exists from (1) to (2) to (3).

AMONG the minerals sometimes formed in contact-metamorphosed siliceous limestones, scawtite has proved one of the most elusive as far as deliberate synthesis is concerned. This is almost certainly related to the fact that this mineral is the only quaternary phase presently known in the $\text{CaO-SiO}_2\text{-H}_2\text{O-CO}_2$ system.

Until relatively recently, *PVT* data in $\text{H}_2\text{O-CO}_2$ mixtures have been lacking and systematic experimentation under metamorphic conditions (elevated pressures and temperatures) has not been forthcoming in the 'scawtite system'. The importance of this system however is great, for its application to cement technology if not to petrology, and it is to be hoped that the examples of Ellis (1959) and Rosenberg and Holland (1962) in studying $\text{H}_2\text{O-CO}_2$ systems at elevated pressures and temperatures will be pursued in combination with many other components.

Occurrences and paragenesis. Scawtite was originally discovered and named by Tilley in 1930. The mineral occurs in vesicles with zeolites and calcite in certain melilite-rich rocks of the hybrid zone at Scawt Hill. Petrographic evidence indicated a late stage of formation for the scawtite, and this indication was later confirmed by Tilley in 1938 through his observations of the phase as pseudomorphs after spurrite, again at Scawt Hill.

After its original discovery, scawtite began to gain recognition in a wide variety of places. Taylor (1935) described it in Montana with gehlenite, vesuvianite, calcite, and sometimes garnet. Murdoch (1955)

noted scawtite as occurring in veins, sometimes with bulfonteinite, in a diopside-wollastonite-spurrite assemblage. McConnell (1954) observed scawtite with tobermorite and calcite in vesicles in a larnite rock at Ballycraigy, and finally Mason (1957) found a scawtite rock with lesser amounts of hydrogrossularite, magnetite, and calcite. Where scawtite has not been clearly a secondary mineral (i.e. in pseudomorphs, vesicles or veins) it has been associated with hydrous phases, e.g. vesuvianite and/or hydrogrossularites, and although there has been no evidence for its spurious synthesis in the $\text{CaO-SiO}_2\text{-CO}_2$ system, there are several indications that it has been formed repeatedly, if not intentionally, during investigations in the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system, Heller and Taylor (1956).

Synthetic studies

On the basis of the few available analyses it seems that the chemical composition of scawtite may be expressed as $\text{Ca}_{14}(\text{OH})_4(\text{Si}_{16-x-y}\text{C}_x\text{H}_{4y})\text{O}_{44}$, based on a 48-oxygen cell (as suggested by McConnell, 1955).

Such a formula, however, encompasses a larger range of compositions than is indicated by the three scawtites analysed (i.e. those from Scawt Hill, Ballycraigy, and Crestmore). Actually, all three lie very close to the $\text{H}_2\text{O-wollastonite-calcite}$ plane in the $\text{CaO-SiO}_2\text{-H}_2\text{O-CO}_2$ system. The scawtite from Scawt Hill is somewhat apart from that of Crestmore and Ballycraigy (and indeed from the synthetic material) which contain appreciable water in the structure.

Deliberate attempts to synthesize scawtite were made around the above composition with $x+y = 4$ and with $x = 1$ or 2 . Mallinkrodt's special bulky silicic acid was used as a source of silica and this was mixed with A.R. grade CaCO_3 and/or $\text{Ca}(\text{OH})_2$ or CaO in the proportions required for $7\text{CaO}.6\text{SiO}_2.2\text{CO}_2$, $7\text{CaO}.6\text{SiO}_2.1\text{CO}_2$, or $7\text{CaO}.6\text{SiO}_2$. These mixtures were then run at elevated temperatures and pressures for varying lengths of time up to four weeks. The majority of the runs in which scawtite was produced yielded a mixture of scawtite with tobermorite, calcite and/or xonotlite. 'Pure' scawtite could only be prepared by using $\text{Ca}(\text{OH})_2$ as the source of lime and taking the stoichiometric amount of CO_2 dissolved in the excess water for the source of CO_2 (this was best obtained from appropriate mixtures of CO_2 -saturated water and freshly boiled distilled water), see fig. 1.

Total pressures ranged from saturated steam pressures to 50,000 psi and temperatures from 25 to 690°C . Total pressure had little if any effect on the formation of scawtite whose formation was restricted

to temperatures between 140 and 300° C. At lower temperatures, tobermorite and calcite appeared to be the stable assemblage, and at higher temperatures, xonotlite and calcite (or wollastonite and calcite) were produced.

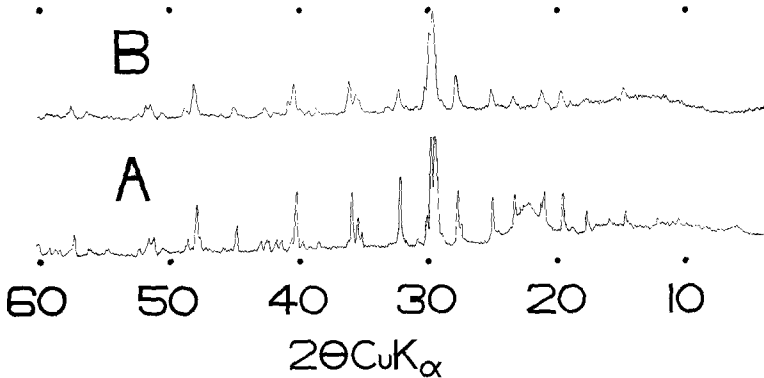


FIG. 1. X-ray powder diffraction patterns of (A) scawtite from Crestmore, California, and of (B) synthetic scawtite (present study).

The range of stability of scawtite of a given composition, as discussed above, is narrow and encroaches on that of xonotlite + H₂O in the CaO-SiO₂-H₂O system. The following reactions take place with rising temperature:

1. Tobermorite + calcite → scawtite + H₂O.
2. Scawtite → xonotlite + calcite + H₂O (see fig. 2).

Since neither of these reactions involves a CO₂-rich vapour phase, the effect of pressure on the temperatures of reaction is understandably small, at least above saturated steam pressures. The anhydrous composition of the Scawt Hill scawtite does not fit into the compatibility 'triangles' of fig. 2, and for this some other explanation has yet to be found.

Though not measured separately, the CO₂ pressures under which scawtite is stable are apparently lower than those which normally exist during the primary thermal metamorphism of impure limestones. A sample of synthetic scawtite and a sample of natural scawtite, separated from a specimen kindly provided by Dr. Brian Mason from his Tokatoka collection, were each made into a thin slurry and gently stirred overnight in CO₂-saturated water at 21° C and 1 atmosphere. After sixteen hours

scawtite could no longer be detected by X-ray powder diffraction and the samples had broken down to calcite and amorphous silica.

The experimental work supports the evidence from natural occurrences that scawtite does not properly belong to the group of useful metamorphic-grade-indicator minerals of the primary decarbonation series

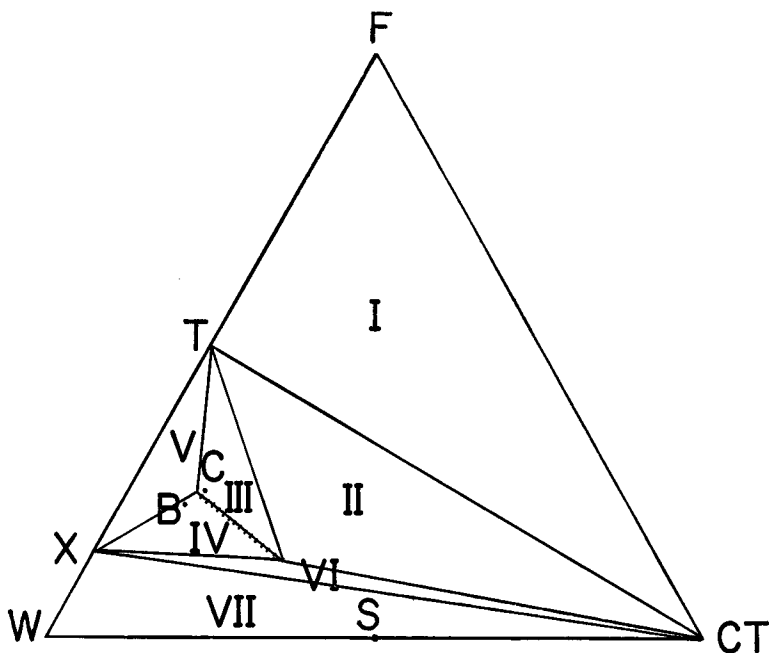


FIG. 2. Scawtite-bearing assemblages in the $\text{CaO-SiO}_2\text{-H}_2\text{O-CO}_2$ system. (I) Tobermorite + calcite + fluid. (II) Tobermorite + scawtite + calcite + fluid. (III) Tobermorite + scawtite + fluid. (IV) Xonotlite + scawtite + fluid. (V) Xonotlite + tobermorite + scawtite + fluid. (VI) Scawtite + xonotlite + calcite + fluid. (VII) Xonotlite + wollastonite + calcite + fluid. *S* = Scawtite from Scawt Hill. *C* = Scawtite from Crestmore. *B* = Scawtite from Ballycraigy. *F* = H_2O component of fluid. *CT* = Calcite. *T* = Tobermorite. *W* = Wollastonite. *X* = Xonotlite.

(see Bowen, 1940). Although scawtite may contain more than twice as much CO_2 as H_2O in its structure, it probably cannot develop until the CO_2 pressure and the temperature in a given environment of metamorphosed siliceous limestones have dropped considerably below those existing at the initial development of the wollastonite facies. Scawtite forms as the hydrous fluids from the igneous source sweep out and replace the carbon dioxide-rich fluids from the limestone source.

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