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NOTES

COMMENTS ON: AN EXPANSIBLE MINERAL HAVING HIGH REHYDRATION ABILITY*

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In their paper on the rehydration after heating to 800°C of an interstratified mineral (mica–montmorillonite) from Satsuma Peninsula, Japan, Tomita and Dozono (1973) state "It has been said that hydrous forms of layer silicates, e.g. montmorillonite, hydrated halloysite, and vermiculite never rehydrate after heating to 800°C" (Greene-Kelly, 1953; Walker, 1951). Similarly Deer *et al.* (1962) report for vermiculite that "the expulsion of inter-layer water can be reversed after heating to temperatures as high as 550°C, and only beyond 700°C is it certain that none can be regained".

This note shows that the rehydration of vermiculite is very dependent both on the time of heating at a particular temperature and on the composition of the vermiculite. Certain vermiculites will rehydrate after heating to 800°C provided that they are not held at this temperature until all the hydroxyl water is lost.

Tomita and Dozono have found that an interstratified mica–montmorillonite mineral will rehydrate after heating to 800°C for 1 hr. Earlier Walker (1951) observed, for a vermiculite from West Chester, that only after heating to about 700°C for 24 hr was dehydration irreversible. In later work, Walker and Cole (1957) and Walker (1961) reported that the vermiculite mineral 'Batavite' does not lose the last trace of its interlayer water until about 800°C compared with a temperature of about 700°C for material from West Chester. Thus, it might be expected that Batavite would rehydrate after heating to 800°C despite the contrary statement regarding vermiculite made by Tomita and Dozono (1973) quoted above.

Although not specifically mentioned in the publications of Walker and Cole (1957) or Walker (1961), Batavite possesses a high capacity to rehydrate after heating to 800°C in differential thermal analysis equipment. In the work done for the publication by Walker and Cole it was noted that if flakes of Batavite were heated in an open-ended silica tube to 800°C in a DTA furnace at 10°C/min and sealed at that temperature, an X-ray spacing of 9·45 Å was obtained. When the tube was broken and the mineral allowed to rehydrate in air, a 14·2 Å reflection typical of the unheated mineral was partially recovered. For this reason in the earlier work of Walker and Cole, samples taken from DTA equipment for X-ray purposes were always sealed in tubes at the temperature of sampling.

The work on Batavite has been repeated using a Rigaku Denki combined DTA and weight-loss equipment. Firstly, flakes were sealed in tubes and heated to 825°C at 20°C/min, with a weight loss of 17·0 per cent. The flakes were then held for 1 hr at 825°C with a further 0·8 per cent loss of weight. Samples sealed while the oven was at a high temperature (~ 500°C) gave a spacing at 9·2 Å. After exposure to the air at ambient temperature, the spacing did not change nor did the sample regain any weight. Secondly, the experiment was repeated with the holding for 1 hr at 825°C eliminated, whereupon the sample picked up 2/3 of its lost weight and showed a substantial recovery of the 14 Å spacing upon exposure to a damp atmosphere for 1 day. Thirdly, the first experiment was repeated for a temperature of 700°C. The loss in weight upon reaching 700°C was 16·7 per cent and after holding for 1 hr at that temperature, 18·0 per cent. Upon exposure to a damp atmosphere for 2 hr the sample regained about 2/3 of its lost weight; a figure not greatly altered after 1 day of exposure. The basal spacing of the heated sample collapsed to a weak 9·2 Å and a stronger 9·8 Å reflection. Upon exposure to the air a strong reflection quickly appeared at 14·7 Å with very weak residual reflections at 9·2 and 9·6 Å. A vermiculite from Llano, Texas when heated to 800°C as in the first and second experiments described above, gave results similar to those for Batavite. Powders obtained by grinding flakes of both Batavite and Llano vermiculite had their rehydration ability destroyed by heating to 800°C. However, Walker (1961) reported that crystals less than 2 μm e.s.d. of the West Chester Mg–vermiculite show a relatively diffuse basal reflection in the region of 9·5 Å at 750°C, compared with the 9·02 Å reflection obtained from the macroscopic crystals.

Weiss and Hofmann (1951) showed that Batavite has a tetrahedral Al:Si ratio of 1:3 and contains only Mg and Al in the octahedral layer. On the other hand, van Olphen (1965) found that Llano vermiculite has an Al:Si ratio of 1:2 in its tetrahedral layer with only Mg and Al octahedrally coordinated. The West Chester vermiculite (Walker and Cole, 1957) has an Al:Si ratio 1:2 in its tetrahedral layer and a considerable amount of Fe^{3+} in the octahedral layer. All have Mg as the sole exchange cation. The rehydration of vermiculites has been ascribed (Walker, 1951) to the strong tendency of the Mg ions to rehydrate once unbound water molecules have been removed. The greater capacity of Batavite and Llano vermiculite to rehydrate over the material from West Chester may be due to the lack of octahedral iron.

Tomita and Dozono were not able to purify their mineral and so could not comment on the reason for its high capacity to rehydrate. However, they did note that Granquist and Kennedy (1967) had reported that for a synthetic ammonium dioctahedral clay the presence of fluoride in hydroxyl sites enhanced the water sorption capacity. It should be noted here that vermiculite minerals seldom contain fluorine. Tomita and Dozono also noted that Wright *et al.*

* Tomita, K. and Dozono, M. *Clays and Clay Minerals* (1973) **21**, 185–190.

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(1972) concluded that for the same clay studied by Granquist and Kennedy the thermally activated substance had protons in the tetrahedral vacancies of the octahedral layer.

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