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An occurrence of todorokite in the deuteric stage of a basalt

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Summary. An occurrence of todorokite having a formula $(Mn^{2+},Ca)Mn_5^{4+}O_{11}.4H_2O$ is recorded from Ardglen, 150 miles N.N.W. of Sydney, New South Wales. The composition of Ardglen todorokite is somewhat simpler than previously recorded occurrences, most of which were in manganese and manganese–base-metal ore deposits. The simpler composition is explained in terms of its occurrence as a late deuteric mineral associated with manganocalcite and zeolites in an altered Tertiary basalt. The manganese is believed to have been derived from the deuteric alteration of the augite of the basalt.

TODOROKITE has a variable composition of the general form $(Mn^{2+},X)(Mn^{4+})_3 O_7 . 2-x H_2O$, where X represents various arrangements of Zn, Mg, Ba, Sr, Ca, Cu, Pb, Na_2, K_2. Most of the published formulae show the presence, in minor amounts, of most of the elements indicated by X, though it is suspected that many of these are either non-essential components or are impurities. Variation in the amount of water of crystallization is also evident from the several published analyses. It is probably isostructural with woodruffite, $(Zn, Mn^{2+})^2 Mn_5^{4+}O_{12} . 4H_2O$.

Todorokite was first described by Yoshimura (1934) from the Syûetu vein of the Todoroki Mine, Japan, and has since been recorded from several other localities; the known occurrences are well reviewed by Straczek *et al.* (1960) and Larson (1962).

Whereas previous occurrences came mainly from manganiferous ore deposits, the material described in this paper came from a small vug in basalt of Tertiary age at Ardglen, some 150 miles N.N.W. of Sydney, Australia.

Ardglen is a small settlement on the eastern margin of the Liverpool Ranges some 150 miles N.N.W. of Sydney and 75 miles W.N.W. of Newcastle, New South Wales. The rocks of the Ardglen area consist of Tertiary basalt overlying Permian marine and freshwater sediments and, in part, overlying marine strata of Carboniferous age. The basalt is a normal olivine bearing plateau basalt strongly altered in places by deuteric fluids. The resulting rock is an earthy aggregate of chlorite, sericite, calcite, traces of epidote, and varying amounts of zeolites of which natrolite, chabazite, and apophyllite are prominent. The zeolites occur particularly in gas cavities in the lava.

The todorokite occurs as a froth-like coating on manganocalcite in small vugs in the altered basalt, and consists of a film of felted, microscopic crystals possessing, in aggregate, a brassy colour, and a distinct metallic sheen. Straczek *et al.* (1960) states that Cuban todorokite is brownish-black to dark brown in colour and has a streak of a similar colour. The streak of Ardglen material is brownish-black and the brassy colour, contrasting with that of the Cuban mineral, is possibly due to a dispersion effect from what appears to be a dry froth of approximately 0·25 mm thick.

A chemical analysis of the mineral was carried out by courtesy of the Chemical Laboratories of N.S.W. Department of Mines: MnO_2 71·50, MnO 12·50, CaO 2·80, K_2O 0·20, H_2O^+ 11·63, H_2O^- 1·26, sum 99·89 %.

The analysis of Ardglen todorokite was made on a very small amount of material and weighings, e.g. for loss of water (H_2O^-), were made on a Cahn Gram Electrobalance. H_2O^+ was determined as loss of weight after heating between 365° and 400° C. MnO_2 was determined by a modification of the method described by Vogel[1] with $KMnO_4$ back titration of excess oxalate. Total manganese was determined by periodate oxidation spectrophotometrically and MnO calculated by difference.

An X-ray analysis of Ardglen todorokite gave:

d	9·40 Å	7·17	4·74	4·30	3·19	2·79	2·49	2·40	2·28	1·97	1·89	1·69
I	8	4	10	1 (d)	1	1	3	3 (d)	3	2	2	4

These data agree within acceptable limits, having regard to compositional variation, with published data for other occurrences.

Crystals of Ardglen todorokite were examined in both transmitted and in reflected light since some doubt is evident in previous descriptions as to whether the mineral should be regarded as transparent or

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[1] A. I. Vogel, Textbook of quantitative inorganic analysis, 3rd edn, Longmans, 1960, p. 297.

opaque. Fig. 1, in reflected light, shows a not insubstantial reflectance with cleavage normal to the basal plane and parallel to the elongation of the crystals. This agrees with the data of Straczek *et al.* (1960). Faint reflection pleochroism and distinct polarization effects in grey to white were observed on natural crystal faces though these observations were difficult because of the extremely small size (0·01–0·05 mm) of the crystals.

FIG. 1. Crystals of todorokite from Ardglen, N.S.W., Australia. Reflected light, × 750.

Discussion. The Ardglen todorokite is of particular interest for two reasons: firstly because of its simple composition compared to other analyses of this mineral, and secondly, in respect to its mode of occurrence.

Previous analyses of todorokite (see, for example, Larson, 1962) indicate extended formulae in which the alkali metals are consistently present in the divalent manganese position, as are, in some cases, copper and lead. Some of these components have been suspected as non-essential and some even as impurities. It will be noted that virtually all previous todorokite came from ore deposits—either manganese or manganese plus sulphides.

The composition of Ardglen todorokite indicates a formula $(Mn^{2+}, Ca)Mn_5^{4+}O_{11}.4H_2O$. The 0·20 % K_2O and traces of SrO and BaO are not incorporated in the formula as it is considered that they are not essential. This simple formula is no doubt related to the mode of occurrence of Ardglen todorokite. Lack of ore minerals in the formative environment accounts for the absence of base metals such as are shown in analyses of todorokite from several other localities. The availability of calcium is evident by the layer of manganocalcite on which the todorokite was precipitated.

The origin of Ardglen todorokite is regarded as part of the deuteric stage of alteration of the Ardglen basalt. Tertiary basalts of eastern Australia, as elsewhere, carry up to 0·3 % manganese contained in the titan-augite. This manganese is liberated during the deuteric alteration of the pyroxene. Of this manganese some would go into the resulting chlorite, some into the calcite deposited in the gas vesicles of the basalt and some would remain to form todorokite.

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