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Woodallite, a new chromium analogue of iowaite from the Mount Keith nickel deposit, Western Australia

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ABSTRACT

Woodallite is a new Cr-rich member of the hydrotalcite group from the large, low-grade Mount Keith nickel deposit, in the northeastern Goldfields district of Western Australia. Woodallite occurs as whorls and clusters of minute platelets up to 6 mm across in lizardite+brucite-altered dunite. Individual platelets are typically 10–100 µm in maximum dimension and are often curved. Associated minerals include chromite, lizardite, iowaite, pentlandite, magnetite, tochilinite and brucite. Electron microprobe analysis gave: Mg 25.90 wt.%; Cr 10.81; Fe 4.86; Al 0.68; Cl 9.89; S 0.03; Si 0.01; Ni 0.01; Na 0.01, yielding (after correction for loss of volatiles) an empirical formula of $Mg_{6.19}(Cr_{1.21}Fe_{0.51}Al_{0.15})_{\Sigma 1.87}(OH)_{16}[Cl_{1.62}(CO_3)_{0.17}(SO_4)_{0.01}]\cdot 4H_2O$, by analogy with the hydrotalcite group. The simplified formula is $Mg_6Cr_2(OH)_{16}Cl_2\cdot 4H_2O$. Combined thermogravimetric analysis and mass spectroscopy showed a two-stage weight loss of 12.7% and 27.3% occurring over the ranges 25–300°C and 300–660°C, respectively. The first weight loss is attributed to loss of interlayer water, chlorine-bearing species (e.g. HCl) and some CO_2, the second to loss of hydroxide water, remaining CO_2 and Cl species. The mineral is deep magenta to purple in colour, transparent, with a resinous to waxy lustre, and a perfect basal {0001} cleavage. Woodallite has a Mohs hardness of 1.5–2, and a pale-pink to white streak. The strongest lines in the X-ray powder pattern are [d_{obs} (I_{obs}) (hkl)] 8.037 (100) (003); 4.021 (48) (006); 2.679 (1) (009); 2.624 (3) (012); 2.349 (5) (015); 2.007 (6) (0,0,12); 1.698 (2) (0,1,11); 1.524 (2) $(2\bar{1}3)$. These lines were indexed on a hexagonal cell with a = 3.103(2), c = 24.111(24) Å, V = 201.14 Å^3 and Z = 3/8. The new mineral is isostructural with the hydrotalcite group and has space group $R\bar{3}m$. The measured density is 2.062 gm/cm^3. Woodallite is uniaxial negative with ω = 1.555 and ε = 1.535 (white light); pleochroism is distinct from violet to pinkish lilac. Woodallite forms as a result of hydrothermal alteration of primary magmatic chromite by Cl-rich solutions at temperatures <320°C. Relict chromite fragments are frequently present in the whorls, and associated magnetite is altered extensively to iowaite. The mineral is named after Roy Woodall, eminent Australian industry geologist.

KEYWORDS: woodallite, new mineral, hydrotalcite group, Mount Keith deposit, Western Australia.

Introduction

THE Mount Keith deposit is a large, low-grade, disseminated nickel sulphide deposit located 94 km NNE of Leinster in the northeastern Goldfields district of Western Australia. The main MKD5 orebody was discovered in 1968 and mining by WMC Resources Ltd. commenced in 1994. Currently, mining by conventional open pit methods occurs at the rate of 50 Mtonnes per annum of which 11 Mtonnes is processed. The orebody is remarkable for the abundance of hydrotalcite group minerals and related phases

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which frequently comprise up to 20 wt.% of run-of-mine ore. Of this group the most abundant species are iowaite, pyroaurite and stichtite. Previous studies on the occurrence and mineral chemistry of hydrotalcite group minerals at Mount Keith are sparse and generally unpublished. An examination of a low temperature alteration product of stichtite and pyroaurite was performed by Hudson and Bussell (1981), which lead to the description of mountkeithite, a pyroaurite type phase with an expanded interlayer. More recent work by the senior author on the mineralogy and distribution of chlorine in the orebody led to a detailed investigation of the mineral chemistry of the hydrotalcite group minerals, which were found to be the dominant hosts of chlorine in Mount Keith ore (Grguric, 1999). During the course of this work, a new chromium analogue of iowaite was identified from the high-grade core of the deposit, in diamond drillhole MKD194. The characterization and description of this mineral is the subject of this paper.

The new mineral, woodallite, is named after Roy Woodall (b. 1930), eminent Australian geologist, who was instrumental in the initiation and development of the nickel and alumina industries in Western Australia. The mineral and the name were approved by the IMA Commission on New Minerals and Mineral Names in 2000 (00-042). The type specimen is held in the collection of the South Australian Museum, Adelaide (G25116), with co-type material held in the Western Australian Museum (WAM M1.2000) and the Museum of Victoria (M46222).

Occurrence

An outline of the general geology and mineralization style of the Mount Keith Ni deposit (27°13′S 120°32′E) is given in Hopf and Head (1998), and a more detailed discussion of the alteration systematics is given in Rödsjö and Goodgame (1999). The MKD5 orebody (av. Ni grade 0.58%) is hosted by a series of Archaean komatiitic dunite and peridotite units which form part of the Agnew-Wiluna Belt, in central Western Australia. Disseminated Ni-Fe-sulphide minerals (dominated by pentlandite, pyrrhotite, millerite and pyrite) occur as an intercumulous phase in sites interstitial to former olivine grains, and the deposit falls into the Group 2B Ni sulphide deposit classification of Lesher (1989). The host cumulate dunites and peridotites have been completely serpentinized and partially carbonated after deformation and metamorphism to upper greenschist facies. This retrograde serpentinization/carbonation event was initiated by infiltration of H_2O-CO_2-rich fluids which exploited early cross-cutting (D1 or D2) faults/shears as conduits (Rödsjö and Goodgame, 1999; Rödsjö, 1999). The infiltrating fluids reacted with the ultramafic wall rock to produce a talc-magnesite assemblage proximal to these conduits, with enveloping magnesite-antigorite haloes. The most distal manifestation of this alteration process is a lizardite-brucite assemblage with associated hydrotalcite group minerals. With the exception of the hydrotalcite group minerals, this sequence of alteration assemblages is essentially identical to that described by Eckstrand (1975) in the Dumont serpentinite complex, Quebec. Petrogenetic indicators suggest hydrothermal alteration at Mount Keith occurred at temperatures below 320°C (Rödsjö and Goodgame, 1999).

The chlorine distribution in the orebody shows a distinct inverse relationship with the intensity of CO_2 metasomatism (Fig. 1). Talc-magnesite zones have whole-rock chlorine contents of <1000 ppm, while least-altered lizardite-brucite-hydrotalcite group zones typically contain 5−15,000 ppm Cl with local maxima of up to 25,000 ppm (Grguric, 1999). The chlorine enrichment is believed to have occurred via a hydrothermal ‘dry-up’ process whereby the dominant H_2O and CO_2 components of the infiltrating fluid were consumed in hydration and carbonation reactions with the host ultramafic, leaving a residual fluid enriched in Cl^- ions and other ionic species. This Cl^--rich brine reacted with magnetite and chromite in distal lizardite-brucite zones to produce iowaite and woodallite, respectively. In zones where the CO_3^{2-}-activity of the fluid was higher, chlorian pyroaurite and chlorian stichtite predominate. Due to the dearth of Al in the dunites and mesocumulate peridotites, hydrotalcite and related Al-rich species are rare. Iowaite and pyroaurite occur in the form of stockworks of cross-fibre veins; as microscale anastomosing veinlets; and as replacement rims on magnetite grains. Woodallite and stichtite occur as whorls and patches replacing former intercumulus chromite grains (Fig. 2). Relict chromite fragments are typically present in the whorls.

The type woodallite specimen was located in a high-Cl, lizardite-brucite alteration zone in diamond drill hole MKD194 at a depth of 226.0 m (Fig. 1). Associated minerals included

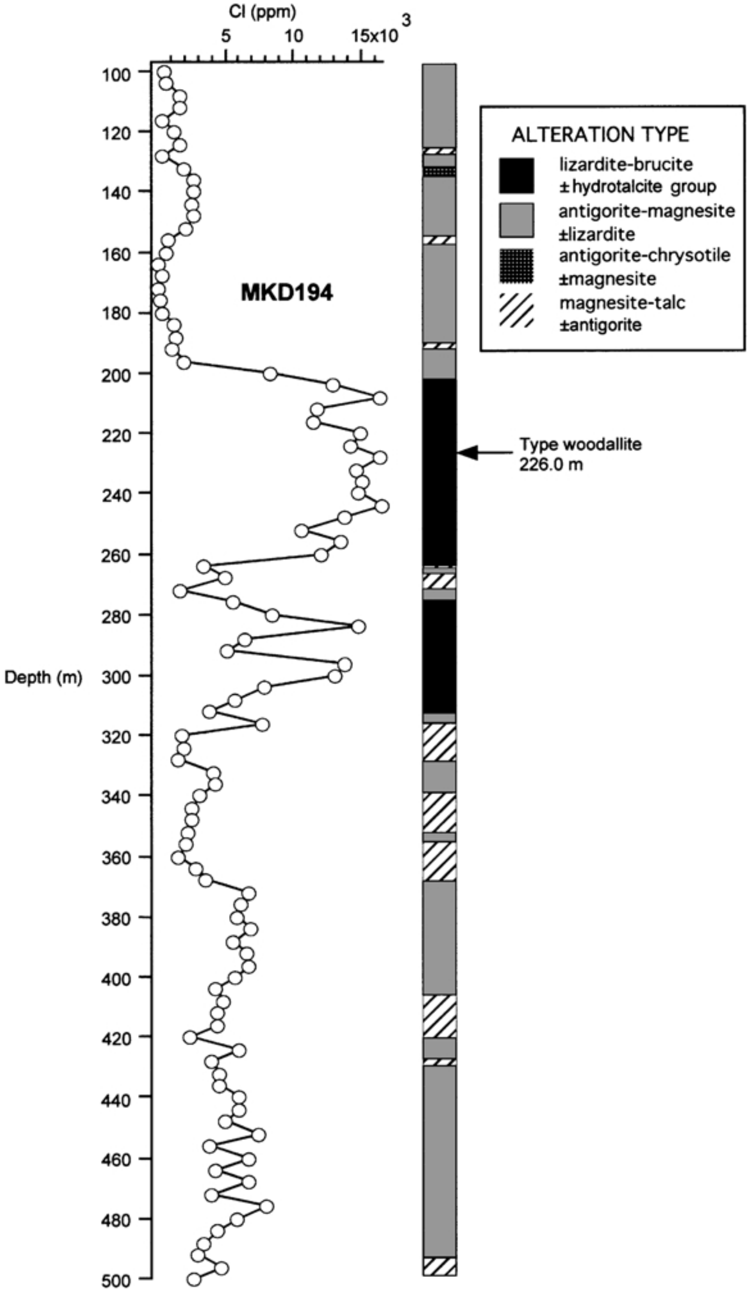

FIG. 1. Downhole profile of diamond drill hole MKD194 showing alteration lithology and whole-rock chlorine content (2 m composite samples). Position of the woodallite type specimen is indicated.

relict chromite, lizardite, brucite, iowaite, pentlandite, magnetite and tochilinite. It is likely that woodallite is relatively abundant in the high-Cl zones of the MKD5 orebody, though micro-analysis is necessary for positive identification because even small amounts of Cr substitution in iowaite result in a strong magenta colouration (Grguric and Pring, 1998).

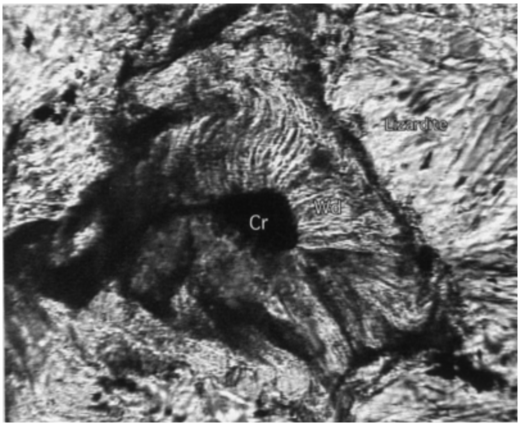

FIG. 2. Thin-section image of the woodallite type sample from drillhole MKD194 showing a whorl of woodallite (Wd) surrounding a core of relict chromite (Cr) in lizardite-rich serpentinite. Note the crenulation of the woodallite lamellae. Transmitted light. Field of view is 0.5 mm wide.

Hydrotalcite group minerals show anion-exchange behaviour related to the interlayer site (Miyata, 1983; Taylor *et al.*, 1991; Hansen and Bender-Koch, 1995). The selectivity of this site for divalent anions, and CO_3^{2-} groups in particular, is known to be considerably greater than for monovalent ions such as Cl^- (Miyata, 1983; Hansen and Taylor, 1991). For this reason Cl contents of hydrotalcite group minerals in the upper weathered zone of the MKD5 orebody tend to be very low or absent. Iowaite is replaced by pyroaurite or mountkeithite (Hudson and Bussell, 1981), while woodallite would be replaced by stichtite or Cr-mountkeithite.

Physical and optical properties

Woodallite occurs as anhedral whorls and compact clusters of minute platelets up to 6 mm across in black lizardite+brucite-altered dunite. Individual platelets are typically 5–100 μm in maximum dimension and are often curved or crenulated (Fig. 2). In this respect the mode of occurrence is identical to that of stichtite in the less Cl-enriched zones of the orebody.

Individual euhedral crystals are not observed because of the lack of open vugs and cavities in the ultramafic host. The colour of woodallite varies from deep magenta to purple and the streak is pale pink to white. The mineral is transparent with a resinous to waxy lustre, the obvious transparency being in marked contrast to that of stichtite when examined in hand specimen. In thin-section woodallite is pale pink. Optical properties were determined using Cargille immersion liquids in white light. Woodallite is uniaxial negative with $\omega = 1.555$ and $\varepsilon = 1.535$ and its pleochroism is distinctive from violet to pinkish lilac. No fluorescence was detected in either short wave (253 nm) or long wave (366 nm) ultraviolet light. Density was measured using the suspension method with tetrabromoethane as a heavy medium, diluted with chloroform. The measured density was found to be 2.062 ± 0.005 gm/cm^3, and the calculated density 2.023 gm/cm^3, based on the empirical formula. Calculated density based on the simplified end-member formula ($Mg_6Cr_2(OH)_{16}Cl_2{\cdot}4H_2O$) is 2.043 gm/cm^3. Woodallite has a Mohs hardness of 1.5–2, and as is characteristic of the entire hydrotalcite group, possesses a perfect basal {0001} cleavage. The cleavage lamellae are flexible but not elastic.

Chemistry

Electron microprobe analyses of woodallite were performed using a JEOL 8900 instrument at CSIRO Minerals in Clayton, Victoria, with additional analyses performed using a Cameca SX50 at CSIRO Division of Exploration and Mining in Floreat, Western Australia. An accelerating voltage of 15 kV was used with a specimen current of 0.067–0.069 mA. Spot size was set at 10 μm in order to reduce beam damage and volatilization. The WDS standards used were spinel (Mg,Al), magnesite (Mg), Cr metal, hematite (Fe), AgCl (Cl), pyrite (S), wollastonite (Si), Ni metal and jadeite (Na). Pure separates (200 mg) of the type material were obtained by hand-picking and analysed for total C using a Leco carbon analyser at Analabs Ltd. The measured C content was assigned to carbonate. Water and carbon dioxide were also measured semi-quantitatively during thermal analysis, discussed in the next section.

Analytical data are presented in Table 1. By analogy with the hydrotalcite group an average of the analyses (corrected for loss of volatiles) yielded the empirical formula; $Mg_{6.19}(Cr^{3+}_{1.21}Fe^{3+}_{0.51}Al^{3+}_{0.15})_{\Sigma 1.87}(OH)_{16}[Cl_{1.62}(CO_3)_{0.17}(SO_4)_{0.01}]{\cdot}4H_2O$. The formula was calculated assuming 16(OH) and charge balance between the interlayer and metal cations. Since sulphide inclusions were not observed at high magnification, low level S detected by microprobe was ascribed to interlayer sulphate. As is characteristic of hydrotalcite group minerals, considerable loosely bound interlayer water (Allmann and Donnay, 1969; Miyata, 1975) is lost during evacuation of the microprobe sample chamber (evident from the development of expanded basal partings), and during specimen heating by the electron beam, resulting in a systematic overestimation of the cation, Cl and S content. A corrected analysis is given in Table 1. The ideal end-member formula for woodallite is $Mg_6Cr_2(OH)_{16}Cl_2{\cdot}4H_2O$.

The atomic Mg:*R* ratio (where $R = Cr^{3+}+Fe^{3+}+Al^{3+}$) varies from 2.81 to 3.62 in the probe data set with an average of 3.31. Although the ideal ratio is 3, analyses of natural hydrotalcite group minerals frequently show ratios >3.0 (e.g. Taylor *et al*., 1991; Ashwal and Cairncross, 1997). In the case of woodallite this ratio was not modified when a magnesite probe standard was substituted for synthetic spinel. This supports the suggestion that the excess of Mg is not an analytical artefact, but as proposed by Ashwal and Cairncross for natural stichtites, may be due to minor substitution of Mg^{2+} into trivalent *R* sites.

Woodallite reacts with dilute acids affording a greenish-brown solution with little or no effervescence (in marked contrast to stichtite). The addition of silver nitrate solution to a dilute nitric acid solution of the mineral results in the formation of dense, white precipitate (AgCl). Before a blowpipe flame woodallite glows brightly but does not fuse, cooling to a dark-grey, magnetic mass.

Thermal analysis

Thermogravimetric analysis was performed using a Setaram Thermal Analyser coupled with a Balzers Thermostar mass spectrometer at CSIRO Minerals, Clayton. A pure sample (50 mg) of the type material was extracted by hand-picking and heated to 1400°C at a fixed rate of 10°C/min. A two-stage weight loss of 12.7% and 27.3% was recorded, occurring over the temperature ranges 25–300°C and 300–660°C, respectively. Based on the composition of the off gases measured by the mass spectrometer, the first weight loss was attributed to loss of interlayer water, chlorine-bearing species (e.g. HCl, HOCl, Cl_2) and some CO_2, while the second was attributed to loss of hydroxide water, remaining CO_2 and Cl species. The total weight loss of 40.0% compares favourably with the theoretical value of 42.7% for the measured composition of the natural material (Table 1), assuming complete volatilization of hydroxide water, interlayer water, CO_2 and Cl. On this basis, ideal end-member woodallite would show a weight loss of 43.2%. Braithwaite *et al*. (1994) noted a similar two-stage weight loss in weakly carbonatian iowaite from Palabora, and measured a total weight loss of 41%.

X-ray crystallography

X-ray powder diffraction patterns of woodallite were obtained using a Philips X'Pert diffractometer with Cu-$K\alpha_{1,2}$ radiation (λ = 1.54060 Å). Owing to the small grainsize and ease of deformation of the type material, a suitable crystal for single crystal XRD could not be obtained. A thin layer of powdered sample was floated onto a zero-background plate, and the diffraction pattern collected over a 2θ range of 5–90°. An indexed list of the resolvable reflections together with *d*-spacings is given in Table 2, and the powder pattern is shown in Fig. 3. A second diffraction data set was obtained using an Inel diffractometer equipped with a CPS120 position-sensitive detector. The powdered sample was packed into a 0.7 mm glass capillary which was rotated during pattern collection. This data set was used to measure relative intensities, as the zero-background plate was suspected of inducing preferred orientation. Peak intensity data for woodallite are given in Table 2. Least-squares refinement of the unit cell using the Philips powder pattern data gave a hexagonal (rhombohedral) cell with a = 3.103(2) Å, c = 24.111(24) Å, Z = 3/8 and cell volume 201.14 Å^3. On the basis of the pattern obtained, woodallite was found to be isostructural with the hydrotalcite group with space group $R\bar{3}m$ (Allmann, 1968; Allmann and Donnay, 1969; Braithwaite *et al*., 1994), and lattice parameters intermediate between those of stichtite and iowaite. The type material appears to be essentially pure, with only two minor impurity peaks detected at *d*-spacing 1.9243 Å and 1.4625 Å (Fig. 3).

Relationship to similar species

The trigonal-rhombohedral (space group $R\bar{3}m$) hydrotalcite group is a group of minerals with the general formula:

$$M_6^{2+}R_2^{3+}(OH)_{16}A{\cdot}4H_2O$$

TABLE 1. Electron microprobe analysis of woodallite.

Element	Range	Mean	Corrected[1]	Ideal[3]
Mg wt.%	21.75–28.90	25.90	22.90	21.93
Cr	10.32–11.31	10.81	9.56	15.64
Fe	4.56–5.19	4.86	4.30	–
Al	0.54–0.82	0.68	0.60	–
Cl	4.43–12.86	9.89	8.71	10.66
S	0.01–0.05	0.03	0.03	–
Si	0.00–0.02	0.01	0.00	–
Ni	0.00–0.04	0.01	0.00	–
Na	0.00–0.03	0.01	0.00	–
CO_3	n.a.	n.a.	1.52[2]	–
OH	n.a.	n.a.	41.40	40.93
H_2O	n.a.	n.a.	10.96	10.84
Total		52.20	100	100

[1] Analysis corrected to allow for H_2O + OH lost in high vacuum and under electron beam. Equivalent to $Mg_{6.19}(Cr_{1.21}Fe_{0.51}Al_{0.15})(OH)_{16}[Cl_{1.62}(CO_3)_{0.17}(SO_4)_{0.01}]\cdot 4H_2O$

[2] Based on total C content of 0.305 wt.% measured by Leco carbon analyser.

[3] Calculated analysis for end-member $Mg_6Cr_2(OH)_{16}Cl_2\cdot 4H_2O$

where $M = Mg^{2+}$, Ni^{2+}, Fe^{2+} but most commonly Mg; $R = Al^{3+}$, Fe^{3+}, Cr^{3+}, Mn^{3+}; and $A = CO_3^{2-}$, SO_4^{2-}, $2Cl^-$, $2OH^-$ (Allmann, 1970; Taylor, 1973; Hansen and Taylor, 1991). The basic structure of this group consists of positively-charged, brucite-type octahedral sheets alternating with H_2O- and *A* anion-occupied interlayers (Allmann, 1968; Allmann and Donnay, 1969; Taylor, 1973). The net positive charge in the brucite-type sheets is due to substitution of trivalent *R* cations for Mg, and structural refinements indicate that Mg and *R* cations are disordered over the octahedral sites (Bellotto *et al.*, 1996). The interlayer water molecules are weakly bound, and the systematics of *A* anion exchange behaviour are well established (Miyata, 1983; Taylor *et al.*, 1991; Hansen and Taylor, 1991; Hansen and Bender-Koch, 1995). Figure 4 shows the general compositional scheme for hydrotalcite group minerals with either Al, Fe or Cr *R* site cations. The composition of woodallite is consistent with a chromium analogue of iowaite or alternatively a chloride analogue of stichtite.

TABLE 2. X-ray powder diffraction data for woodallite.

I/I_0	d_{obs}	d_{calc}	*hkl*
100	8.0361	8.0369	003
48	4.0205	4.0185	006
1	2.6794	2.6790	009
3	2.6239	2.6235	012
5	2.3488	2.3478	015
6	2.0072	2.0092	0,1,12
1	1.7946	1.7948	1,0,10
2	1.6977	1.6987	0,1,11
1	1.5511	1.5519	$2\bar{1}0$
2	1.5237	1.5237	$2\bar{1}3$ 1,0,13
1	1.4479	1.4477	$2\bar{1}6$ 0,1,14
1	1.3394	1.3419	021 $2\bar{1}9$
1	1.3140	1.3117	024 1,0,16
0	1.2945	1.2946	205
0	1.2271	1.2282	$2,\bar{1},12$ 208
1	1.1475	1.1481	0,0,21 1,0,19

The *R* site compositions of Mount Keith hydrotalcite group minerals are plotted in ternary Al-Fe-Cr-space in Fig. 5. Hydrotalcite group minerals in the Mount Keith deposit form as a result of hydrothermal alteration of spinels in a Mg-rich ultramafic host. Consequently, their *R* site composition is controlled by the composition of the precursor spinel phase which is either primary magmatic chromite, or magnetite generated during serpentinization of olivine. Stichtite and woodallite

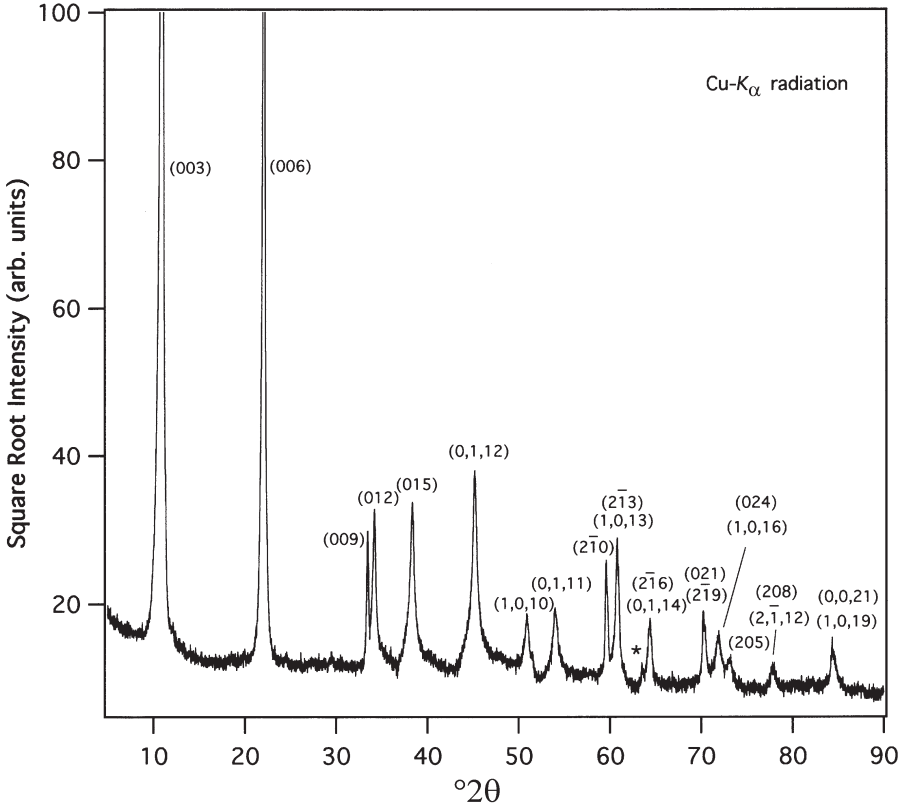

FIG. 3. X-ray powder diffraction pattern of woodallite. Impurity peak is indicated by an asterisk.

are found to contain a significant Al component due to the presence of a hercynitic component in the precursor magmatic chromite (Barnes, 1998), while pyroaurite and iowaite derived from magnetite are essentially Al free (Fig. 5). Ashwal and Cairncross (1997) compared the *R* site composition of stichtites from 14 localities with the composition of associated relict spinels and in several cases found the stichtites to be depleted in Al relative to the precursor chromite or 'ferritchromite'. A similar trend is observed for Mount Keith woodallite and stichtite (Fig. 5).

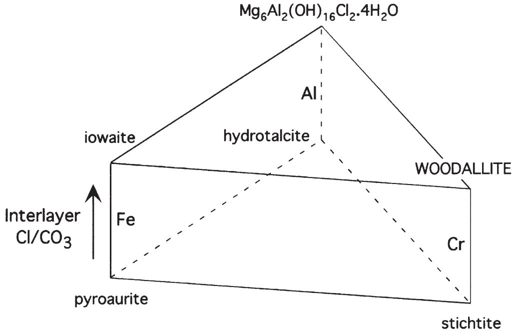

FIG. 4. Compositional scheme for hydrotalcite group minerals with *R* site Al, Fe and Cr (apices of triangle). Vertical axis represents interlayer anion composition.

Most hydrotalcite group minerals show a predominance of divalent *A* anions in the interlayer site, which is probably related to the aforementioned higher selectivity of this site for divalent anions (CO_3^{2-} in particular) over monovalent species (Miyata, 1983; Hansen and Taylor, 1991). Woodallite and iowaite are notable exceptions, and the presence of a dominant chloride component in the interlayer suggest formation under conditions of very high fluid Cl^- activities and or very low CO_3^{2-} activities. The facility with which interlayer Cl^- is

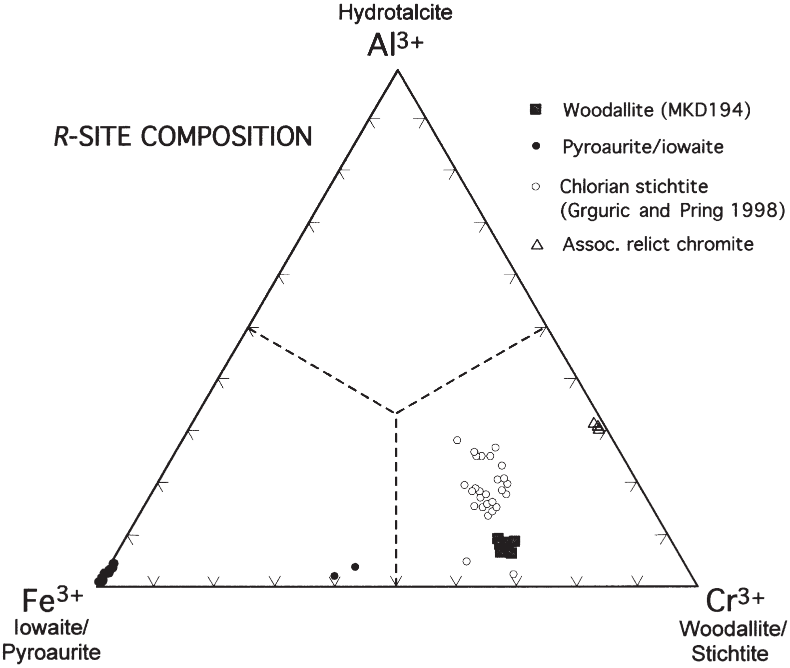

FIG. 5. *R* site compositions of Mount Keith hydrotalcite group minerals in ternary Al-Fe-Cr space. Compositions of relict chromites associated with woodallite and stichtite are also plotted.

exchanged for carbonate and sulphate ions at low temperatures means that in the weathering environment iowaite and woodallite would be rapidly altered to pyroaurite and stichtite, or sulphate equivalents. As an illustration, iowaite in Mount Keith ore is converted to sulphate-pyroaurite and pyroaurite in the Mount Keith grinding and flotation circuit, which involves exposure to sulphate-rich (9500 ppm SO_4^{2-}) process water for less than a few hours at ambient temperature (Grguric, 1999). Although the chloride ion content of the process water is very high (32,000 ppm), Cl^- in the interlayer is preferentially exchanged for divalent anions. After several weeks, finely powdered woodallite shows an increase in effervescence when dissolved in dilute acid suggesting that where the surface area of the sample is high, partial alteration to stichtite can occur simply by exposure to moist air.

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