# The decomposition of konyaite: importance in $CO_2$ fixation in mine tailings

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# ABSTRACT

The sodium-magnesium hydrated double salt konyaite, Na<sub>2</sub>Mg(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O, has been studied by singlecrystal X-ray diffraction and thermogravimetry on synthetic samples and by quantitative X-ray diffraction utilizing the Rietveld method on natural samples from the Mount Keith mine, Western Australia. Konyaite crystallizes in space group  $P2_1/c$ , with the cell parameters: a = 5.7594(10), b = 23.914(4), c = 8.0250(13) Å,  $\beta = 95.288(9)^\circ$ , V = 1100.6(3) Å<sup>3</sup> and Z = 4. The crystal structure has been refined to  $R_1 = 3.41\%$  for 2155 reflections [F<sub>0</sub>>4 $\sigma$ (F<sub>0</sub>)] and 6.44\% for all 3061 reflections, with all atoms located.

Quantitative phase analysis utilizing the Rietveld method was undertaken on five samples of konyaite-bearing mine tailings from the Mount Keith Nickel Mine, Western Australia. Konyaite was found to decompose over time and after 22 months had transformed to other sulphate and amorphous phases. Blödite did not increase in any of the samples indicating that konyaite may not always transform to blödite. Over the same time frame, synthetic konyaite completely decomposed to a mixture of thenardite (Na<sub>2</sub>SO<sub>4</sub>), hexahydrite (MgSO<sub>4</sub>·6H<sub>2</sub>O), blödite (Na<sub>2</sub>Mg(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O) and löweite (Na<sub>12</sub>Mg<sub>7</sub>(SO<sub>4</sub>)<sub>13</sub>). Detection of konyaite and other Mg-rich sulphates is important in terms of CO<sub>2</sub> fixation. Magnesium bound to sulphate mineral phases reduces the overall potential of tailings piles to lock up atmospheric carbon in Mg carbonates, such as hydromagnesite. Amorphous sulphates are also highly reactive and may contribute to acid mine drainage if present in large quantities, and may dissolve carbonate phases which have already sequestered carbon.

**Keywords:** konyaite, synthesis, decomposition, crystal structure, mine tailing, Mount Keith, Rietveld method, carbon sequestration, double salt, acid mine drainage, Mars, Australia.

## Introduction

ATMOSPHERIC CO<sub>2</sub> is fixed within secondary carbonate minerals in the mineral waste from some ultramafic mines (Wilson *et al.*, 2006, 2009). In tailings rich in sulphide minerals, secondary sulphate phases commonly form (e.g. Agnew and Taylor, 2000; Jambor *et al.*, 2000; Acero *et al.*, 2007). Both secondary Mg-sulphate

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minerals and Mg-carbonate minerals form by weathering of Mg-bearing gangue minerals in ultramafic mineral waste (Dipple *et al.*, 2009). Only the Mg-carbonate minerals trap and store  $CO_2$  and as a consequence the formation of secondary sulphate minerals is deleterious for trappping atmospheric  $CO_2$ .

Crystallographic methods of quantifying  $CO_2$  fixation within minerals require that all phases are detectable in X-ray powder diffraction patterns. Hydrous sulphate minerals, like those that form in some ultramafic mine tailings, are subject to phase changes and can become X-ray amorphous as a result of changes in relative humidity and temperature (e.g. Chipera and Vaniman, 2007).

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Should the decomposition of sulphate minerals to X-ray amorphous phases prove to be more common than previously thought, their presence may impede quantification of CO<sub>2</sub> trapping within naturally occuring ultramafic formations and engineered environments like mine tailings storage facilities. Furthermore, this may have an impact upon remote mineralogical studies on the Martian surface, where Mg-sulphate minerals are thought to be common (e.g. Feldman *et al.*, 2004).

Konyaite, Na<sub>2</sub>Mg(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O, was first described by van Doesburg et al. (1982) from the Great Konya Basin in Turkey. This mineral has only been recorded from several localities, although experimental observations suggest that it should be more common than its decomposition product blödite, Na2Mg(SO4)2·4H2O (e.g. Keller et al., 1986; Leduc et al., 2009). Little is known about the stability of konyaite and its role in the geological environment. Van Doesburg et al. (1982) suggested that konvaite was a metastable phase, although this was questioned by Timpson et al. (1986). The ease with which this mineral can be precipitated in the laboratory (e.g. van Doesburg et al., 1982; Leduc et al., 2009) and its extreme rarity compared to blödite raises questions about the ultimate fate of konyaite in the environment.

Konyaite forms as a rare component within efflorescent crusts of halide and sulphate minerals at the surface of serpentine-rich tailings at the waste storage facility at the Mount Keith Nickel Mine, Western Australia (Fig. 1). Secondary hydromagnesite,  $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ , is known to be trapping and storing atmospheric  $CO_2$  at Mount Keith (Dipple *et al.*, 2009).



FIG. 1. Efflorescent crusts of hydromagnesite and of halide and sulphate minerals on the surface of serpentinerich tailings, Mount Keith, Western Australia.

Hydromagnesite occurs in significant abundance within and just below the efflorescent crusts and is present at lesser abundances at depth within the tailings (Dipple *et al.*, 2009; Wilson, 2009). Because pure konyaite could not be separated from the crusts at Mount Keith, efforts were made to synthesize sufficient quantities for analysis. Here we demonstrate the decomposition of the double salt, konyaite, to several combinations of less hydrous and single-salt phases. Both konyaite and blödite from the Mount Keith Nickel Mine are shown to decompose to X-ray amorphous phases, which have implications for detection of these minerals on Mars and for measurement of  $CO_2$  trapping in ultramafic rocks on Earth.

## Secondary minerals at the Mount Keith mine

The MKD5 orebody at the Mount Keith Nickel Mine in the North Eastern Goldfields district of Western Australia is the largest nickel producer in Australia (Grguric, 2003). The deposit at Mount Keith occurs in the NNW/SSE-trending Agnew-Wiluna greenstone belt in the Archaean Yilgarn Craton (Hill et al., 1990). Conventional open-pit mining methods are practised at Mount Keith (Grguric, 2003). The mining operation produces ~350,000 tonnes of greenhouse gases (cited as CO<sub>2</sub> equivalent) and ~11 Mt of ultramafic tailings each year (BHP Billiton, 2005). Tailings consist primarily of antigorite and lizardite with hydrotalcite-group minerals (i.e. iowaite and woodallite with uncommon pyroaurite, stichtite, and mountkeithite - Mills et al., 2011). Minor brucite, talc, magnetite, chromite, quartz, magnesite, dolomite, calcite and trace vermiculite and Ni-, Fe- and Cusulphide minerals are common. Dipple et al. (2009) and Wilson (2009) describe efflorescent crusts of halide and sulphate minerals which occur at the surface of tailings throughout the wastestorage facility at Mount Keith. They found that halite, hexahydrite and blödite are the dominant phases in the efflorescences. Minor amounts of konyaite, löweite, epsomite, and gypsum are less common, while secondary hydromagnesite occurs within and just below the efflorescent crusts and is preserved at depth within the tailings upon burial beneath freshly deposited tailings.

### Experimental

# Synthesis

Konyaite was synthesized by mixing 5.0 g of MgSO<sub>4</sub>·7H<sub>2</sub>O with 5.0 g of Na<sub>2</sub>SO<sub>4</sub> in 200 ml of

distilled water in a 250 ml Pyrex beaker. This beaker was placed in a larger beaker containing water to better regulate the temperature and kept at  $35(2)^{\circ}$ C on a hot plate at between ~50-70% relative humidity. The initial pH was 9.04, with the pH decreasing at a rate of ~0.7 units/day. The reaction was complete after 4 days and the pH had declined to 6.29 within 24 h of completion. Konvaite crystallized as an intergrown colourless mass of platy crystals, with {010} as the dominant form. Small white opaque balls of konyaite up to 0.5 mm formed on the surface of the platy mass after the sample was removed from the hot plate. A small amount of thenardite (<5 wt.%), Na<sub>2</sub>SO<sub>4</sub>, was observed in bulk powder patterns, but it was possible to select small amounts of pure konyaite for further analyses, as both minerals have different morphologies. Pure konyaite was also confirmed via powder X-ray diffraction (XRD).

Konyaite was also synthesized using a method similar to that described by van Doesburg *et al.* (1982) and Leduc *et al.* (2009). 1.3 g of MgSO<sub>4</sub>·7H<sub>2</sub>O was mixed with 1.3 g of Na<sub>2</sub>SO<sub>3</sub> in 50 ml of distilled water in a covered Petri dish and kept at  $35(2)^{\circ}$ C on a hot plate. The initial pH was 8.51, with the pH decreasing to 6.19 just under 24 hours before completion. The reaction was complete after 3 weeks, with konyaite crystals forming on the underside of the lid. The former method is preferred due to the ease of measurement of the pH and the ability to obtain crystals suitable for structure analysis in under a week.

# Single-crystal methods

The single-crystal study was completed using a Bruker X8 ApexII single-crystal diffractometer at the Department of Chemistry of the University of British Columbia. Crystals obtained from the synthesis were intergrown, so a large platy {010} crystal was dissected using a scalpel. A konvaite fragment 0.20 mm  $\times$  0.10 mm  $\times$  0.05 mm in size was used for collection of intensity data at 293 K (Table 2). The intensity data were processed with the Bruker Apex program suite, with data reduction using the SAINT program (Bruker, 2003) and absorption correction by the multi-scan method using SADABS (Bruker, 2003). In the final stages of manuscript completion the structure of konyaite was published by Leduc et al. (2009); therefore, we give here only a brief treatment of our single-crystal results which are consistent with those of Leduc et al. (2009), for comparison.

# Thermogravimetric analysis

Simultaneous thermogravimetric analyses (TGA) were obtained from 13.09 mg of hand-picked "fresh" synthetic material and 19.73 mg of 22 month old synthetic material. The samples were analysed under N<sub>2</sub> gas using a Perkin Elmer Pyris 6 thermogravimetric analyser (Department of Chemistry, The University of British Columbia) over the temperature range  $30-900^{\circ}$ C, with a heating rate of 5°C/min.

## Quantitative X-ray powder diffraction

Quantitative phase analysis (OPA), utilizing the Rietveld method (Rietveld, 1969), was undertaken on five samples of konyaite-bearing mine tailings from the Mount Keith Nickel Mine, Western Australia. These samples were collected in September and October of 2006 (Southern Hemisphere spring) from depths of either 0-10 cm below the surface of the tailings deposits (06MKG2-9-1, 06MKG8-3-1, 06MKG8-7-1, 06MKG10-9-1) or from 2-5 cm below the surface of the tailings (06MK40-4). In all cases, gangue minerals were thoroughly cemented by secondary efflorescent minerals. Samples were left in a drying hood for a minimum of 1 week and were then homogenized mechanically with a spatula. Samples that were stored in our laboratory were exposed to ambient conditions of temperature and relative humidity. Temperature in our laboratory varied between 20 and 30°C and ambient relative humidity in Vancouver, BC, Canada varies between approximately 60% and 80% over the course of a typical year (Environment Canada, 2010). From each dried and homogenized sample, a 50 to 100 g sample was taken and pulverized using a tungsten carbide ringmill. 3 g aliquots of pulverized sample were weighed to a precision of  $\pm 0.001$  g. A 10 wt.% spike of annealed synthetic fluorite was added to each 3 g aliquot. The spiked aliquots were then ground for 10 min in a McCrone micronizing mill to reduce the mean grain size and to ensure homogenization. Grinding was undertaken under anhydrous ethanol using agate grinding elements. Ground samples were dried at room temperature under a fume hood and were disaggregated using an agate mortar and pestle once dry.

A specimen was prepared from each sample by mounting the powder into a back-loading aluminium cavity holder using the method described by Raudsepp and Pani (2003). X-ray powder diffraction data were collected on a Siemens D5000  $\theta$ -2 $\theta$  diffractometer equipped with a VÅNTEC-1 detector. The long, finefocus Co X-ray tube was operated at 35 kV and 40 mA. Data for Rietveld refinement were collected with a step size of 0.02°2 $\theta$  and counting time of 1 s/step over a range of 3–80°2 $\theta$ .

Rietveld refinements were completed using Rietveld refinement software TOPAS 3 (Bruker, 2004) using the fundamental-parameters approach (Cheary and Coelho, 1992). Sources of crystalstructure data for mineral phases in the tailings samples are listed in Table 1. The method of Wilson et al. (2006) was used to compensate for structural disorder in lizardite and antigorite. Peak intensities for each serpentine mineral were extracted using the Pawley method (Pawley, 1981), independent of atomic scattering, from powder XRD patterns of high-purity standards. Fourth-order symmetrized harmonics were used to model anisotropic peak shape in lizardite and antigorite (Järvinen, 1993). The weight-percent abundance of antigorite and lizardite are given together, because the method of Wilson et al. (2006) cannot quantify more than one disordered phase per sample and cannot account for additional, amorphous phases. The woodallite in the mine tailings was fitted using a modified structure based on that of iowaite (Braithwaite *et al.*, 1994). The lattice parameters of iowaite were replaced with those given for woodallite by Grguric *et al.* (2001) and the Fe<sup>3+</sup> in the structure was replaced with  $Cr^{3+}$ .

Second or third-order Chebychev polynomials were used to model the background and a 1/x term was included to assist in fitting the background curve at small diffraction angles. Cell parameters and Lorentzian crystallite size were refined for all phases and zero error was refined for each powder XRD diffraction pattern. The method of Brindley (1945) was used to correct for micro-absorption contrast between phases, assuming a mean particle radius of 2.5 µm. Preferred orientation of hydrotalcite-group minerals was modelled using the March-Dollase correction (March, 1932; Dollase, 1986).

# Qualitative powder XRD

Powder XRD data for qualitative analyses were collected using a Bruker D8 Advance diffractometer at the Department of Earth and Ocean Sciences, The University of British Columbia, using Co- $K\alpha$  radiation. Hand-picked konyaite was crushed lightly in ethanol to avoid a potential phase transition and dispersed on a zero-background plate. Data were collected at 40 kV and

Mineral	Formula	Source
Antigorite	Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	Uehara (1998)
Blödite	$Na_2Mg(SO_4)_2 \cdot 4H_2O$	Vizcayno and Garcia-Gonzalez (1999)
Brucite	Mg(OH) <sub>2</sub>	Catti et al. (1995)
Calcite	CaCO <sub>3</sub>	Maslen et al. (1995)
Dolomite	$CaMg(CO_3)_2$	Ross and Reeder (1992)
Fluorite	CaF <sub>2</sub>	Batchelder and Simmons (1964)
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	Cole and Lancucki (1974)
Halite	NaCl	Nickels et al. (1949)
Hexahydrite	MgSO <sub>4</sub> ·6H <sub>2</sub> O	Zalkin et al. (1964)
Hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	Akao and Iwai (1977)
Iowaite	$Mg_{6}Fe_{2}^{3+}(OH)_{16}Cl_{2}\cdot 4H_{2}O$	Braithwaite et al. (1994)
Konyaite	$Na_2Mg(SO_4)_2 \cdot 5H_2O$	This study
Lizardite-1T	$Mg_3Si_2O_5(OH)_4$	Mellini and Viti (1994)
Magnesite	MgCO <sub>3</sub>	Markgraf and Reeder (1985)
Magnetite	$Fe^{2+}Fe_2^{3+}O_4$	Tsukimura et al. (1997)
Quartz	SiO <sub>2</sub>	Glinnemann et al. (1992)
Thenardite	$Na_2SO_4$	Hawthorne and Ferguson (1975)
Vermiculite	(Mg,Fe,Al) <sub>3</sub> (Al,Si) <sub>4</sub> O <sub>10</sub> ·4H <sub>2</sub> O	Shirozu and Bailey (1966)
Woodallite	$Mg_6Cr_2(OH)_{16}Cl_2 \cdot 4H_2O$	Grguric et al. (2001), Braithwaite et al. (1994

TABLE 1. Sources of crystal-structure data for Rietveld refinement.

40 mA. The sample was covered (to avoid contamination) and kept at room temperature and 40% relative humidity between sequential runs. Data were analysed using the *ICDD PDF-4+* 2008 database using the program *DIFFRAC*<sup>plus</sup> *EVA 14* (Bruker, 2008).

# **Experimental Results and Discussion**

#### Single-crystal structure determination

The crystal structure of konyaite was solved in  $P2_1/c$  (No. 14), by direct methods using *SHELXS*-97 (Sheldrick, 2008) and subsequent Fourier and difference Fourier syntheses, followed by anisotropic full-matrix least-squares refinements on  $F^2$ . The final model with 10 hydrogen atoms determined was  $R_1 = 3.41\%$  for 2155 reflections  $[F_0>4\sigma(F_0)]$  and 6.44% for all 3061 reflections. As there are only minor differences between these results and those of Leduc *et al.* (2009), detailed description is not warranted. The refined atomic coordinates, site occupancies and displacement parameters are given in Table 3 and polyhedral bond distances in Table 4. Note that the cell parameters for the crystal studied here [a =5.7594(10), b = 23.914(4), c = 8.0250(13) Å,  $\beta =$ 95.288(9)°, V = 1100.6(3) and Z = 4] are smaller than all those given previously for konyaite.

#### Quantitative phase analysis

Rietveld refinement results for five samples of konyaite-bearing mine tailings from Mount Keith are given in Table 5 and in Figs 2 and 3. Refinements were done on (1) an aliquot taken from a subsample of each sample (sub1-1) all of which were pulverized and analysed within several months of collection; (2) a second aliquot of the same subsample (sub1-2), which was analysed 1.5 to 2 y after being pulverized; and (3) an aliquot from a second, different subsample (sub2-1) of each tailings sample,

TABLE 2. Summary of data-collection conditions and refinement parameters for konyaite.

<b>Crystal data</b> Cell parameters Space group	a = 5.7564(10)  Å b = 23.914(4)  Å c = 8.0250(13)  Å $\beta = 95.288(9) ^{\circ}$ $V = 1100.6(3) \text{ Å}^{3}$ Z = 4 $P2_{1}/c$
Data collection	
Temperature (K) $\lambda$ (Mo- $K\alpha$ ) Crystal shape, size <sup>°20</sup> max Reflection range Total no. of reflections No. of unique reflections No. of reflections, $F > 4\sigma(F)$ Absorption correction $R_{merg}$ on $F^2$	293(2) 0.71073 plate, 0.20 mm × 0.10 mm × 0.05 mm 59.4 $-7 \le h \le 7; -29 \le k \le 33; -11 \le l \le 11$ 14519 3061 2155 $\mu = 0.687 \text{ mm}^{-1}$ 0.0537
Refinement	
No. of parameters refined	204
$R_1, F \ge 4\sigma(F)$ $R_2$ all data	0.0341
$WR_2$ ( $F^2$ )*, all data	0.0861
GoF	0.968
$\Delta \sigma_{\min}, \ \Delta \sigma_{\max} \ (e/\AA^3)$	-0.362, 0.347

\*  $w = 1/[\sigma^2(F_o^2) + (0.0484P^2 + 0P)], P = [2F_c^2 + Max(F_o^2, 0)]/3.$ 

for konyaite.	
(Å <sup>2</sup> )	
parameters	
lisplacement	
and e	
coordinates	
Atomic	
TABLE 3.	

Atom	X	у	И	$U_{\mathrm{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
S1	0.21295(9)	0.509125(19)	0.29840(7)	0.01293(13)	0.0129(3)	0.0113(2)	0.0144(3)	-0.00046(18)	0.0004(2)	0.00049(17)
S2	0.49462(10)	0.332195(19)	0.17467(7)	0.01510(14)	0.0137(3)	0.0133(2)	0.0180(3)	0.00038(18)	-0.0003(2)	-0.00028(18)
MgI	0.03518(13)	0.64080(3)	0.31838(9)	0.01360(18)	0.0123(4)	0.0127(3)	0.0157(4)	-0.0006(3)	0.0007(3)	0.0000(3)
Nal	0.27761(18)	0.45040(3)	-0.04907(12)	0.0240(2)	0.0281(6)	0.0207(4)	0.0218(5)	-0.0023(4)	-0.0057(4)	-0.0002(4)
Na2	-0.31311(18)	0.44526(4)	0.34401(12)	0.0244(2)	0.0289(6)	0.0230(4)	0.0207(5)	0.0006(4)	-0.0005(4)	-0.0015(4)
01	0.2066(3)	0.56761(5)	0.3603(2)	0.0181(3)	0.0201(9)	0.0130(6)	0.0207(8)	-0.0032(6)	-0.0015(7)	0.0035(6)
02	-0.2828(3)	0.60147(6)	0.3067(2)	0.0176(3)	0.0133(9)	0.0187(7)	0.0208(9)	0.0020(6)	0.0014(7)	-0.0022(6)
03	0.0403(3)	0.62514(7)	0.0618(2)	0.0208(4)	0.0193(10)	0.0253(8)	0.0183(9)	0.0037(6)	0.0047(8)	0.0043(7)
04	0.3462(3)	0.68275(6)	0.3573(2)	0.0212(4)	0.0191(9)	0.0171(7)	0.0266(10)	0.0007(6)	-0.0019(8)	-0.0029(6)
05	0.2715(3)	0.47355(6)	0.4428(2)	0.0248(4)	0.0300(11)	0.0189(7)	0.0244(9)	0.0082(6)	-0.0035(8)	0.0004(6)
06	0.3943(3)	0.50444(6)	0.1832(2)	0.0229(4)	0.0213(10)	0.0250(7)	0.0237(9)	-0.0066(6)	0.0091(8)	-0.0022(6)
07	-0.0127(3)	0.49378(6)	0.2132(2)	0.0222(4)	0.0167(9)	0.0225(7)	0.0259(9)	-0.0009(6)	-0.0061(8)	-0.0030(6)
08	-0.1336(3)	0.71310(6)	0.2410(2)	0.0244(4)	0.0292(11)	0.0177(7)	0.0251(10)	-0.0017(7)	-0.0046(9)	0.0055(7)
60	0.0042(4)	0.65095(8)	0.5725(2)	0.0303(4)	0.0196(11)	0.0489(10)	0.0233(10)	-0.0147(8)	0.0058(8)	-0.0117(8)
010	0.6961(3)	0.29487(6)	0.1884(2)	0.0252(4)	0.0210(10)	0.0177(7)	0.0356(11)	-0.0043(7)	-0.0045(8)	0.0061(6)
011	0.2895(3)	0.30311(6)	0.0934(2)	0.0253(4)	0.0221(10)	0.0234(8)	0.0285(10)	0.0042(7)	-0.0083(8)	-0.0076(6)
012	0.5440(3)	0.38201(6)	0.0786(2)	0.0263(4)	0.0218(10)	0.0176(7)	0.0402(11)	0.0102(7)	0.0064(8)	-0.0004(6)
013	0.4449(3)	0.35015(7)	0.3428(2)	0.0283(4)	0.0215(10)	0.0439(10)	0.0194(10)	-0.0044(7)	0.0014(8)	0.0056(7)
HI	-0.214(5)	0.7134(12)	0.143(3)	0.039(9)						
H2	-0.138(5)	0.6461(15)	0.607(5)	0.068(12)						
H3	-0.290(6)	0.5810(12)	0.391(4)	0.045(10)						
H4	0.180(5)	0.6215(13)	0.023(4)	0.047(10)						
H5	0.434(6)	0.6798(14)	0.460(4)	0.055(10)						
H6	-0.411(4)	0.6201(11)	0.297(4)	0.036(8)						
H7	0.065(7)	0.6791(13)	0.638(5)	0.071(12)						
H8	-0.178(6)	0.7398(12)	0.308(4)	0.060(11)						
6H	0.330(7)	0.7186(10)	0.349(5)	0.065(11)						
H10	-0.029(7)	0.6539(14)	0.004(5)	0.073(13)						

# DECOMPOSITION OF KONYAITE

S1	05	1.4520(16)	Na1	O6	2.3166(18)
	O7	1.4585(17)		O7	2.3397(18)
	O6	1.4615(19)		O12	2.4061(18)
	O1	1.4857(14)		O2	2.4133(19)
		× /		O6	2.504(2)
<s-o></s-o>		1.464		O3	2.567(2)
				O7	2.991(2)
S2	O10	1.4602(17)			
	O12	1.4610(16)	<na-o></na-o>		2.505
	O13	1.4687(19)			
	O11	1.4708(17)	Na2	O7	2.404(2)
				O1	2.415(2)
<s-o></s-o>		1.465		O6	2.4710(19)
				O5	2.5843(19)
Mg1	01	2.0223(15)		O13	2.667(2)
	08	2.0515(17)		O5	2.675(2)
	O4	2.0517(18)		O12	2.679(2)
	O2	2.0532(18)		O9	2.948(2)
	09	2.078(2)			
	03	2.0958(19)	<na-o></na-o>		2.605
<mg-o></mg-o>		2.059			

TABLE 4. Polyhedral bond distances (Å) in konyaite.

which was both pulverized and analysed ~2 y after collection. It is expected that Rietveld refinement results for sub1-1 aliquots of each sample (pulverized and analysed in early 2007) are more likely to give modal abundances close to those observed in the field.

In the sub1-1 aliquots of all five samples, serpentine minerals (plus any unidentifiable amorphous content) were present at abundances of 63.5 to 78.7 wt.% (Table 5, Fig. 4). Three samples contained hexahydrite at abundances of 1.0-5.1 wt.%. Blödite and konyaite were detected in the five samples at abundances of 0.6 to 6.4 wt.% and 1.6 to 3.1 wt.%, respectively. Hydromagnesite was not detected in three of the samples, but was present at 2.4 and 5.9 wt.% in the remaining two.

Samples 06MKG2-9-1 and 06MKG10-9-1 (sub1-1) contain 0.9 wt.% and 2.2 wt.% of CO<sub>2</sub>, which has been mineralized as hydromagnesite (Table 5). These two samples contain sulphate minerals with enough Mg to mineralize an additional 1.6 wt.% and 0.3 wt.% of CO<sub>2</sub>, respectively. In the remaining three samples, which contain no hydromagnesite, sequestration potentials between 0.5 wt.% and 1.2 wt.% CO<sub>2</sub> have been lost to precipitation of sulphate minerals.

The sub1-2 aliquots (analysed 1.5 to 2 y after being pulverized) had significantly different abundances of sulphate minerals from those measured in the sub1-1 aliquots in 2007. Notably, konyaite was no longer detectable in any of the five samples. Furthermore, the amount of blödite did not increase in any of the samples (contrary to the observations of van Doesburg et al., 1982). In one sample, 06MKG2-9-1, instead of producing more blödite, the decomposition of 1.6 wt.% konvaite appears to have resulted in 1.9 wt.% of thenardite and an additional 1.6 wt.% of hexahydrite. The relative error for measurements of phases below ~6 wt.% increases rapidly under the data collection conditions used in our laboratory (Raudsepp et al., 1999; Dipple et al., 2002; Wilson et al., 2006) and can be as high as 50% relative on lowabundance phases. Thus, these results are broadly consistent with decomposition of konyaite to thenardite + hexahydrite. In the sub1-2 aliquots of the other four samples, the amount of blödite appears to have decreased in one sample (06MK40-4) and blödite was no longer detectable in the others (i.e. 06MKG8-3-1, 06MKG8-7-1 and 06MKG10-9-1). In the three samples in which hexahydrite was initially present (06MKG2-9-1, 06MKG8-3-1 and

Sample	90 —	MKG2-9	-1	90 —	MKG8-3		- 00	MKG8-7		— 06N	AKG10-9	-1	- 00	6MK40-4	
Subsample and aliquot Ground Analysed	sub1-1 2007 2007	sub1-2 2007 2008	sub2-1 2008 2008	sub1-1 2007 2007	sub1-2 2007 2008	sub2-1 2008 2008	sub1-1 2007 2007	sub1-2 2007 2008	sub2-1 2008 2008	sub1-1 2007 2007	sub1-2 2007 2008	sub2-1 2008 2008	sub1-1 2007 2007	sub1-2 2007 2008	sub2-1 2008 2008
Serpentine group $\pm$ amorphous	63.5	64.9	56.4	73.0	72.0	75.0	78.7	79.6	76.6	77.9	82.6	78.6	77.7	83.0	81.6
Blödite Gypsum Hexahydrite Konyaite Thenardite	6.4 5.1 1.6	6.4 6.7 1.9	15.1 1.9	2.5 0.4 5.0 1.6	1.6 6.3	2.8 3.6	0.9 1.0 3.1	1.2	1.2	0.6			3.0	0.5	0.4
Calcite Dolomite Hydromagnesite Magnesite	3.7 2.4 0.7	2.8 1.4 0.6	2.0 2.4 1.3	1.7	2.5 2.9	2.5 2.5	0.2 0.7 4.7	2.2 5.1	0.5 3.2 4.6	5.9 0.6	4.0 0.9	1.2 4.9 0.6	1.1 5.7	2.1 4.3	2.2 5.6
Brucite Halite Hydrotalcite group Magnetite and chromite Quartz Vermiculite	10.7 2.3 3.3 0.4	$13.2 \\ 1.0 \\ 1.0 $	18.0 1.4 1.5	6.5 1.1 3.6	5.8 1.3 3.6	5.4 2.0 3.1 3.0	4.5 2.6 0.5	5.8 3.0 0.2	6.8 1.8 0.3	7.0 3.7 2.1 0.1	7.3 3.0 2.1 0.1	8.2 3.8 2.5 0.1	3.3 2.2 0.3 0.3	$\begin{array}{c} 0.5 \\ 3.7 \\ 2.2 \\ 3.5 \\ 0.1 \\ 0.1 \end{array}$	4.2 3.2 0.2 0.2
Total $R_{Nr_{\rm T}^2}$ $R_{D}$	100.0 4.9 3.1 2.1	100.0 5.9 3.3 2.0	100.0 5.1 2.9 2.3	100.0 4.5 3.1 2.1	100.0 6.6 4.2 1.4	100.0 5.2 3.3 2.0	100.0 4.1 3.0 2.1	100.0 7.0 4.7 1.2	100.0 4.7 3.1 2.2	100.0 4.2 3.0 2.2	100.0 5.1 3.2 2.0	100.0 5.4 3.4 2.0	100.0 3.9 3.0 2.2	100.0 4.6 3.1 2.2	100.0 4.4 2.9 2.3
Mg in serpentine (wt.%) SP** of serp. (wt.% CO <sub>2</sub> ) Mg in sulphates (wt.%) %Mg (of secondary mins.) SP** in sulph. (wt.% CO <sub>2</sub> ) Mg in hydromag. (wt.%) %Mg (of secondary mins.) CO <sub>2</sub> sequestered (wt.%)	16.7 24.2 1.1 64.1 1.6 1.6 35.9 0.6 35.9 0.6	$\begin{array}{c} 17.1\\24.7\\1.2\\6.0\\1.7\\0.4\\0.4\\0.5\\0.5\end{array}$	$\begin{array}{c} 14.8\\21.5\\11.3\\67.8\\1.9\\1.9\\0.6\\32.2\\0.9\end{array}$	$\begin{array}{c} 19.2 \\ 27.8 \\ 0.8 \\ 1.2 \\ 1.2 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \end{array}$	$\begin{array}{c} 18.9\\ 27.4\\ 0.7\\ 0.7\\ 1.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\end{array}$	$\begin{array}{c} 19.7 \\ 28.6 \\ 0.6 \\ 0.8 \\ 0.0 \\ 0.0 \\ 0.0 \\ 0.0 \end{array}$	20.7 30.0 0.4 0.6 0.0 0.0 0.0	$\begin{array}{c} 20.9\\ 30.3\\ 0.1\\ 0.1\\ 0.2\\ 0.0\\ 0.0\\ 0.0\end{array}$	20.2 29.2 0.4 0.6 0.0 0.0 0.0	$\begin{array}{c} 20.5\\ 29.7\\ 0.2\\ 0.3\\ 0.3\\ 89.2\\ 2.2\\ 2.2\end{array}$	21.7 31.5 0.0 0.0 0.0 1.0 1.0 1.5	$\begin{array}{c} 20.7\\ 29.9\\ 0.0\\ 0.0\\ 0.0\\ 1.3\\ 1.3\\ 1.9\\ 1.9\end{array}$	$\begin{array}{c} 20.5\\ 29.6\\ 0.4\\ 0.5\\ 0.0\\ 0.0\\ 0.0\\ 0.0\end{array}$	$\begin{array}{c} 21.8\\ 31.6\\ 0.0\\ 0.1\\ 0.0\\ 0.0\\ 0.0\\ 0.0\end{array}$	$\begin{array}{c} 21.5\\ 31.1\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\\ 0.0\end{array}$

TABLE 5. Rietveld refinement results for konyaite-bearing mine tailings.

\*  $R_{\nu\nu}$  is the weighted pattern index, a function of the least-squares residual;  ${}^{\dagger}\chi^2$  is the reduced chi-squared statistic for the least-squares fit;  $\ddagger$  d is the Durbin-Watson statistic, a measure of serial correlation for the least-squares fit;  $\ast$ \* SP is the sequestration potential in wt.% CO<sub>2</sub> that could potentially be sequestered by a mineral or group of minerals (calculated in terms of CO<sub>2</sub> trapped within hydromagnesite).





FIG. 2. Rietveld refinement results plotted for aliquots sub1-1 and sub1-2 of five samples from Mt. Keith. Columns labelled '1' give results for sub1-1 aliquots and those labelled '2' give results for sub1-2 aliquots (analysed ~2 y after sample collection). (a) Abundances of Mg and Na sulphate minerals; (b) weight difference of sulphate minerals between sub1-2 and sub1-1 aliquots; (c) sum of abundances for sulphate and serpentine minerals; (d) abundance of serpentine minerals; (e) weight difference of serpentine minerals between sub1-2 and sub1-1 aliquots.

06MKG8-7-1), the abundance either remained constant within error (as defined by Wilson *et al.*, 2006) or increased in the sub1-2 aliquots. In two samples (06MKG10-9-1 and 06MKG40-4) an increase in the abundance of serpentine + amorphous material was observed to be concurrent with a decrease in the abundance of sulphate minerals. The significant increase in the refined abundances for serpentine + amorphous material in samples 06MKG10-9-1 and 06MK40-4 and the concurrent and comparable decrease in the abundance of konyaite and blödite may reflect decomposition of these minerals to X-ray amorphous phases.

Comparison of the values for sequestration potentials associated with serpentine in the sub1-2 aliquots (Table 5) suggests that in some cases (notably for 06MKG10-9-1 and 06MK40-4) the presence of amorphous content could have led to overestimates of several wt.%  $CO_2$  in the sub1-2 aliquots. In the sub1-1 aliquots, serpentine minerals represent between 93.8% and 99.0% of the unused potential of the tailings samples to sequester  $CO_2$ . The remaining unused sequestration potential is tied up in sulphate minerals. Under the alkaline conditions that prevail in the tailings storage facility at Mount Keith, chemical weathering of serpentine minerals will tend to proceed relatively slowly (e.g. Bales and Morgan, 1985). Therefore, it is important for  $CO_2$ sequestration purposes that much of the Mg released from serpentine minerals by weathering goes into the production of hydromagnesite.

In order to test whether the decomposition of konyaite was solely the result of grinding, each of the five samples was resampled in November 2008 and new aliquots (sub2-1) of tailings were pulverized and analysed. Again, konyaite was

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FIG. 3. Rietveld refinement plots for a sample of konyaite-bearing tailings from the Mount Keith Nickel Mine, Western Australia (06MKG10-9-1). Results for the sub1-1 aliquot of 06MKG10-9-1 are given in (*a*) and results for the sub1-2 aliquot are given in (*b*). Uppermost lines = observed data overlain by the calculated pattern; curves beneath observed and calculated patterns = calculated patterns for each phase; grey line below = residual pattern; short vertical lines = positions of Bragg reflections for each phase.



FIG. 4. Powder XRD pattern of sulphate mine tailings (konyaite has already transformed to blödite). Blödite and halite have decomposed to an amorphous phase after being contained in a desiccator in a moist environment.

absent in all samples, confirming that decomposition does not depend on pulverization for the samples studied. For the most part, results for other phases were similar to those in the first subsample (sub1-1 and sub1-2), but varied because this represented resampling of large (>1 kg) samples and homogenization of unpulverized samples can be difficult. Notably, blödite was present in aliquot sub2-1 of two of the samples from which it had disappeared in sub1-2 (06MKG8-3-1 and 06MKG8-7-1).

## Qualitative powder XRD

Separately, we prepared a smear mount from the sub2-1 aliquot of 06MKG2-9-1 which was rich in both blödite and halite and placed it in a desiccator with water to simulate a moist wet environment. Within 5 days the blödite had completely decomposed to an amorphous sulphate phase and halite had also decomposed completely (Fig. 4). No peaks corresponding to the formation of other sulphate phases were observed.

After 22 months the synthetic konyaite was reanalysed to compare the decomposition to that of the natural konyaite. The samples were kept in a sealed plastic vial in a draw for the entire time. Over this period, the konyaite had transformed completely to a mixture of thenardite (31.46 wt.%), hexahydrite (17.41 wt.%), blödite (25.36 wt.%) and löweite (25.78 wt.%). It appears that transformation of konyaite  $\rightarrow$  blödite  $\rightarrow$ löweite  $\rightarrow$  thenardite + hexahydrate occurs at a slower rate in the synthetic sample than in the natural samples, where löweite is rarely observed. The reaction rate of synthetic konvaite may be slower in this case due to decreased interaction with the atmosphere, whilst the blödite  $\rightarrow$  löweite transition might be favoured due to drier storage conditions. These observations further confirm that reaction rates are very dependent on relative humidity and temperature and several decomposition routes are possible.

#### Thermogravimetric analysis

The decomposition of 'fresh' synthetic konyaite shows two major mass losses at ~170 and 250°C, while decomposition of the 22 month old sample shows two major mass losses at ~135 and 240°C (Fig. 5). For the fresh sample, 18.27% of water was lost, while 15.16% of water was liberated in the 22 month old sample. The smaller amount of mass loss in the older sample is consistent with transformation of konyaite to other sulphate phases. Based on this mass-loss data, as well as the decomposition noted from the sample above, the following reactions describe the decomposition of konyaite:

- 1. konyaite  $\rightarrow$  blödite + H<sub>2</sub>O
- 2. 7 konyaite  $\rightarrow$  löweite + thenardite + 25 H<sub>2</sub>O
- 3. 2 konyaite  $\rightarrow$  blödite + thenardite + hexahydrite

Our mass-loss results appear to be slightly different to those obtained by van Doesburg *et al.* (1982) who reported a major loss at 92°C (reportedly corresponding to blödite transformation) and one at 124°C (reportedly corresponding to the formation of löweite). Our data show that the transformation of konyaite is not this simple, and that thenardite and hexahydrite are important decomposition products.

# Implications for CO<sub>2</sub> fixation

Wilson *et al.* (2009) recently described the crystallographic trapping of atmospheric  $CO_2$  within the structure of hydromagnesite and



FIG. 5. TGA data for (*a*) fresh synthetic konyaite and (*b*) 22 month old synthetic konyaite.

related secondary magnesium carbonate minerals at the Clinton Creek and Cassiar chrysotile deposits in Canada. Wilson *et al.* (2006, 2009) suggested that trapping and storing CO<sub>2</sub> within secondary magnesium carbonate minerals, like the hydromagnesite found at Mount Keith, represents a viable method for sequestering atmospheric CO<sub>2</sub> into mine tailings. Weathering of serpentine-rich mine tailings has the potential to trap and store nearly 0.4 times the mass of these minerals in CO<sub>2</sub> by producing magnesium carbonate minerals (Lackner *et al.*, 1995).

Rietveld refinement results provide a weightpercent measure of each mineral phase detectable in a sample of mine tailings. Modal abundances from Rietveld refinement results can be used to (1) estimate the potential of mine tailings to sequester CO<sub>2</sub> into magnesium carbonate minerals, (2) quantify the amount of CO<sub>2</sub>-sequestration potential that is being lost to precipitation of sulphate minerals, and (3) estimate the amount of CO<sub>2</sub> trapped and stored within secondary carbonate minerals. However, konyaite and other sulphate minerals compete with carbonate minerals for the Mg<sup>2+</sup> that is released by dissolution of serpentine minerals. Thus, production of secondary sulphate minerals in mine tailings diminishes the amount of CO<sub>2</sub> that can be stored in those tailings. Although sulphate minerals are gradually leached from inactive tailings at Mount Keith (Wilson, 2009), their presence in active tailings as a result of sulphide mineral oxidation limits CO<sub>2</sub> fixation on the timescale of interest to mining operations. Also, the decomposition of Na-Mg-sulphate minerals (this study) and Mg-sulphate minerals (e.g. Chipera and Vaniman, 2007) to X-ray amorphous phases may hinder quantitative mineralogical analyses and lead to mis-estimates for sequestration potential and carbon fixation in mine tailings and natural geological formations. However, we have shown here that these mis-estimates can be mitigated, allowing for accurate quantification of CO<sub>2</sub> fixation in secondary carbonate minerals.

The use of an internal standard (e.g. synthetic fluorite or diamond) for quantitative powder XRD ensures that the weight percent abundance of hydromagnesite is not overestimated for samples containing amorphous material. Using this method, the abundances of hydromagnesite in all three aliquots of samples 06MKG2-9-1 and 06MKG10-9-1 were largely consistent, indicating that quantification of hydromagnesite is relatively unaffected by sulphate mineral transformations. Nonetheless, the use of structureless pattern fitting for antigorite and lizardite in samples containing amorphous material may result in overestimates for these phases and their potential to sequester CO<sub>2</sub> upon weathering. Furthermore, because amorphous sulphate phases cannot be detected with X-ray powder diffraction data, the amount of sequestration potential lost to these minerals cannot be measured in this way.

Decomposition of sulphate minerals like konayite and blödite may have an impact on early detection of acid-mine drainage from routine monitoring by X-ray powder diffraction. Also, amorphous phases are problematic in terms of mineral reaction rates. Amorphous sulphate phases (most commonly ferric iron or aluminium) have been widely documented as occurring in mine tailings from the breakdown of sulphide minerals (e.g. Strömberg and Banwart, 1994) and also act to dissolve and break down pre-existing mineral phases and subsequently create acid mine drainage (e.g. Valente and Gomez, 2009). Increased reactivity of amorphous sulphate phases may pose further problems for the sequestering of carbon, whereby if undetected substantial amounts may dissolve carbonate phases releasing CO<sub>2</sub> into the atmosphere. Undetected sulphate phases are also likely to change the transformation pathways substantially if heat treatment is applied effecting metallurgical processes. Mills et al. (2009) and Madsen et al. (2010) showed the dramatic effects minor impurities had in the transformation of plumbojarosite at high temperatures.

Therefore, the combined use of quantitative X-ray powder diffraction with an internal standard and complimentary chemical analysis is an effective method for both environmental monitoring and remote mineralogical studies. Measurement of  $CO_2$  fixation within minerals, detection of acid generation in sulphide-bearing mine tailings, and identification of hydrous minerals in astro-biological studies of other solar system bodies may be impacted by the presence of amorphous sulphate minerals. Our results suggest that the decomposition of sulphate mineral phases may be more common than previously thought.

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