

## FLUORO-POTASSICHASTINGSITE FROM THE GREENWOOD MINE, ORANGE COUNTY, NEW YORK: A NEW END-MEMBER CALCIC AMPHIBOLE

MARIAN V. LUPULESCU<sup>§</sup>

*New York State Museum, Division of Research and Collections, 3140 CEC, Madison Ave., Albany, New York 12230, USA*

JOHN RAKOVAN

*Department of Geology, Miami University, Oxford, Ohio 45056, USA*

M. DARBY DYAR

*Mount Holyoke College, 405 Clapp, South Hadley, Massachusetts 01075-6419, USA*

GEORGE W. ROBINSON

*A.E. Seaman Mineral Museum, Michigan Technological University, Houghton, Michigan 49931, USA*

JOHN M. HUGHES

*Office of the Provost, The University of Vermont, Burlington, Vermont 05405, USA*

### ABSTRACT

Fluoro-potassichastingsite, ideally  $\text{KCa}_2(\text{Fe}^{2+}_4\text{Fe}^{3+})\text{Si}_6\text{Al}_2\text{O}_{22}\text{F}_2$ , is found in compact aggregates of crystals up to 1 cm size on the waste-rock dump at the Greenwood mine, in Harriman State Park, Tuxedo, Orange County, New York, USA. It is associated with magnetite, diopside, enstatite, pyrrhotite, chalcopyrite, pyrite and, rarely, phlogopite. Fluoro-potassichastingsite is transparent, black to greenish in very thin fragments, and non-fluorescent in ultraviolet light; it has a vitreous luster and a greenish gray streak. The Mohs hardness is 6,  $D_{\text{meas}}$  is 3.289 g/cm<sup>3</sup>, and  $D_{\text{calc}}$  is 3.37 g/cm<sup>3</sup>. The {110} cleavage is perfect, and the fracture is conchoidal. It is biaxial negative, with  $\alpha$  1.668(2),  $\beta$  1.688(2),  $\gamma$  1.698(2),  $2V_{\text{meas}}$  40–70°,  $2V_{\text{calc}}$  70°,  $Y = b$ ,  $Z \wedge c = 23^\circ$ , and  $r < v$ . The observed pleochroism is  $X$  bluish green,  $Y$  green to brownish green,  $Z$  blue to light blue. The Gladstone–Dale compatibility index is superior, with  $1 - (K_p/K_c) = 0.012$  (based on empirical formula and calculated density). The mineral is monoclinic, space group  $C2/m$ ,  $a$  9.9480(3),  $b$  18.1777(6),  $c$  5.3302(2) Å,  $\beta$  105.140(1)°,  $V$  930.41(8) Å<sup>3</sup>, and  $Z = 2$ . The strongest eight X-ray powder-diffraction lines [ $d$  in Å( $hkl$ )] are: 8.499(100)(110), 3.151(76)(310), 2.830 (53)(330), 3.299(32)(240), 2.722(23)(151), 2.402(17)(350), 3.401(11)(131), and 1.661(10)(461). Combined electron-microprobe and Mössbauer data yield: SiO<sub>2</sub> 40.49, TiO<sub>2</sub> 0.11, Al<sub>2</sub>O<sub>3</sub> 10.29, V<sub>2</sub>O<sub>3</sub> 0.03, Cr<sub>2</sub>O<sub>3</sub> 0.01, Fe<sub>2</sub>O<sub>3</sub> 4.49, FeO 19.80, CaO 11.13, MgO 6.68, MnO 0.20, K<sub>2</sub>O 2.93, Na<sub>2</sub>O 1.24, F 2.23, Cl 0.61, H<sub>2</sub>O 0.70, O = (F+Cl) –1.08, sum 99.86 wt.%, which corresponds to the following crystal-chemical formula based on 24 [O + (OH) + F + Cl]:  $^A(\text{K}_{0.59}\text{Na}_{0.25})_{\Sigma 0.84} \text{ } ^B(\text{Ca}_{1.87}\text{Na}_{0.13})_{\Sigma 2.00} \text{ } ^C(\text{Fe}^{2+}_{2.60}\text{Mg}_{1.56}\text{Fe}^{3+}_{0.53}\text{Al}_{0.26}\text{Mn}_{0.03}\text{Ti}_{0.01})_{\Sigma 4.99} \text{ } ^T(\text{Si}_{16.36}\text{Al}_{1.64})_{\Sigma 8.00} \text{ } ^O_{22.68} \text{ } ^{3+}[\text{F}_{1.11}(\text{OH})_{0.73}\text{Cl}_{0.16}]_{\Sigma 2.00}$ . The ICP–MS analyses on a crystal fragment different than the one analyzed for major elements yielded the following trace-element concentrations (ppm): Cu 278.9, Rb 162.5, Y 343.2, La 257, Ce 568, Nd 156. The new species and name have been approved by IMA–CNMMN (2005–006).

**Keywords:** fluoro-potassichastingsite, end member, calcic amphibole, structure determination, Grenville rocks, Hudson Highlands, New York.

### SOMMAIRE

La fluoro-potassichastingsite, de composition idéale  $\text{KCa}_2(\text{Fe}^{2+}_4\text{Fe}^{3+})\text{Si}_6\text{Al}_2\text{O}_{22}\text{F}_2$ , se présente en agrégats compacts de cristaux atteignant un diamètre de 1 cm; nous l'avons découvert dans les haldes de la mine Greenwood, dans le parc étatal Harriman, à Tuxedo, comté de Orange, état de New York. Lui sont associées magnétite, diopside, enstatite, pyrrhotite, chalcopyrite, pyrite et, plus rarement, phlogopite. La fluoro-potassichastingsite est transparente, noire à verdâtre où les esquilles sont très minces, et

<sup>§</sup> E-mail address: mlupules@mail.nysed.gov

non fluorescente en lumière ultraviolette; elle possède un éclat vitreux et une rayure gris verdâtre. La dureté de Mohs est 6, la densité mesurée est  $3.289 \text{ g/cm}^3$ , et la densité calculée est  $3.37 \text{ g/cm}^3$ . Le clivage  $\{110\}$  est parfait, et la fracture est conchoïdale. Il s'agit d'un minéral biaxe négatif, avec  $\alpha$  1.668(2),  $\beta$  1.688(2),  $\gamma$  1.698(2),  $2V_{\text{mes}}$  40–70°,  $2V_{\text{calc}}$  70°,  $Y = b$ ,  $Z \wedge c = 23^\circ$ , et  $r < v$ . Les cristaux sont pléochroïques,  $X$  vert bleuâtre,  $Y$  vert à vert brunâtre, et  $Z$  bleu à bleu pâle. L'indice de compatibilité de Gladstone–Dale est dans la catégorie supérieure, avec  $1 - (K_p/K_c) = 0.012$  (compte tenu de la formule empirique et la densité calculée). Le minéral est monoclinique, groupe spatial  $C2/m$ ,  $a$  9.9480(3),  $b$  18.1777(6),  $c$  5.3302(2) Å,  $\beta$  105.140(1)°,  $V$  930.41(8) Å<sup>3</sup>, et  $Z = 2$ . Les huit raies les plus intenses du spectre de diffraction, méthode des poudres [ $d$  en Å( $hkl$ )] sont: 8.499(100)(110), 3.151(76)(310), 2.830(53)(330), 3.299(32)(240), 2.722(23)(151), 2.402(17)(350), 3.401(11)(131), et 1.661(10)(461). Une combinaison des données acquises avec une microsonde électronique et par spectroscopie de Mössbauer a donné: SiO<sub>2</sub> 40.49, TiO<sub>2</sub> 0.11, Al<sub>2</sub>O<sub>3</sub> 10.29, V<sub>2</sub>O<sub>3</sub> 0.03, Cr<sub>2</sub>O<sub>3</sub> 0.01, Fe<sub>2</sub>O<sub>3</sub> 4.49, FeO 19.80, CaO 11.13, MgO 6.68, MnO 0.20, K<sub>2</sub>O 2.93, Na<sub>2</sub>O 1.24, F 2.23, Cl 0.61, H<sub>2</sub>O 0.70, O = (F+Cl) –1.08, pour un total de 99.86% (poids), ce qui correspond à la formule cristallochimique suivante, fondée sur une base de 24 [O + (OH) + F + Cl]: <sup>A</sup>(K<sub>0.59</sub>Na<sub>0.25</sub>)<sub>Σ0.84</sub> <sup>B</sup>(Ca<sub>1.87</sub>Na<sub>0.13</sub>)<sub>Σ2.00</sub> <sup>C</sup>(Fe<sup>2+</sup><sub>2.60</sub>Mg<sub>1.56</sub>Fe<sup>3+</sup><sub>0.53</sub>Al<sub>0.26</sub>Mn<sub>0.03</sub>Ti<sub>0.01</sub>)<sub>Σ4.99</sub> <sup>T</sup>(Si<sub>6.36</sub>Al<sub>1.64</sub>)<sub>Σ8.00</sub> O<sub>22.68</sub> <sup>O3</sup>[F<sub>1.11</sub>(OH)<sub>0.73</sub>Cl<sub>0.16</sub>]<sub>Σ2.00</sub>. Les analyses ICP–MS d'un cristal autre que celui qui a servi pour les éléments majeurs ont donné les concentrations en éléments traces suivantes (ppm): Cu 278.9, Rb 162.5, Y 343.2, La 257, Ce 568, Nd 156. La nouvelle espèce a reçu l'approbation du comité CNMNC de l'IMA (2005–006).

(Traduit par la Rédaction)

**Mots-clés:** fluoro-potassichastingsite, pôle, amphibole calcique, affinement de la structure, socle de Grenville, Hudson Highlands, New York.

## INTRODUCTION

In our study of Grenville-age amphibole-bearing rocks of New York State, we found an amphibole in the Hudson Highlands that is a new end-member of the calcic amphibole group, here named fluoro-potassichastingsite. The new mineral is the fluorine- and potassium-dominant analogue of hastingsite. Potassium-dominant amphiboles are well documented (Deer *et al.* 1997, Mazdab 2003), and seven of them are formally recognized by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA). However, fluoro-potassicrichterite (Oberti *et al.* 1992) and fluoro-potassic-magnesian-arfvedsonite (Hogarth 2006) are the only potassium- and fluorine-dominant amphiboles previously approved by the commission.

Relatively few data on fluorine- and potassium-rich amphiboles and their geological environments are available. Mazdab (2003) compiled data on potassic amphiboles, recalculated the empirical formulae, and listed two naturally occurring K- and F-rich amphiboles in addition to fluoro-potassicrichterite: "potassic-fluoro-magnesian-arfvedsonite" (renamed fluoro-potassic-magnesian-arfvedsonite, Burke & Leake 2004), and "potassic-fluoro-magnesian-ikatophorite" (renamed fluoro-potassic-magnesian-ikatophorite, but not yet IMA approved: Burke & Leake 2004).

In this study, we present the physical, optical, compositional and structural properties of the new mineral species fluoro-potassichastingsite. The mineral and the name were approved by IMA–CNMNC (2005–006), and the type material is deposited in the Mineral Collection at New York State Museum under the catalogue number 21205.

## OCCURRENCE

Fluoro-potassichastingsite was collected from the dump of the Greenwood (Patterson) iron mine. The mine, located in Hudson Highlands, in Harriman State Park, Town of Tuxedo, Orange County, New York, was first opened in 1838, and was a source of iron during the Civil War. It was last worked in 1880. The mineral forms compact aggregates of crystals up to 1 cm, associated with magnetite, diopside, enstatite, pyrrhotite, chalcopyrite, pyrite and, rarely, phlogopite. Magnetite shows spinel exsolution on  $\{111\}$  in polished thin sections, and rare molybdenite is locally associated with Fe sulfides. The sulfide sequence paragenetically overlaps the oxide sequence and is accompanied by halogen- and potassium-rich amphiboles. The Greenwood mine belongs to a belt of iron deposits (Fe oxide, Fe oxide + Fe sulfide, Fe oxide + Fe sulfide + U oxide, Fe oxide + REE minerals) that extends from New York's Hudson Highlands region south into the Reading Prong of New Jersey and Pennsylvania. Some of these iron deposits were mined until the beginning of the 20<sup>th</sup> century.

These iron deposits are hosted by a sequence of gneisses, amphibolites and rare small bodies of marble that form the Proterozoic belt of the Hudson Highlands region in New York. This uplifted area experienced Grenville age metamorphism and deformation, with ages of peak metamorphism of  $1010 \pm 7$  to  $1160 \pm 4$  Ma (Gates *et al.* 2001). Many late-Grenville shear zones with widths of 1–2 km, most of which exhibit a right-lateral shear sense, cross-cut and transpose the older contact-metamorphic units (Gates *et al.* 2000). These shear zones were the pathways for potassium- and halogen-rich crustal fluids that generated the fluoro-potassichastingsite.

## PHYSICAL PROPERTIES

Fluoro-potassichastingsite occurs as brittle, black, prismatic crystals. It is transparent and green in very thin fragments, has a greenish gray streak, a vitreous luster, and a Mohs hardness of 6. The crystals display perfect cleavage on {110} and have a conchoidal fracture. The density measured by gas displacement using AccuPyc 1330 (helium) is 3.289 g/cm<sup>3</sup>, and the density calculated from the empirical formula is 3.37 g/cm<sup>3</sup>.

## OPTICAL PROPERTIES

Fluoro-potassichastingsite is biaxial negative. The indices of refraction measured with oils are  $\alpha$  1.668(2),  $\beta$  1.688(2),  $\gamma$  1.698(2);  $2V_{\text{meas}}$  ranges from 40 to 70°, and  $2V_{\text{calc}}$  is equal to 70°. Dispersion is weak,  $r < v$ , and the optical orientation is  $Y = b$  with  $Z \wedge c \approx 23^\circ$ . The mineral is pleochroic with  $X$  bluish green,  $Y$  greenish to brownish green, and  $Z$  blue to light blue. It is non-fluorescent in both long- and short-wave UV light. The Gladstone–Dale compatibility index, based on the empirical formula and calculated density, is superior, with  $1 - (K_p/K_C) = 0.012$ .

## CHEMICAL COMPOSITION

Several fragments from the holotype crystal were detached, mounted in epoxy, polished and coated with carbon under vacuum for wavelength-dispersion electron-microprobe analysis using a JEOL Superprobe 733. The operating conditions were: accelerating voltage 15 kV, beam current 15 nA, with a beam diameter of 20  $\mu\text{m}$ . Standards used were kyanite (Si, Al), synthetic forsterite (Mg), synthetic fayalite (Fe), synthetic diop-

side (Ca), jadeite (Na), rutile (Ti), synthetic tephroite (Mn), orthoclase (K), synthetic V<sub>2</sub>O<sub>5</sub> (V), chromite (Cr), topaz (F) and sodalite (Cl). The data were reduced using a ZAF correction routine (Table 1). The concentrations of trace elements (Table 2) were determined by ICP–MS with a PerkinElmer – Sciex Elan 6100 DRC using the low-pressure HF digestion method and the following standards: NIST–278 and NIST–688. The mineral has relatively high levels of Cu, Zn, Rb, Sr, Zr, Ba, Y, and REE. Concentrations of some trace elements (*e.g.*, V and Zn) are close to those in K-rich hastingsite from other Fe-oxide deposits (Mazdab 2003).

The amount of H<sub>2</sub>O determined by hydrogen extraction (0.79%) differs from the amount of H<sub>2</sub>O calculated (0.70%) assuming 2 (OH<sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>). If we use the water content determined by hydrogen extraction to calculate the empirical formula, we have 2.09 [F<sub>1.10</sub>(OH)<sub>0.83</sub>Cl<sub>0.16</sub>] and O<sub>21.91</sub> and the neutrality of the formula is compromised. The amount of H<sub>2</sub>O calculated from stoichiometry allows us to fill (F, OH, Cl) to 2 *apfu*.

Combining the mean of 12 electron-microprobe analyses (Table 1) with Mössbauer data to acquire Fe<sup>2+</sup>O and Fe<sup>3+</sup><sub>2</sub>O<sub>3</sub>, gives the following empirical formula for the holotype material, on the basis of 24 [O + (OH) + F + Cl] and the recalculation scheme presented in Leake *et al.* (1997): <sup>A</sup>(K<sub>0.59</sub>Na<sub>0.25</sub>)<sub>Σ0.84</sub> <sup>B</sup>(Ca<sub>1.87</sub>Na<sub>0.13</sub>)<sub>Σ2.00</sub> <sup>C</sup>(Fe<sup>2+</sup><sub>2.60</sub>Mg<sub>1.56</sub>Fe<sup>3+</sup><sub>0.53</sub>Al<sub>0.26</sub>Mn<sub>0.03</sub>Ti<sub>0.01</sub>)<sub>Σ4.99</sub> <sup>T</sup>(Si<sub>6.36</sub>Al<sub>1.64</sub>)<sub>Σ8.00</sub> O<sub>22.68</sub> <sup>O3</sup>[F<sub>1.11</sub>(OH)<sub>0.73</sub>Cl<sub>0.16</sub>]<sub>Σ2.00</sub> or, ideally, KCa<sub>2</sub>(Fe<sup>2+</sup><sub>4</sub>Fe<sup>3+</sup><sub>1</sub>)Si<sub>6</sub>Al<sub>2</sub>O<sub>22</sub>F<sub>2</sub>. Thus this amphibole falls within the compositional field of fluoro-potassichastingsite.

## MÖSSBAUER SPECTROSCOPY

Approximately 25 mg of sample was crushed to a fine powder with sugar under acetone before mounting in a sample holder confined by cello tape. The resultant thickness of the sample gave 1.04 mg Fe/cm<sup>2</sup>. A room-temperature Mössbauer spectrum to determine Fe<sup>2+</sup> and Fe<sup>3+</sup> content was acquired in the Mineral Spectroscopy Laboratory at Mount Holyoke College and corrected for Compton background. A source of 45 mCi <sup>57</sup>Co in Rh was used on a WEB Research Co. spectrometer;

TABLE 1. BULK COMPOSITION OF FLUORO-POTASSICHAUSTINGSITE FROM THE GREENWOOD MINE, NEW YORK

SiO <sub>2</sub> wt.%	40.49	40.13	– 41.17	Si <i>apfu</i>	6.36
TiO <sub>2</sub>	0.11	0.01	– 0.19	<sup>27</sup> Al	1.64
Al <sub>2</sub> O <sub>3</sub>	10.29	10.16	– 10.58	ΣT	8.00
V <sub>2</sub> O <sub>5</sub>	0.03	0.004	– 0.10		
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.00	– 0.02	<sup>27</sup> Al	0.26
FeO	23.84	23.38	– 24.38	Fe <sup>3+</sup>	0.53
CaO	11.13	11.05	– 11.27	Fe <sup>2+</sup>	2.60
MgO	6.68	6.53	– 6.82	Mg	1.56
MnO	0.20	0.17	– 0.22	Mn	0.03
K <sub>2</sub> O	2.93	2.82	– 3.05	Ti	0.01
Na <sub>2</sub> O	1.24	1.19	– 1.33	ΣC	4.99
F	2.23	2.04	– 2.31	Ca	1.87
Cl	0.61	0.57	– 0.67	Na	0.13
H <sub>2</sub> O*	0.70			ΣB	2.00
O=F	–0.94				
O=Cl	–0.14			Na	0.25
Total	99.86			K	0.59
				ΣA	0.84
%Fe <sup>2+</sup>	19.8			F	1.11
Fe <sub>2</sub> O <sub>3</sub> (MS)	4.49			Cl	0.16
FeO (MS)	19.80			H*	0.73

MS: wt.% Fe<sub>2</sub>O<sub>3</sub> and FeO determined by Mössbauer spectroscopy. \* Determined by stoichiometry. The electron-microprobe data were converted to a structural formula on the basis of 24 [O + (OH) + F + Cl].

TABLE 2. AVERAGE LEVELS OF TRACE ELEMENTS IN FLUORO-POTASSICHAUSTINGSITE

Li ppm	11.4	Cs ppm	0.3	Dy ppm	63.2
Ni	19.5	Ba	77.5	Ho	12.9
Cu	278.9	La	257	Er	38.9
Zn	75.3	Ce	568	Tm	6.8
Rb	162.5	Pr	70.8	Yb	49
Sr	65.7	Nd	156	Lu	7.9
Y	343.2	Eu	2.8	Hf	2.8
Zr	47.8	Sm	53.2	Pb	1.5
Nb	31.9	Gd	46.7	Th	6.1
Sn	32.1	Tb	9.5	U	1.1

The concentrations of the trace elements were determined on a crystal of fluoro-potassichastingsite different than the one used for the crystal-chemical formula (Table 1).

run time was one day. Results were calibrated against an  $\alpha$ -Fe foil of 6  $\mu\text{m}$  thickness and 99% purity. The error on site assignments in this sample is estimated to be roughly  $\pm 1$ –3%; errors on Mössbauer parameters are probably  $\pm 0.05$  mm/s.

The spectrum was fitted using the WMOSS software of WEB Research Co., an implementation of the Voigt-based fitting method developed by Rancourt & Ping (1991). This method has been shown to be the most appropriate for samples in which the Fe atoms do not have homogeneous environments, but rather have different nearest-neighbor and next-nearest-neighbor environments. Various combinations of constraints for the parameters of each distribution were used, but these permutations did not affect the relative peak-areas by more than  $\pm 1$ –2% (*i.e.*, within the stated error).

Quadrupole-splitting distributions (QSDs) were used to represent the contributions of octahedral  $\text{Fe}^{2+}$  in this spectrum. Following the established conventions for fits using quadrupole-splitting distribution,  $\gamma$ , the Lorentzian full peak-width and half-maximum intensity, was constrained to be 0.20 mm/s, which is roughly the natural line-width of Fe. The ratio of Lorentzian heights of the two lines in an elemental quadrupole doublet,  $h_+/h_-$ , was constrained for all components to be equal to one. The values for  $\delta_0$  (the value of isomer shift,  $\delta$ , where the distributed hyperfine parameter has a value of zero) and  $\delta_1$  (the coupling of  $\delta$  to the distributed hyperfine parameter) were constrained to be the same (but allowed to vary as a group) for the  $\text{Fe}^{2+}$

subcomponents based upon the assumption that these all represent  $\text{Fe}^{2+}$  atoms at  $M$  sites. The remaining parameters, including the center of the Gaussian component of the  $\Delta$  distribution ( $\Delta_0$ ), the width of the quadrupole-splitting distribution ( $\delta_\Delta$ ), and the relative area of the doublets ( $A$ ), were allowed to vary freely. Isomer shift ( $\delta$ ) is calculated using  $\delta = \delta_1 * \Delta_0 + \delta_0$ . Details relating to the application of these parameters can be found in Rancourt & Ping (1991).

Peak areas were corrected for recoil-free fraction ( $f$ ) effects by use of the room-temperature correction factor calculated on the basis of wet chemical *versus* Mössbauer data for hornblende (Dyar *et al.* 1993). We recognize that  $f$  values are highly composition-dependent, but there are no  $f$  determinations for hastingsite in the literature. Therefore, we use the only value currently available for amphibole, which comes from Dyar *et al.* (1993).

The Mössbauer spectrum of the sample is shown in Figure 1. Results are given in Table 3. At room temperature, each spectrum is composed of two QSD  $^{57}\text{Fe}^{2+}$  subcomponents and one  $^{57}\text{Fe}^{3+}$  component. The two  $^{57}\text{Fe}^{2+}$  components have similar octahedral isomer shifts ( $\delta$ ) of 1.18 and 1.19 mm/s, but dramatically different values of quadrupole splitting,  $\Delta$  (2.15 and 2.49 mm/s). Traditionally, these doublets have been assigned to  $^{57}\text{Fe}^{2+}$  and  $^{57}\text{Fe}^{2+}$ , respectively (*cf.* Gunter *et al.* 2003). The  $^{57}\text{Fe}^{3+}$  component has  $\delta = 0.29$  mm/s. This value is slightly low for octahedrally coordinated  $\text{Fe}^{3+}$ .

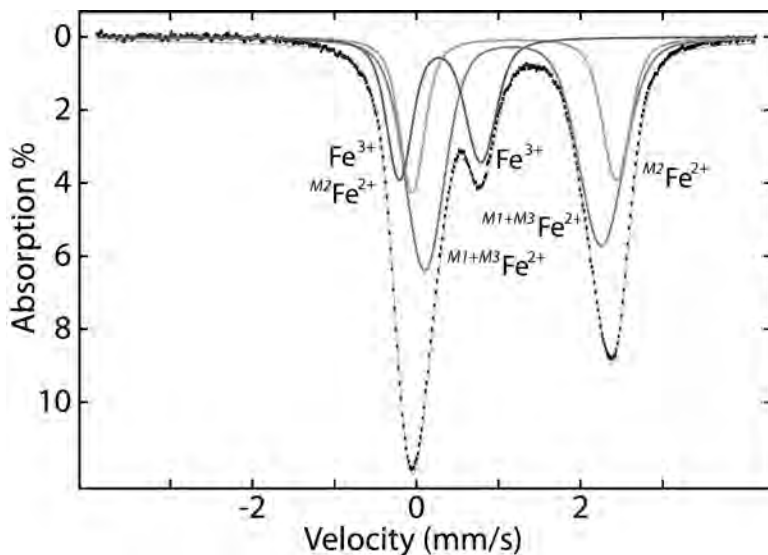


FIG. 1. Mössbauer spectrum of fluoro-potassichastingsite (powdered sample) taken at room temperature. The spectrum, based on the results given in Table 3, shows the quadrupole splitting distribution of the octahedrally coordinated  $\text{Fe}^{2+}$ . A detailed discussion of the results is given in the text.

Results are given in mm/s relative to the center point of a spectrum obtained by calibration with a Fe foil (Table 3). The value A represents the relative area of each doublet, and % present is the percentage of the total Fe at each site, corrected for the recoil-free fraction effect using the amphibole corrections from Dyar *et al.* (1993). The reduced  $\chi^2$  value for this fit was 2.352.

X-RAY POWDER DIFFRACTION

X-ray powder-diffraction data (Table 4) were obtained using a Scintag X2 X-ray diffractometer with CuK $\alpha$  X-radiation. Operating conditions were 45 kV and 35 mA. The unit-cell parameters refined from the powder data using quartz as an internal standard are *a* 9.9503(14), *b* 18.1756(15), *c* 5.3292(11) Å,  $\beta$  105.160(14)°, *V* 930.282(227) Å<sup>3</sup> with *Z* = 2.

CRYSTAL STRUCTURE

The crystal fragment selected for X-ray diffraction, approximately 175 × 155 × 52 μm, was mounted on a Bruker Apex CCD diffractometer equipped with graphite-monochromated MoK $\alpha$  radiation. Refined cell-parameters and other crystal data are listed in Table 5. Data were collected for an approximate sphere of reciprocal space, and were integrated and corrected for Lorentz and polarization factors using the Bruker program SAINTPLUS (Bruker AXS Inc., 2001). Refined unit-cell parameters derived from the single-crystal data are *a* 9.9480(3), *b* 18.1777(6), *c* 5.3302(2) Å,  $\beta$  105.140(1)°, *V* 930.41(8) Å<sup>3</sup> and *Z* = 2. The structure was refined using the standard C2/*m* amphibole model (Hawthorne 1983) and the Bruker SHELXTL v. 6.14 package of programs, with neutral-atom scattering factors and terms for anomalous dispersion. The refinement was undertaken with anisotropic-displacement parameters for all atoms except those on the A(2) and M(4)' sites. The A site was found to be modeled best using the A(*m*) and A(2) splitting of the site, as defined by Hawthorne (1983). Occupancy was released for refinement, and the site scattering was modeled using K scattering factors for both sites. Difference maps also

clearly show splitting of M(4) into M(4) and M(4)' sites, with 0.64 e<sup>-</sup> Å<sup>-3</sup> at M(4)'. Scattering at these sites was modeled with Ca and Fe, respectively, and occupancies were released for refinement. The data did not support a constrained refinement of the tetrahedral sites, so they were modeled with Si scattering; the occupancies were released and refined to values less than 1. The T(1) site exhibits the largest deviation from 1. This is interpreted to mean that Al most strongly partitions at the T(1) site, as is known for most amphiboles (Oberti *et al.* 1995); however, the refined site-occupancy indicates that some Al also occupies the T(2) site. Both of these interpretations are supported by the mean bond-distances for the two tetrahedral sites. Sites M(1), M(2) and M(3) were refined with variable occupancy using Fe and Mg scattering factors assuming that the occupancy Fe + Mg = 1. The scattering at the O(3) site was refined using F and O scattering factors assuming F + O = 1. Occupancies

TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR FLUORO-POTASSICHASTINGSITE

<i>d</i> <sub>obs</sub> Å	<i>d</i> <sub>calc</sub> Å	<i>h</i> <i>k</i> <i>l</i>	<i>d</i> <sub>obs</sub> Å	<i>d</i> <sub>calc</sub> Å	<i>h</i> <i>k</i> <i>l</i>
9.064	9.086	2 0 2 0	1.910	1.910	5 5 1 0
8.499	8.491	100 1 1 0	1.896	1.897	2 4 6 1
4.802	4.802	6 2 0 0	1.832	1.831	3 5 3 0
4.544	4.543	6 0 4 0	1.769	1.769	2 5 1 2
3.401	3.401	11 1 3 1	1.699	1.699	2 7 3 3
3.299	3.300	32 2 4 0	1.661	1.661	10 4 6 1
3.151	3.153	76 3 1 0	1.650	1.650	9 4 8 0
3.026	3.029	2 0 6 0	1.628	1.628	4 1 11 0
2.956	2.956	5 2 2 1	1.601	1.601	6 6 0 0
2.830	2.830	53 3 3 0	1.591	1.591	1 7 5 3
2.764	2.764	5 3 3 1	1.553	1.553	2 6 0 2
2.722	2.722	23 1 5 1	1.512	1.512	5 5 5 1
2.609	2.610	9 0 6 1	1.468	1.468	5 3 11 0
2.563	2.563	7 2 0 2	1.453	1.453	10 0 12 1
2.402	2.402	17 3 5 0	1.415	1.415	2 6 6 0
2.362	2.361	6 3 5 1	1.369	1.369	5 0 8 3
2.351	2.35	7 4 2 1	1.349	1.349	1 7 13 1
2.317	2.316	2 7 1 1	1.338	1.338	2 6 8 1
2.306	2.304	1 3 1 2	1.324	1.324	5 1 13 1
2.176	2.175	8 2 6 1	1.309	1.309	1 6 8 0
2.054	2.053	2 2 8 0	1.305	1.305	2 3 9 3
2.041	2.041	1 4 0 2	1.282	1.282	1 6 8 2
2.029	2.029	7 3 5 1	1.210	1.210	1 5 11 2
2.016	2.016	5 3 7 0	1.201	1.201	2 6 10 0
1.940	1.940	<1 4 2 1	1.135	1.135	3 7 9 0

The pattern was measured with CuK $\alpha$  radiation.

TABLE 3. MÖSSBAUER PARAMETERS FOR FLUORO-POTASSICHASTINGSITE

	<sup>57</sup> Fe <sup>2+</sup>	<sup>57</sup> Fe <sup>3+</sup>	Fe <sup>3+</sup>
$\Delta_0$	2.15	2.49	0.99
$\delta_0$	0.98	0.52	0.57
$\bar{\delta}_0$	1.09	1.09	0.23
$\delta_1$	0.04	0.04	0.06
$\bar{\delta}$	1.18	1.19	0.29
A	51.7	24.1	22.2
% present	54.7	25.5	19.8

The values presented in the table are expressed in mm/s. An explanation of the symbols used in the left column is provided in the text.

TABLE 5. CRYSTAL DATA AND DETAILS CONCERNING THE STRUCTURE REFINEMENT OF FLUORO-POTASSICHASTINGSITE

Unit-cell parameters, space group	
<i>a</i> 9.9480(3), <i>b</i> 18.1777(6), <i>c</i> 5.3302(2) Å, $\beta$ 105.140(1)°, C2/ <i>m</i>	
Frame width, scan time, number of frames	0.20°, 10 s, 4500
Detector distance	5 cm
Effective transmission	0.9030 – 1.000
<i>R</i> <sub>int</sub> (before, after SADABS absorption correction)	0.0339 – 0.0161
Measured reflections, full sphere	7974
Unique reflections, refined parameters	1,190, 116
<i>R</i> 1 for 1137 <i>F</i> <sub>o</sub> > 4 $\sigma$ ( <i>F</i> <sub>o</sub> )	0.0242
<i>R</i> 1 for all 1190 data	0.0247
Largest difference peaks	+1.60, -1.03 e <sup>-</sup> Å <sup>-3</sup>
Goodness-of-fit	1.084



(based on the scattering factors used to model the site scattering) are listed in Table 6, which also presents the atom parameters. The presence of F (dominant), OH and Cl in our sample makes the determination of the H position, associated with the O3 oxygen, problematical. As shown by Oberti *et al.* (1995), the H lies along a path defined by F, O3 and Cl. It is thus "lost" in the average electron-density resulting from the presence of these three constituents. Refinement of the H position with a fixed O3–H distance (in the range 0.82–0.87) did result in a slightly better refinement. Because of the observations of Oberti *et al.* (1995), however, the H was left out of our structure model. The largest difference-peak in the refinement ( $1.6 \text{ e}^- \text{ \AA}^{-3}$ ) lies near the predicted H position. Selected interatomic distances are presented in Table 7. A table of structure factors is available from the Depository of Unpublished Data on the MAC website [document Fluoro-potassichastingsite CM47\_909].

Using quadratic-programming methods, Wright *et al.* (2000) proposed a method of optimizing the occupancy of cation sites in minerals with multiply-occupied cation sites; the optimized formula minimizes the differences between the formula obtained from the results of the chemical analysis and that obtained by single-crystal structure refinement (using site scattering and bond valence, which is a function of bond distance). Using that method, *via* the program OCCQP, with the structure refinement and chemical data obtained in this study, the structural formula of the holotype fluoro-potassichastingsite (with the proportion of halogen determined from chemical data only) is:  $A^{(m)}(K_{0.61}Na_{0.11}Ca_{0.05})_{\Sigma 0.77} A^{(2)}(K_{0.02}Ca_{0.01})_{\Sigma 0.03} M^{(4)}(Ca_{1.85}Na_{0.04})_{\Sigma 1.89} M^{(4)}(Mn^{2+}_{0.03})_{\Sigma 0.03} M^{(3)}(Fe^{2+}_{0.55}Mg_{0.45})_{\Sigma 1.00} M^{(2)}(Fe^{2+}_{0.85}Mg_{0.27}Fe^{3+}_{0.38}Al_{0.51})_{\Sigma 2.01} M^{(1)}(Fe^{2+}_{1.06}Mg_{0.92}Al_{0.02})_{\Sigma 2.00} T^{(1)}(Si_{2.80}Al_{1.20})_{\Sigma 4.00} T^{(2)}(Si_{3.66}Al_{0.34})_{\Sigma 4.00} O_{22}[F_{1.11}(OH)_{0.73}Cl_{0.16}]_{\Sigma 2.00}$ . Several hard constraints were used in the OCCQP calculation according to crystal-chemical knowledge of the amphiboles. The  $M(4)$  and  $M(4)'$  site occupancies were allowed to vary in the OCCQP

calculations. The sum of the occupancies on these two sites is 1.92 *apfu*. Minor vacancies are shown but may not be real.

## DISCUSSION

The paragenetic relationships at the Greenwood mine show that fluoro-potassichastingsite formed after the magnetite ore and was synchronous with the sulfide sequence. The mineral replaced hastingsite and diopside, developed as an intergranular phase between diopside crystals, and formed compact aggregates with crystals up to 1 cm in size. It is a product of potassium-halogen metasomatism and is somewhat similar to the products of alkali chloride metasomatism (Barton & Johnson 2000) that accompany occurrences of iron oxide, lead–zinc, REE–uranium mineralization (Mazdab 2003), and Cu–Au  $\pm$  Co  $\pm$  As mineralization (Williams 1998).

Only limited data exist on the K- and F-rich amphiboles; they have been observed in both magmatic and metasomatic environments (Table 8).

Similarly, experimental data on fluorine- and potassium-dominant amphiboles are sparse. Gilbert & Briggs (1974) and Gilbert *et al.* (1982) have experimentally studied the stability of fluoro-potassicrichterite and concluded that the "low pressure difference in the F- and OH-stabilities ( $\sim 300^\circ\text{C}$ ) is diminished with increasing pressure ( $\sim 150^\circ\text{C}$ )". Foley (1991), in his work on the high-pressure stability of fluoro-potassicrichterite, showed that the Gilbert & Briggs generalization is reversed at pressures above 30 kbar. The difference in the thermal stability of fluoro-potassicrichterite and its OH analogue increases between 35 and 50 kbar,

TABLE 7. SELECTED INTERATOMIC DISTANCES (Å) IN FLUORO-POTASSICHASTINGSITE

A(m) –	O7	2.536(6)	A(2) –	O5 × 2	2.56(7)
	O7	2.576(6)		O7 × 2	2.81(2)
	O6 × 2	2.926(3)		O6 × 2	2.75(5)
	O5 × 2	3.015(4)		Mean	2.64
	O5 × 2	3.111(4)			
Mean		2.902			
M(4) –	O4 × 2	2.350(2)	M(4)' –	O2 × 2	2.07(8)
	O2 × 2	2.412(3)		O4 × 2	2.291(3)
	O6 × 2	2.549(3)		O6 × 2	2.91(9)
	O5 × 2	2.710(2)		Mean	2.42
	Mean	2.505			
M(1) –	O1 × 2	2.056(1)	M(2) –	O4 × 2	1.992(1)
	O2 × 2	2.126(1)		O2 × 2	2.102(1)
	O3 × 2	2.168(1)		O1 × 2	2.104(1)
	Mean	2.116		Mean	2.066
M(3) –	O1 × 4	2.103(1)	M(3) –	O1 × 4	2.103(1)
	F3 × 2	2.127(2)		F3 × 2	2.127(2)
	Mean	2.111		Mean	2.111
T(1) –	O7	1.660(1)	T(2) –	O4	1.601(1)
	O1	1.661(2)		O2	1.628(2)
	O6	1.681(1)		O5	1.648(1)
	O5	1.687(1)		O6	1.659(2)
	Mean	1.672(3)		Mean	1.634

TABLE 6. POSITIONAL PARAMETERS, EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETER, AND REFINED SITE-OCCUPANCY OF ATOMS IN FLUORO-POTASSICHASTINGSITE

Site	x	y	z	$U_{eq}$	Occupancy
A(m)	0.5248(5)	0	0.0522(10)	0.0428(19)	$K_{0.30(7)}$
A(2)	0.500	-0.034(5)	0	0.01(2)	$K_{0.61(3)}$
M(4)	0	0.2799(16)	0.500	0.02(2)	$Ca_{0.93(12)}$
M(4)'	0	0.255(6)	0.500	0.014(11)	$Ca_{0.015(7)}$
M(1)	0	0.09116(3)	0.500	0.0095(2)	$Fe_{0.515(3)}Mg_{0.481(5)}$
M(2)	0.500	0.32197(3)	0	0.0075(1)	$Fe_{0.815(3)}Mg_{0.381(5)}$
M(3)	0	0	0	0.0085(3)	$Fe_{0.542(5)}Mg_{0.458(6)}$
T(1)	0.27871(5)	0.08541(3)	0.30210(10)	0.0079(2)	$Si_{0.929(4)}$
T(2)	0.29054(5)	0.17262(3)	0.81095(10)	0.0073(2)	$Si_{0.944(4)}$
O(1)	0.10586(15)	0.08896(8)	0.21650(28)	0.0141(3)	$O_1$
O(2)	0.12106(14)	0.17519(8)	0.73056(27)	0.0136(3)	$O_2$
O(3)	0.11559(25)	0.0000	0.71592(37)	0.0284(7)	$F_{0.99(5)}O_{0.01(5)}$
O(4)	0.36705(15)	0.24911(8)	0.79186(28)	0.0153(3)	$O_3$
O(5)	0.34741(14)	0.13728(8)	0.10438(26)	0.0154(3)	$O_4$
O(6)	0.34365(14)	0.11953(8)	0.60240(27)	0.0157(3)	$O_5$
O(7)	0.3364(2)	0	0.2937(4)	0.0185(4)	$O_6$

TABLE 8. OCCURRENCES OF K- AND F-RICH AMPHIBOLES

Occurrences, localities	K- and F-rich amphibole	Ref.
Kakortokite pegmatite Kola Peninsula, Russia	"fluoro-potassic-magnesiokatophorite"	1
Fenite veins in quartzite and biotite schists, Gatineau area, Quebec, Canada	"fluoro-potassic-magneso-arfvedsonite"	2
Lamproite West Kimberly, Australia	titanian fluoro-potassicrichterite	3
Calcareous ejecta Monte Somma, Italy	fluoro-potassicrichterite	4
Calc-silicate band in marble Bufa del Diente, Mexico	fluoro-potassicrichterite	5
Marble Pargas, Finland	fluorian potassicpargasite	6

References: 1: Mazdab (2003), 2: Hogarth *et al.* (1987), Hogarth (2006), 3: Oberti *et al.* (1992), 4: Della Ventura *et al.* (1992), 5: Heinrich (1994), 6: Robinson *et al.* (1997). The quotation marks indicate that the name differs slightly from that in the original articles to reflect current usage in the order of prefixes.

the smallest being at intermediate pressures, such as 20–35 kbar.

The formation of fluoro-potassichastingsite at the Greenwood mine is related to a metasomatic – hydrothermal event that has generated the relatively high-temperature sulfide sequence (pyrrhotite – chalcopyrite ± molybdenite ± pyrite) that overlapped the Fe oxide sequence. For most of the above-mentioned occurrences, the source for potassium and fluorine is probably igneous (Heinrich 1994), but we have no reason to attribute the same origin to the fluids that generated fluoro-potassichastingsite. These halogen-rich fluids are probably of crustal origin, with potassium likely having been leached from the host microcline gneiss. The fluids that generated the sulfide sequence reacted with diopside and hastingsite to form fluoro-potassichastingsite, as a more stable amphibole species, than its precursor(s) at the prevailing conditions. The genesis of such amphiboles and their associated minerals is currently under investigation, the results of which are planned for a future publication.

#### ACKNOWLEDGMENTS

New York State Museum partially funded this project (ML). The structure portion of this work was supported by NSF grant EAR-0003201 (JM and JR). The authors strongly appreciate the very helpful and constructive comments of Drs. Roberta Oberti, Frank Mazdab and Robert F. Martin, which greatly improved the manuscript.

#### REFERENCES

- BARTON, M.D. & JOHNSON, D.A. (2000): Alternative brine sources for Fe-oxide (–Cu–Au) systems: implications for hydrothermal alteration and metals. *In* Hydrothermal Iron Oxide Copper–Gold and Related Deposits: a Global Perspective. Australian Mineral Foundation, Perth, Australia (43–60).
- BURKE, E.A.J. & LEAKE, B.E. (2004): "Named amphiboles": a new category of amphiboles recognized by the International Mineralogical Association (IMA), and the proper order of prefixes to be used in amphibole names. *Can. Mineral.* **42**, 1881–1883.
- DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1997): *Rock-Forming Silicates*. 2B. *Double-Chain Silicates* (2<sup>nd</sup> ed.). The Geological Society, London, U.K.
- DELLA VENTURA, G., PARODI, G.C. & MARAS, A. (1992): Potassium-fluor-richterite, a new amphibole from San Vito, Monte Somma, Campania, Italy. *Rendiconti Lincei, Sci. Fis. Nat., Ser. 9*, **3**(3), 239–245.
- DYAR, M.D., MACKWELL, S.J., MCGUIRE, A.V., CROSS, L.R. & ROBERTSON, J.D. (1993): Crystal chemistry of Fe<sup>3+</sup> and H<sup>+</sup> in mantle kaersutites: implications for mantle metasomatism. *Am. Mineral.* **78**, 968–979.
- FOLEY, S. (1991): High-pressure stability of the fluor- and hydroxy-endmembers of pargasite and K-richterite. *Geochim. Cosmochim. Acta* **55**, 2689–2694.
- GATES, A.E., KROL, M.A. & VALENTINO, D.W. (2000): Dextral strike-slip tectonic escape in the final assembly of Rodinia in the Appalachians, Hudson Highlands, NY. *Geol. Soc. Am., Abstr. Program, Northeastern Section* **32**, 20.
- GATES, A., VALENTINO, D., CHIARENZELLI, J. & HAMILTON, M. (2001): Ages and tectonic events in the Hudson Highlands, NY: results from SHRIMP analyses. *Geol. Soc. Am., Abstr. Program, Northeastern Section* **33**(1), 79–80.
- GILBERT, M.C. & BRIGGS, D.F. (1974): Comparison of the stabilities of OH- and F-potassic richterites – a preliminary report. *Trans. Am. Geophys. Union (Eos)* **55**, 480–481 (abstr.).
- GILBERT, M.C., HELZ, R.T., POPP, R.K. & SPEAR, F.S. (1982): Experimental studies of amphibole stability. *In* Amphiboles: Petrology and Experimental Phase Relations (D.R. Veblen & P.H. Ribbe, eds.). *Rev. Mineral.* **9B**, 229–353.
- GUNTER, M.E., DYAR, M.D., TWAMLEY, B., FOIT, F.F., JR., & CORNELIUS, S.B. (2003): Composition, Fe<sup>3+</sup>/ΣFe, and crystal structure of non-asbestiform and asbestiform amphiboles from Libby, Montana, U.S.A. *Am. Mineral.* **88**, 1970–1978.

- HAWTHORNE, F.C. (1983): The crystal chemistry of the amphiboles. *Can. Mineral.* **21**, 173-480.
- HEINRICH, W. (1994): Potassium-fluor-richterite in metacherts from the Bufa del Diente contact-metamorphic aureole, NE Mexico. *Mineral. Petrol.* **50**, 259-270.
- HOGARTH, D.D. (2006): Fluoro-potassic-magnesio-arfvedsonite,  $\text{KNa}_2\text{Mg}_5\text{Si}_8\text{O}_{22}\text{F}_2$ , from the Outaouais region, Quebec, Canada. *Can. Mineral.* **44**, 289.
- HOGARTH, D.D., CHAO, G.Y. & TOWNSEND, M.G. (1987): Potassium- and fluorine-rich amphiboles from the Gatineau area, Quebec. *Can. Mineral.* **23**, 739-753.
- LEAKE, B.E., WOOLLEY, A.R., ARPS, C.E.S., BIRCH, W.D., GILBERT, M.C., GRICE, J.D., HAWTHORNE, F.C., KATO, A., KISCH, H.J., KRIVOVICHEV, V.G., LINTHOUT, K., LAIRD, J., MANDARINO, J.A., MARESCHE, W.V., NICKEL, E.H., ROCK, N.M.S., SCHUMACHER, J.C., SMITH, D.C., STEPHENSON, N.C.N., UNGARETTI, L., WHITTAKER, E. J. W. & GUO YOUZHI (1997): Nomenclature of amphiboles; report of the subcommittee on amphiboles of the International Mineralogical Association, Commission on New Minerals and Mineral Names. *Can. Mineral.* **35**, 219-246.
- MAZDAB, F.K. (2003): The diversity and occurrence of potassium-dominant amphiboles. *Can. Mineral.* **41**, 1329-1344.
- OBERTI, R., UNGARETTI, L., CANNILLO, E. & HAWTHORNE, F.C. (1992): The behavior of Ti in amphiboles. I. Four- and six-coordinate Ti in richterite. *Eur. J. Mineral.* **4**, 425-439.
- OBERTI, R., UNGARETTI, L., CANNILLO, E., HAWTHORNE, F. C. & MEMMI, I. (1995): Temperature-dependent Al order-disorder in the tetrahedral double chain of  $C2/m$  amphiboles. *Eur. J. Mineral.* **7**, 1049-1063.
- RANCOURT, D.G. & PING, J.Y. (1991): Voigt-based methods for arbitrary-shape static hyperfine parameter distributions in Mössbauer spectroscopy. *Nucl. Instrum. Methods Phys. Res.* **B58**, 85-97.
- ROBINSON, G.W., GRICE, J.D., GAULT, R.A. & LALONDE, A.E. (1997): Potassicpargasite, a new member of the amphibole group from Pargas, Turku-Pori, Finland. *Can. Mineral.* **35**, 1535-1540.
- WILLIAMS, P.J. (1998): An introduction to the metallogeny of the McArthur River – Mount Isa – Cloncurry minerals province. In *Metallogeny of the McArthur River – Mount Isa – Cloncurry Mineral Province* (P.J. Williams, ed.). *Econ. Geol.* **93**, 1120-1131.
- WRIGHT, S.E., FOLEY, J.A. & HUGHES, J.M. (2000): Optimization of site occupancies in minerals using quadratic programming. *Am. Mineral.* **85**, 524-531.

Received January 3, 2006, revised manuscript accepted May 8, 2009.