The Canadian Mineralogist
Vol. 41, pp. 479-488 (2003)

SYNTHESIS AND PROPERTIES OF V^{3+} ANALOGUES OF JAROSITE-GROUP MINERALS

John E. DUTRIZAC[§] and Tzong T. CHEN

CANMET, Natural Resources Canada, 555 Booth Street, Ottawa, Ontario K1A 0G1, Canada

Abstract

The V^{3+} analogues of natrojarosite, jarosite, rubidium-substituted jarosite, dorallcharite, hydronium jarosite, ammoniojarosite and plumbojarosite were synthesized using a conventional hydrolysis procedure. Although a temperature of 100°C was acceptable for most of the syntheses, a reaction temperature of 140°C was needed to give a satisfactory yield of the V^{3+} analogue of hydronium jarosite. Also, the V^{3+} analogue of plumbojarosite was synthesized by reacting an excess of $PbSO_4$ at 150°C, and subsequently dissolving any unreacted $PbSO_4$ at room temperature with ammonium acetate solution. Efforts to synthesize the V^{3+} analogue of argentojarosite were unsuccessful, as trivalent vanadium reduced the silver ion to metallic silver. The V^{3+} analogues of jarosite-group minerals commonly form spheroidal aggregates composed of individual crystals to 3 μm in diameter. According to X-ray powder-diffraction data, all the precipitates have the *R*3*m* structure of jarosite-group minerals; however, no ~11 Å reflection was detected in the V^{3+} analogue of plumbojarosite, indicating a lack of order involving the Pb^{2+} ions and associated vacancies. The densities of the V^{3+} analogues were also measured; relatively low values were obtained because of V-site vacancies in the structure.

Keywords: trivalent vanadium, jarosite, jarosite-group minerals, synthesis, X-ray powder-diffraction patterns, jarosite analogues.

Sommaire

Nous avons synthétisé les composés analogues de la natrojarosite, jarosite, jarosite substituée par le rubidium, dorallcharite, hydronium jarosite, ammoniojarosite et plumbojarosite contenant du V^{3+} en utilisant une démarche conventionnelle d'hydrolyse, Quoiqu'une température de 100°C est acceptable pour la plupart des synthèses, nous avons eu besoin de chauffer à 140°C pour obtenir une quantité suffisante de l'analogue à V^{3+} de la hydronium jarosite. De plus, l'analogue à V^{3+} de la plumbojarosite a été synthétisé par réaction d'un excédent de $PbSO_4$ à 150°C, avec dissolution par la suite du $PbSO_4$ non réagi à température ambiante avec une solution d'acétate d'ammonium. Nos efforts pour synthétiser l'analogue à V^{3+} de l'argentojarosite n'ont pas réussi, parce que le vanadium trivalent a réduit l'ion Ag^+ à l'argent métallique. Les analogues vanadifères (V^{3+}) des minéraux du groupe de la jarosite se présentent en général en aggrégats sphéroïdes faits de cristaux individuels atteignant 3 μm de diamètre. Selon les données de diffraction X, méthode des poudres, tous les précipités adoptent la structure *R*3*m* des minéraux de ce groupe; toutefois, aucun signe d'une réflexion à ~11 Å n'a été décelé dans l'analogue vanadifère de la plumbojarosite, ce qui témoigne d'un manque d'ordre impliquant les ions Pb^{2+} et les lacunes associées. Nous avons aussi mesuré la densité de ces analogues à V^{3+}; les valeurs sont relativement faibles à cause des lacunes dans le site V des structures.

(Traduit par la Rédaction)

Mots-clés: vanadium trivalent, jarosite, minéraux du groupe de la jarosite, synthèse, diffraction X, méthode des poudres, analogues de la jarosite.

Introduction

Jarosite-group minerals occur widely in nature, and the precipitation of jarosite-type compounds [$MFe_3(SO_4)_2(OH)_6$, where M = K, Na, NH_4, Ag, H_3O, *etc.*] is commonly used in the metallurgical industry to eliminate dissolved iron, and other impurities, from processing solutions in a readily filterable form (*e.g.,* Dutrizac & Jambor 2001). Jarosite precipitation is especially effective in eliminating certain trivalent ions, which substitute for Fe^{3+} in the jarosite structure. Thus, the presence of Al (Stoffregen *et al.* 2001), Cr (Lengauer *et al.* 1994), In (Dutrizac & Mingmin 1993) and Ga (Dutrizac & Chen 2000) is extensively controlled during jarosite precipitation.

[§] *E-mail address*: jdutriza@nrcan.gc.ca

The jarosite group consists of seven minerals, in addition to two synthetic members for which no mineral equivalent is known (Table 1). All the compounds have the general formula $M\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$, but in plumbojarosite and mercury-substituted jarosite (the least stable of all jarosite-type compounds), the *M* cation is divalent. Consequently, only half of the *M* sites are filled, and ordering of the cation and vacancies results in a superstructure in which the *c* axis of the unit cell is doubled (Jambor 1999).

Vanadium is a common element in many ores and concentrates, and in coal and petroleum; it has a complex chemistry and usually occurs in the trivalent, tetravalent and pentavalent oxidation states (Schindler *et al.* 2000, Cotton & Wilkinson 1962). Despite its widespread occurrence in nature, relatively little is known about the behavior of vanadium during jarosite precipitation. Kolitsch & Pring (2001) observed that V^{3+} substitutes to a minor extent for Fe^{3+} and Al^{3+} in mineral members of the alunite supergroup, but they concluded that the vanadate ion (*i.e.*, $V^{5+}O_4$) does not substitute for SO_4, likely because of the much larger size of the polymerized vanadate species (Schindler *et al.* 2000). Tetravalent vanadium exists in acid media as the vanadyl ion, VO^{2+}, but this species is not believed to substitute extensively for Fe^{3+} in jarosite-type compounds (Kolitsch & Pring 2001). Nevertheless, V^{3+} is readily oxidized to V^{4+}, and the possibility of a limited substitution of V^{4+} for V^{3+} or Fe^{3+} in jarosite-type compounds exists. Tudo *et al.* (1973) and Tudo & Laplace (1977) reported the synthesis of the V^{3+} analogues of hydronium jarosite [*i.e.*, $(H_3O)V_3(SO_4)_2(OH)_6$] and of ammonium jarosite [*i.e.*, $(NH_4)V_3(SO_4)_2(OH)_6$] by the thermal decomposition of the respective hydrated double sulfate salts under vacuum. However, the procedure requires close control of the temperature and appears to be applicable only for species having a volatile *M* ion, such as H_3O or NH_4. Dobley *et al.* (2000) synthesized the V^{3+} analogue of natrojarosite using a redox-based technique at 200°C, and showed its structure to be similar to that of natrojarosite. It seems, however, that a two-phase product was made, and no compositional data of the product were provided. Dutrizac & Chen (2002) showed that the V^{3+} analogue of jarosite could be prepared by conventional hydrolysis procedures (Dutrizac & Jambor 2001), and described the parameters affecting the precipitation reaction. Grohol & Nocera (2002) developed a method to synthesize stoichiometric, well-developed crystals of the V^{3+} analogues of jarosite, natrojarosite, rubidium-substituted jarosite, ammoniojarosite and dorallcharite, using a new redox-based hydrothermal technique. These compounds were subsequently used for the measurement of the magnetic properties of the synthesized species (Grohol *et al.* 2001, Papoutsakis *et al.* 2002). The first naturally occurring V^{3+} mineral of the alunite supergroup (Jambor 1999) was recently discovered by Kolitsch *et al.* (1999). Although springcreekite is a barium phosphate species $[BaV_3(PO_4)_2(OH,H_2O)_6]$, its existence suggests that other end-member V^{3+} analogues of jarosite-group minerals may well eventually be discovered.

TABLE 1. JAROSITE-GROUP MINERALS AND RELATED COMPOUNDS

Formula	Mineral name*
$KFe_3(SO_4)_2(OH)_6$	jarosite
$NaFe_3(SO_4)_2(OH)_6$	natrojarosite
$RbFe_3(SO_4)_2(OH)_6$	no mineral equivalent
$AgFe_3(SO_4)_2(OH)_6$	argentojarosite
$(NH_4)Fe_3(SO_4)_2(OH)_6$	ammoniojarosite
$TlFe_3(SO_4)_2(OH)_6$	dorallcharite
$Pb_{0.5}Fe_3(SO_4)_2(OH)_6$	plumbojarosite
$Hg_{0.5}Fe_3(SO_4)_2(OH)_6$	no mineral equivalent
$(H_3O)Fe_3(SO_4)_2(OH)_6$	hydronium jarosite

* where applicable.

The above discussion suggests the existence of a number of V^{3+} analogues of jarosite-type compounds. To shed additional light on these species, efforts were made to synthesize the V^{3+} analogues of natrojarosite, jarosite, rubidium-substituted jarosite, argentojarosite, dorallcharite, hydronium jarosite, ammoniojarosite, mercury-substituted jarosite and plumbojarosite, using conventional procedures of hydrolysis that are currently in use in the hydrometallurgical industry. The results of the synthesis experiments, and the characterization of the resulting precipitates, are presented in this paper.

SYNTHESIS AND CHARACTERIZATION

The V^{3+} analogues of natrojarosite, jarosite, rubidium-substituted jarosite, argentojarosite, dorallcharite and ammoniojarosite were precipitated from 400 mL of solution contained in a 500 mL reaction vessel heated on a temperature-controlled (±1°C) hot plate. The reaction vessel was sealed with a ground glass lid, and the contents of the vessel were stirred using a magnetic stirring bar. Reagent-grade VCl_3 was dissolved in distilled water to give a 0.4 M V^{3+} solution. The as-prepared solution was filtered to remove the small amount of insoluble matter that invariably was present. A significant stoichiometric excess of the appropriate M_2SO_4 salt [*e.g.*, 0.4 M Na_2SO_4, 0.4 M K_2SO_4, 0.4 M $(NH_4)_2SO_4$, *etc.*] was added such that an independent source of sulfate usually was not required. The reaction vessel was then heated to 100°C for 24 h to precipitate the desired V^{3+} analogue; for example,

$$2\,K_2SO_4 + 3\,VCl_3 + 6\,H_2O \rightarrow KV_3(SO_4)_2(OH)_6 + 6\,HCl + 3\,KCl \qquad (1).$$

The V^{3+} analogue of hydronium jarosite was prepared by heating a 0.4 M VCl_3 – 0.4 M Li_2SO_4 solution to 140°C for 24 h. The Li_2SO_4 provided the necessary sulfate concentration, but Li does not form a jarosite-type compound (Dutrizac & Jambor 1987a), such that the resulting V^{3+} analogue of hydronium jarosite was

Li-free. Various efforts were made to synthesize the V^{3+} analogue of plumbojarosite using both sulfate and concentrated chloride media. Although the syntheses from 0.4 M VCl_3 – 4.0 M LiCl – 0.3 M Li_2SO_4 solutions containing 20 g/L $PbCl_2$ yielded only the V^{3+} analogue of hydronium jarosite containing up to 3.6 wt% Pb, syntheses from sulfate solutions produced the V^{3+} analogue of plumbojarosite. For the latter experiments, 30 g/L of $PbSO_4$ were slurried for 24 h in 0.4 M VCl_3 – 0.5 M $MgSO_4$ solutions at pH 1.8 at 150°C in an autoclave. The resulting precipitate was washed four times at room temperature in 1 L portions of 4 M ammonium acetate solution to dissolve the excess $PbSO_4$ selectively (Dutrizac *et al.* 1980).

At the completion of all the synthesis experiments, the resulting slurry was filtered hot, and the precipitate was washed with copious amounts of warm distilled water. The precipitate was then air-dried at room temperature for at least 24 h to avoid any superficial oxidation of the vanadium. The air-dried products were dissolved and then subjected to chemical analysis using inductively coupled plasma (ICP) spectroscopy. The precipitates were also subjected to X-ray powder-diffraction analysis using a Rigaku rotating anode diffractometer with Cu$K\alpha_1$ radiation at 50 kV and 180 mA, at a step scan of 0.02° and a scan rate of 4° per minute in 2θ. The X-ray-diffraction patterns were indexed on the basis of the *R*3*m* cell of jarosite, and all the detected reflections with relative intensities ≥2% were indexed on the basis of this cell. Cell parameters were calculated by a least-squares refinement method using the JADE program. Some of the precipitates were examined by scanning electron microscopy (SEM) with energy-dispersion X-ray analysis (EDX). Polished sections were prepared, and these were analyzed quantitatively using the electron microprobe to illustrate their homogeneity. The samples were analyzed with a JEOL 8900 Superprobe, using 15 kW, 20 nA beam current, a defocused beam and a counting period of 10 s. Probed natural jarosite-group minerals and synthetic electronic-grade compounds were used as standards. The theoretical densities of the V^{3+} analogues of the jarosite-group minerals were calculated from the refined unit-cell dimensions assuming three formula units per unit cell. Pycnometric determinations of densities were made using distilled water as the immersing fluid and ultrasonic vibration to remove trapped air bubbles. The pycnometric apparatus was calibrated with natural quartz, the density of which was found to be 2.64 ± 0.01 g/cm^3 (theoretical value 2.65 g/cm^3). The details of the synthesis procedures and characterization techniques have been presented previously (Dutrizac & Kaiman 1976, Dutrizac 1983, Chen & Dutrizac 1990).

RESULTS AND DISCUSSION

Chemical characterization

The V^{3+} analogues of natrojarosite, jarosite and rubidium-substituted jarosite were readily synthesized at 100°C using the procedures described above, which have been shown to be near-optimum for the precipitation of alkali jarosite species (Dutrizac 1983) and the V^{3+} analogue of jarosite (Dutrizac & Chen 2002). Results of the chemical analyses of the synthesized V^{3+} analogues of natrojarosite, jarosite and rubidium-substitued jarosite are presented in Table 2, together with the stoichiometric compositions. The chloride contents were consistently less than 0.05 wt%, validating the use of VCl_3 as the source of V^{3+}. The analyses indicate modest deficiencies in *M*-site occupancy (0.15–0.24 mol) and vanadium-site occupancy (0.27–0.55 mol). The *M*-site deficiency is related to the substitution of the hydronium ion (H_3O^+) (Ripmeester *et al.* 1986); the charge imbalance caused by the deficiency in the occupancy of the vanadium site may be related to the partial oxidation of V^{3+} to V^{4+} and the modest incorporation of V^{4+} in the structure (Dutrizac & Chen 2002). Grohol & Nocera (2002) postulated that charge neutrality in V-deficient V^{3+} analogues of jarosite-type compounds is maintained by the partial protonation of the OH^- groups. A similar mechanism has been proposed to rationalize the charge imbalance caused by Fe deficiencies in jarosite-group minerals (Kubisz 1964, Dutrizac & Jambor 2001), but an additional factor could also be the partial protonation of the $SO_4{}^{2-}$ species to

TABLE 2. COMPOSITIONS OF THE SYNTHESIZED V^{3+} ANALOGUES OF NATROJAROSITE, JAROSITE AND RUBIDIUM-SUBSTITUTED JAROSITE

	Natrojarosite		Jarosite		Rb-substituted jarosite	
	synthetic	theor.	synthetic	theor.	synthetic	theor.
Na wt%	3.81	4.89	–	–	–	–
K	–	–	7.08	8.04	–	–
Rb	–	–	–	–	13.09	16.05
V	30.13	32.52	26.43	31.44	26.64	28.70
SO_4	41.60	40.88	40.76	39.53	37.19	36.09
H_3O + OH	24.46	21.71	25.73	20.99	23.08	19.16
Formula	$Na_{0.76}(H_3O)_{0.24}$ $V_{2.73}(SO_4)_{2.00}$ $(OH)_{6.00}$		$K_{0.85}(H_3O)_{0.15}$ $V_{2.45}(SO_4)_{2.00}$ $(OH)_{6.00}$		$Rb_{0.79}(H_3O)_{0.21}$ $V_{2.70}(SO_4)_{2.00}$ $(OH)_{6.00}$	

TABLE 3. COMPOSITIONS OF THE SYNTHESIZED V^{3+} ANALOGUES OF AMMONIOJAROSITE, DORALLCHARITE AND HYDRONIUM JAROSITE

	Ammoniojarosite		Dorallcharite		Hydronium jarosite	
	synthetic	theor.	synthetic	theor.	synthetic	theor.
NH_4 wt%	3.00	3.87	–	–	–	–
Tl	–	–	23.57	31.37	–	–
H_3O	–	–	–	–	–	4.08
V	30.48	32.87	24.45	23.46	30.60	32.80
SO_4	41.93	41.32	32.88	29.49	41.18	41.23
H_3O + OH	24.59	21.94	19.10	15.68	28.22	21.89
Formula	$(NH_4)_{0.79}(H_3O)_{0.21}$ $V_{2.74}(SO_4)_{2.00}$ $(OH)_{6.00}$		$Tl_{0.67}(H_3O)_{0.33}$ $V_{2.80}(SO_4)_{2.00}$ $(OH)_{6.00}$		$(H_3O)_{1.00}V_{2.80}$ $(SO_4)_{2.00}$ $(OH)_{6.00}$	

HSO_4^- (Paktunc & Dutrizac 2003, submitted). Possibly, all three mechanisms play a role in maintaining the charge balance in the precipitates of the V^{3+} analogues of jarosite-type compounds.

In Table 3, we present the compositional data for the V^{3+} analogues of ammoniojarosite, dorallcharite and hydronium jarosite. The V^{3+} analogue of dorallcharite was prepared using the same conditions as those employed for the V^{3+} analogues of the alkali-bearing members of the jarosite-group (Table 2). However, because of the lower solubility of Tl_2SO_4, a solution containing 0.23 M Tl_2SO_4 was used, and Li_2SO_4 was added to give an overall sulfate concentration of 0.4 M SO_4. The resulting precipitate, however, had an excessive Tl content, and X-ray powder-diffraction analysis indicated the presence of TlCl. Reducing the concentration of Tl_2SO_4, to 0.05 M (with 0.35 M Li_2SO_4 to maintain the total sulfate concentration at 0.4 M) still yielded precipitates containing a faint trace of TlCl. However, reducing the thallium concentration to 0.03 or 0.04 M Tl_2SO_4 resulted in precipitates containing no detectable TlCl, and a concentration of 0.03 M Tl_2SO_4 (with 0.37 M Li_2SO_4) was selected for the final syntheses. Although a small quantity of the V^{3+} analogue of hydronium jarosite could be synthesized at 100°C from 0.4 M VCl_3 – 0.4 M Li_2SO_4 solutions at a pH of 1.8, greater yields were obtained by heating a similar solution to 140°C for 24 h in a Parr 2-L autoclave. Of course, the addition of Li_2SO_4 is required as the independent source of sulfate for the precipitation reaction (Equation 1). There is a deficiency in the NH_4 and Tl site occupancies (0.21 mol and 0.33 mol, respectively) that is likely compensated by hydronium ion substitution (Ripmeester *et al.* 1986). All the species show a characteristic 0.20–0.26 mol deficiency in vanadium-site occupancy.

In Table 4, we summarize the compositional data for the synthesized V^{3+} analogues of plumbojarosite and Pb-bearing hydronium jarosite. The V^{3+} analogue of plumbojarosite has a significant Pb content, as well as a characteristic 0.28 mol deficiency in vanadium site-occupancy. From a compositional perspective, it is clearly the V^{3+} analogue of plumbojarosite, having 82% Pb-site occupancy in the ideal $Pb_{0.5}V_3(SO_4)_2(OH)_6$ formula. In contrast, the Pb-bearing V^{3+} analogue of hydronium jarosite has only a modest 0.08 mol Pb content and a 0.84 mol H_3O content, but a similar deficiency at the vanadium site.

TABLE 4. COMPOSITIONS OF THE SYNTHESIZED V^{3+} ANALOGUES OF PLUMBOJAROSITE AND Pb-BEARING HYDRONIUM JAROSITE

	Plumbojarosite		Pb-bearing hydronium jarosite	
	synthetic	theor.	synthetic	theor.
Pb wt%	15.50	18.82	3.64	–
H_3O	–	–	–	4.08
V	25.37	27.76	29.41	32.80
SO_4	35.18	34.90	40.04	41.23
H_3O + OH	23.95	18.52	26.91	21.89
Formula	$Pb_{0.41}(H_3O)_{0.18}V_{2.72}(SO_4)_{2.00}(OH)_{6.00}$		$Pb_{0.08}(H_3O)_{0.84}V_{2.77}(SO_4)_{2.00}(OH)_{6.00}$	

Various efforts were made to synthesize the V^{3+} analogue of argentojarosite using the preferred conditions identified for argentojarosite precipitation (Dutrizac & Jambor 1987b). However, the addition of soluble Ag_2SO_4 to the VCl_3 solution resulted in the immediate precipitation of insoluble AgCl, as well as a small amount of the V^{3+} analogue of hydronium jarosite. Accordingly, the V^{3+} chloride was converted to the sulfate salt, and the syntheses were repeated. When Ag_2SO_4 was added to the $V_2(SO_4)_3$ solution and heated to ~90°C, extensive amounts of a dark grey precipitate formed. Chemical analysis of the products indicated Ag contents >50%, V contents of ~25%, but SO_4 contents of <1%. X-ray powder-diffraction analysis showed the presence of major metallic silver and a poorly crystallized vanadium oxide species, possibly related to corvusite, $(Na,Ca)(V^{5+},V^{4+},Fe^{2+})_8O_{26}\bullet4H_2O$. The experiments were repeated several times under a range of conditions, but we invariably found metallic silver as the dominant product of reaction:

$$Ag^+ + V^{3+} \rightarrow Ag^\circ + V^{4+} \qquad (2).$$

Thus it seems that silver ions in solution are able to oxidize V^{3+} to V^{4+}, with the resultant reduction of the silver ions to the metallic state, thereby rendering them unavailable for the precipitation of the V^{3+} analogue of argentojarosite.

A single synthesis of the V^{3+} analogue of mercury-substituted jarosite was attempted from a 0.4 M VCl_3 – 4.0 M LiCl – 0.3 M Li_2SO_4 solution, to which was added 20 g/L of $HgCl_2$. After 24 h of reaction at 100°C, a modest amount of $(H_3O)V_3(SO_4)_2(OH)_6$ formed, but the precipitate contained <200 ppm Hg. The synthesis of mercury jarosite is known to be very difficult (Dutrizac & Kaiman 1976), and no further efforts were made to prepare $Hg_{0.5}V_3(SO_4)_2(OH)_6$.

Morphology of the precipitates

Figure 1 provides a general view of the V^{3+} analogue of jarosite, as observed in a loose powder mount on the SEM, and Figure 2 illustrates the same precipitate at a higher magnification. The precipitate occurs as spheroidal or cauliflower-like aggregates of individual crystals of $KV_3(SO_4)_2(OH)_6$ <3 μm across. The size of the individual crystals is so small, however, that individual faces are distinguishable in some cases only. Nevertheless, the higher magnification used in Figure 2 reveals a number of crudely formed rhombohedral (pseudocubic) crystals of the V^{3+} analogue of jarosite. The spheroidal or cauliflower-like morphology illustrated in Figure 1 is characteristic of the V^{3+} analogues of most of the jarosite-type compounds synthesized in this study.

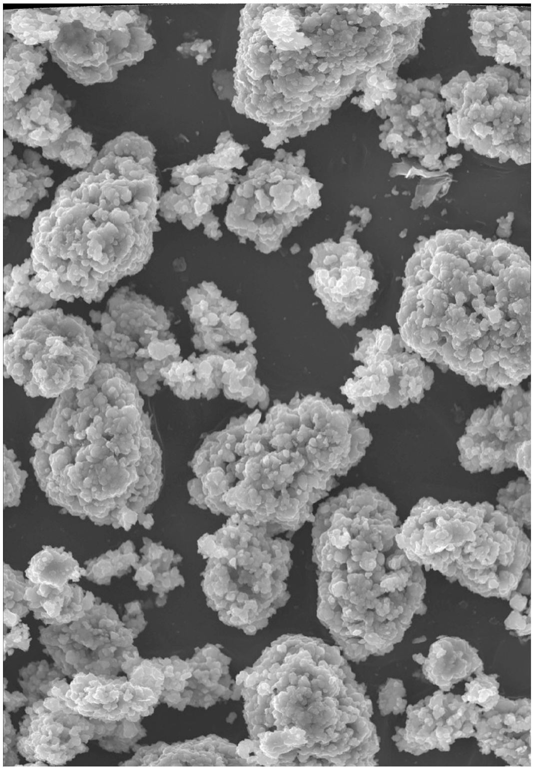

FIG. 1. Secondary electron micrograph of the precipitated V^{3+} analogue of jarosite. Approximate width of the field of view: 70 µm.

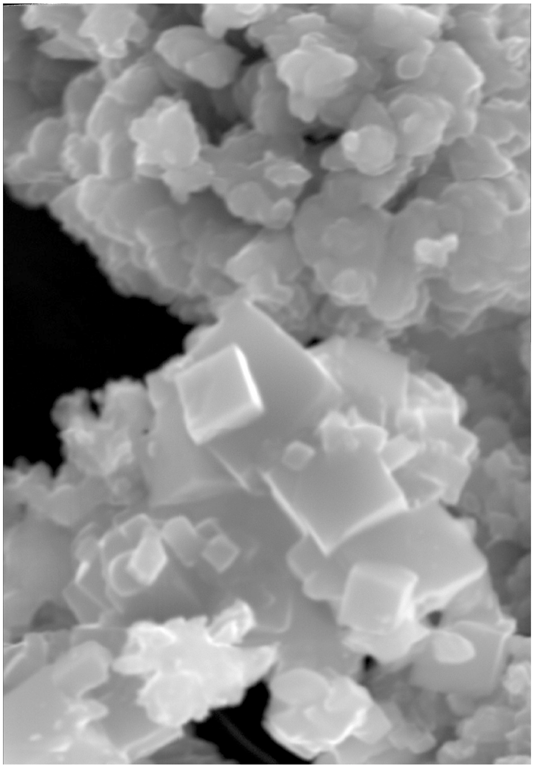

FIG. 2. Detailed structure of the precipitated V^{3+} analogue of jarosite. Approximate width of the field of view: 11 µm.

The precipitated V^{3+} analogue of natrojarosite also shows a few poorly developed faces when examined at high magnification, as indicated in Figure 3. The V^{3+} analogue of ammoniojarosite seems to be more euhedral, and consists of numerous intergrown plates (Fig. 4) 1–3 µm across. Both of these morphologies are commonly exhibited by synthetic iron-bearing jarosite-type precipitates. In contrast, the precipitates made in the autoclaves at elevated temperatures all exhibit euhedral habits, seen at high magnification. The V^{3+} analogue of hydronium jarosite (Fig. 5) and the V^{3+} analogue of plumbojarosite (Fig. 6) both exhibit the rhombohedral (pseudocubic) morphology characteristic of many jarosite precipitates.

Polished sections of the precipitates also were prepared. X-ray maps of the various precipitates indicate the uniform distribution of the *M* ion, vanadium and sulfur throughout the particles, suggesting the precipitation of single-phase species. This conclusion is also supported by the results of quantitative electron-microprobe analyses of some of the precipitates, which indicate a relatively uniform composition. For example, the electron-microprobe analysis of one of the $KV_3(SO_4)_2(OH)_6$ precipitates yielded 7.0 (±0.1) wt% K, 30.8 (±0.5) wt% V, 15.0 (±0.3) wt% S and 53.4 (±0.5) wt% O by difference, where the values in parentheses are the 1σ standard deviations.

X-ray data

The interplanar *d*-values and relative intensities of the peaks of X-ray powder diffractograms for the V^{3+} analogues of natrojarosite, jarosite, rubidium-substituted jarosite and ammoniojarosite are presented in Table 5; the analogous data for the V^{3+} analogues of dorallcharite, hydronium jarosite and plumbojarosite are given in Table 6. Generally, the X-ray powder-diffraction patterns of the V^{3+} analogues of jarosite-type compounds are similar to those of the analogous Fe^{3+}-bearing members. Also, the data reflect the anticipated trends as one ion is replaced by another. For example, the *c* parameter increases systematically as the size of the alkali ion increases from Na^+ to K^+ to Rb^+, whereas the *a* parameter decreases slightly. The X-ray powder-diffraction data for the V^{3+} analogue of plumbojarosite do not re-

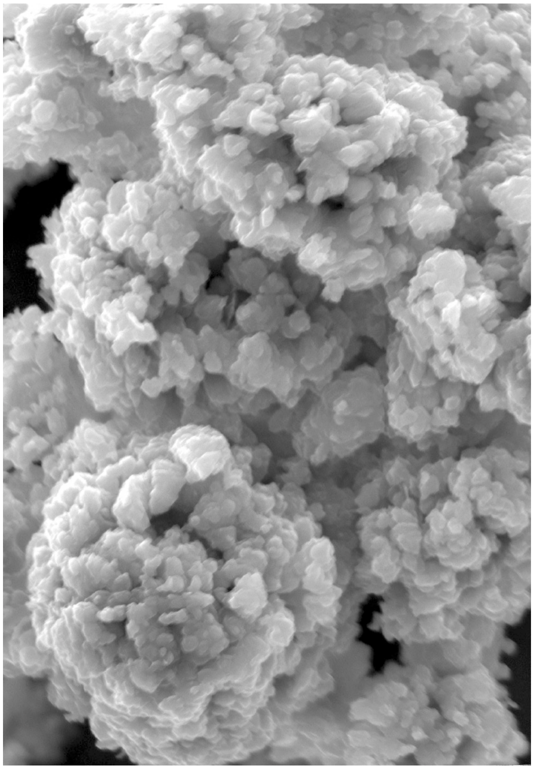

FIG. 3. Secondary electron micrograph of the precipitated V^{3+} analogue of natrojarosite. Approximate width of the field of view: 24.5 μm.

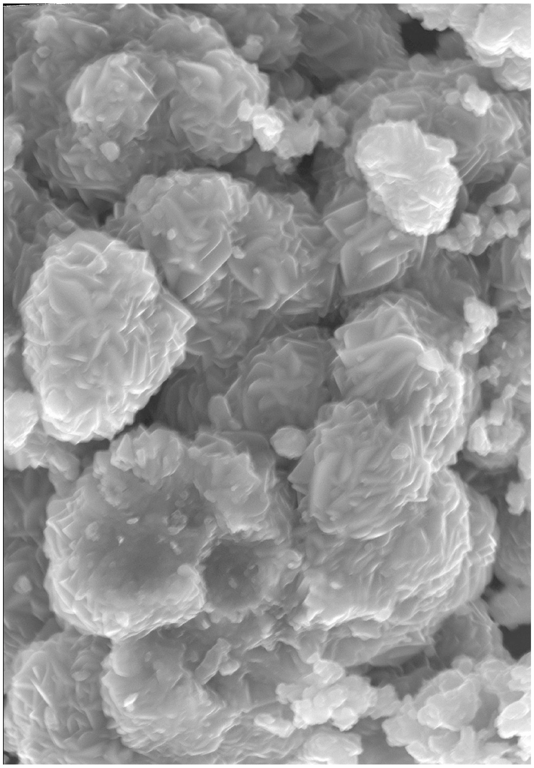

FIG. 4. Secondary electron micrograph of the precipitated V^{3+} analogue of ammoniojarosite. Approximate width of the field of view: 21 μm.

veal a ~11 Å reflection, which is common in most natural examples of plumbojarosite and in many synthetic samples, indicating that the Pb^{2+} ions and vacancies are not ordered in the present material.

Only limited X-ray data have been published previously for the V^{3+} analogues of natrojarosite, jarosite, rubidium-substituted jarosite and dorallcharite (Dobley *et al.* 2000, Grohol & Nocera 2002). The trends identified by them are similar to those found in the current study, although the *d* values are slightly different. Grohol & Nocera (2002) reported the following single-crystal *a* and *c* parameters, where the values in parentheses are those calculated in the present work from X-ray powder-diffraction data: for $NaV_3(SO_4)_2(OH)_6$, 7.2857 (7.300) and 16.851 (16.861) Å, for $KV_3(SO_4)_2(OH)_6$, 7.2737 (7.281) and 17.399 (17.246) Å, for $RbV_3(SO_4)_2(OH)_6$, 7.281 (7.288) and 17.835 (17.576) Å, and for $TlV_3(SO_4)_2(OH)_6$, 7.283 (7.283) and 17.919 (17.772) D. There is generally good agreement among the corresponding *a* values, but the *c* values of Grohol & Nocera (2002) are greater than the present values except for the V^{3+} analogue of natrojarosite. Dobley *et al.* (2000) also determined the cell parameters of the V^{3+} analogue of natrojarosite. Their *a* value of 7.282 Å is comparable to the values noted above, but their *c* parameter, at 16.889 Å, is higher. The differences certainly reflect variations in the extent of incorporation of the hydronium ion and the degree of V-site deficiency among the different products.

Density data

The calculated and measured densities of the V^{3+} analogues of the jarosite-group minerals are presented in Table 7, where the calculated values are based on the refined unit-cell parameters, assuming three formula units per cell. In all instances, the measured densities are lower than the calculated values, and this reflects the modest substitution of the hydronium ion for the *M* ion, as well as the persistent deficiency in V-site occupancy. It also reflects the difficulty of making density determinations on powdery materials. The densities vary only slightly as the *M* ion varies, because the mass and volume of the unit cell are largely determined by the V–

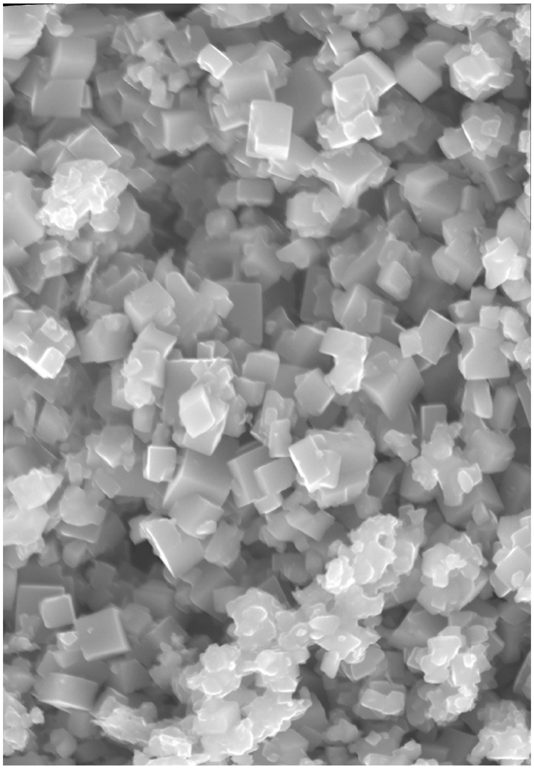

FIG. 5. Secondary electron micrograph of the precipitated V^{3+} analogue of hydronium jarosite made at 140°C. Approximate width of the field of view: 28 μm.

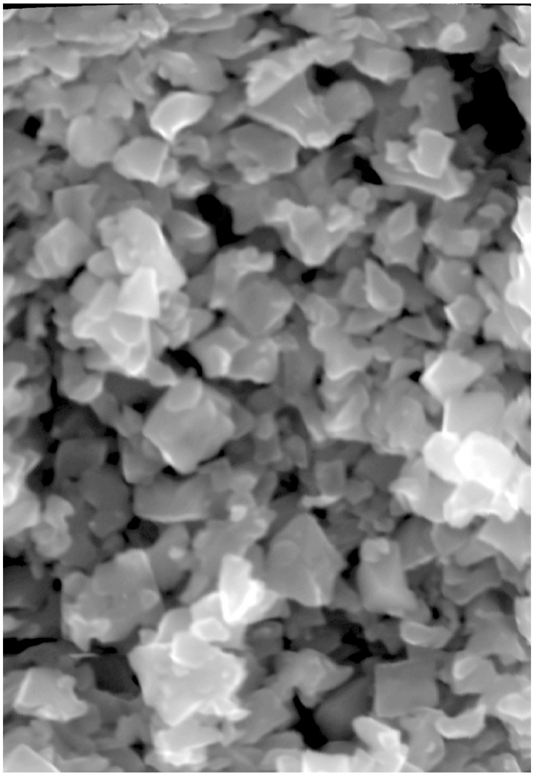

FIG. 6. Secondary electron micrograph of the precipitated V^{3+} analogue of plumbojarosite made at 150°C. Approximate width of the field of view: 9 μm.

SO_4–OH network. The V^{3+} analogue of ammonium jarosite is the least dense of all the precipitates studied, and the V^{3+} analogue of plumbojarosite is the most dense. The density of the V^{3+} analogue of plumbojarosite is not exceptionally high, however, because this compound contains only ½ Pb^{2+} per formula weight. Table 7 also presents the density values calculated by Grohol & Nocera (2002); given the differences in composition between the respective precipitates, there is fair agreement between their values and ours.

CONCLUSIONS

1. The V^{3+} analogues of natrojarosite, jarosite, rubidium-substituted jarosite, dorallcharite and ammoniojarosite were synthesized at 100°C by hydrolytic precipitation.
2. The V^{3+} analogue of hydronium jarosite was prepared at 140°C by hydrolyzing a V^{3+} solution in the presence of Li_2SO_4 as the source of sulfate.
3. The V^{3+} analogue of plumbojarosite was prepared by reacting an excess of $PbSO_4$ with a V^{3+} solution at 150°C in an autoclave, and subsequently dissolving any unreacted $PbSO_4$ in concentrated ammonium acetate media.
4. Efforts to synthesize the V^{3+} analogues of argentojarosite and of mercury-substituted jarosite were unsuccessful.
5. Chemical analyses, refined unit-cell parameters and pycnometrically determined densities of the precipitates show a modest incorporation of H_3O^+ and persistent deficiencies in V-site occupancy for all the synthesized analogues.

ACKNOWLEDGEMENTS

The authors extend their appreciation to CANMET staff members J. Wilson for the X-ray-diffraction analyses and to D.J. Hardy and C. Soriano for assistance with the experimental program. The authors also thank Associate Editor Mati Raudsepp and referees Uwe Kolitsch and Dirk Baron for their numerous constructive comments, which significantly improved the final form of the paper.

TABLE 5. X-RAY DIFFRACTION DATA FOR THE V^{3+} ANALOGUES OF NATROJAROSITE, JAROSITE, RUBIDIUM-SUBSTITUTED JAROSITE AND AMMONIOJAROSITE

(*hkl*)	*d*(cal)	*d*(obs)	*I*(rel)	(*hkl*)	*d*(cal)	*d*(obs)	*I*(rel)	(*hkl*)	*d*(cal)	*d*(obs)	*I*(rel)	(*hkl*)	*d*(cal)	*d*(obs)	*I*(rel)
Synthetic $NaV_3(SO_4)_2(OH)_6$ *a* = 7.300 (±0.015) *c* = 16.861 (±0.030)				Synthetic $KV_3(SO_4)_2(OH)_6$ *a* = 7.281 (±0.001) *c* = 17.246 (±0.002)				Synthetic $RbV_3(SO_4)_2(OH)_6$ *a* = 7.288 (±0.005) *c* = 17.576 (±0.013)				Synthetic $(NH_4)V_3(SO_4)_2(OH)_6$ *a* = 7.268 (±0.012) *c* = 17.504 (±0.035)			
101	5.920	5.967	8	101	5.922	5.928	16	101	5.940	5.945	31	101	5.923	5.919	13
003	5.620	5.663	16	003	5.748	5.766	9	012	5.126	5.136	20	012	5.110	5.141	65
012	5.058	5.092	84	012	5.090	5.096	58	110	3.644	3.644	23	110	3.634	3.645	10
110	3.650	3.663	12	110	3.640	3.643	21	021	3.106	3.097	100	021	3.097	3.102	100
104	3.507	3.520	7	021	3.101	3.101	62	202	2.970	2.966	9	006	2.917	2.938	6
021	3.107	3.118	84	113	3.075	3.076	100	006	2.929	2.928	7	024	2.555	2.566	9
113	3.061	3.071	100	015	3.026	3.026	6	024	2.563	2.564	14	303	1.974	1.976	14
015	2.975	2.984	7	202	2.961	2.961	4	211	2.364	2.358	8	027	1.957	1.957	4
006	2.810	2.818	13	006	2.874	2.877	11	122	2.302	2.301	7	220	1.817	1.822	20
024	2.529	2.535	13	024	2.545	2.544	13	303	1.980	1.979	28	223	1.734	1.739	4
122	2.299	2.303	3	107	2.294	2.296	26	220	1.822	1.820	22	119	1.714	1.717	4
107	2.251	2.256	31	303	1.974	1.974	29	208	1.803	1.804	3	134	1.621	1.625	4
303	1.973	1.977	34	027	1.941	1.941	5	223	1.739	1.733	3	401	1.567	1.568	4
027	1.916	1.919	10	009	1.916	1.916	3	312	1.716	1.715	2	042	1.548	1.548	9
009	1.873	1.877	5	220	1.820	1.820	26	315	1.567	1.566	4	404	1.480	1.485	3
220	1.825	1.828	30	208	1.779	1.779	3	226	1.547	1.547	12	045	1.435	1.436	3
131	1.744	1.739	5	223	1.735	1.736	3	0.2.10	1.535	1.533	6	232	1.424	1.428	4
208	1.753	1.757	3	312	1.714	1.714	5	404	1.485	1.484	4	413	1.337	1.337	5
223	1.736	1.739	5	134	1.620	1.621	4	045	1.439	1.437	4				
312	1.716	1.720	6	128	1.598	1.598	4	232	1.428	1.428	2				
134	1.619	1.621	6	401	1.570	1.570	3	410	1.377	1.376	2				
401	1.573	1.576	5	315	1.559	1.560	3	413	1.340	1.340	7				
042	1.553	1.556	5	042	1.550	1.552	4								
226	1.530	1.533	12	226	1.537	1.538	9								
232	1.429	1.432	6	0.2.10	1.513	1.513	10								
309	1.400	1.402	3	404	1.480	1.480	3								
324	1.371	1.373	2	232	1.426	1.426	5								
413	1.340	1.341	7	410	1.376	1.376	2								
407	1.321	1.322	2	413	1.338	1.338	6								
229	1.307	1.308	2												
327	1.242	1.244	5												

$CuK_{\alpha 1}$ radiation: λ = 1.54056 Å : Rigaku rotating anode diffractometer

REFERENCES

CHEN, T.T. & DUTRIZAC, J.E. (1990): Practical mineralogical techniques for the characterization of hydrometallurgical products. *In* Process Mineralogy IX (W. Petruk, R.D. Hagni, S. Pignolet-Brandom & D.M. Hausen, eds.). Minerals, Metals and Materials Society, Warrendale, Pennsylvania (289-309).

COTTON, F.A. & WILKINSON, G. (1962): *Advanced Inorganic Chemistry.* Interscience Publishers, New York, N.Y. (673-681).

DOBLEY, A., ZAVALIJ, P.Y. & WHITTINGHAM, M.S. (2000): Sodium trivanadium(III) bis(sulfate) hexahydroxide. *Acta Crystallogr.* **C56**, 1294-1295.

DUTRIZAC, J.E. (1983): Factors affecting alkali jarosite precipitation. *Metall. Trans.* **14B**, 531-539.

________ & CHEN, T.T. (2000): The behaviour of gallium during jarosite precipitation. *Can. Metall. Quart.* **39**, 1-14.

________ & ________ (2002): The behaviour of vanadium (III) during jarosite precipitation. *In* Vanadium – Geology, Processing and Applications (M.F. Taner, P.A. Riveros, J.E. Dutrizac, M. Gattrell & L. Perron, eds.). Can. Inst. Mining, Metallurgy and Petroleum, Montreal, Canada (183-204).

________, DINARDO, O. & KAIMAN, S. (1980): Factors affecting lead jarosite formation. *Hydrometallurgy* **5**, 305-324.

________ & KAIMAN, S. (1976): Synthesis and properties of jarosite-type compounds. *Can. Mineral.* **14**, 151-158.

________ & JAMBOR, J.L. (1987a): Behaviour of cesium and lithium during the precipitation of jarosite-type compounds. *Hydrometallurgy* **17**, 251-265.

________ & ________ (1987b): The behaviour of silver during jarosite precipitation. *Trans. Inst. Mining Metall.* **96**, C206-C218.

________ & ________ (2001): Jarosites and their application in hydrometallurgy. *In* Sulfate Minerals – Crystallography, Geochemistry, and Environmental Significance (C.N. Alpers, J.L. Jambor & D.K. Nordstrom, eds.). *Rev. Mineral. Geochem.* **40**, 405-452.

________ & MINGMIN, D. (1993): The behaviour of indium during jarosite precipitation. In *World Zinc '93* (I.G. Matthew, ed.). Austral. Inst. Mining Metall., Parkville, Australia (365-372).

TABLE 6. X-RAY DIFFRACTION DATA FOR THE V^{3+} ANALOGUES OF DORALLCHARITE, HYDRONIUM JAROSITE AND PLUMBOJAROSITE

(*hkl*)	*d*(cal)	*d*(obs)	*I*(rel)	(*hkl*)	*d*(cal)	*d*(obs)	*I*(rel)	(*hkl*)	*d*(cal)	*d*(obs)	*I*(rel)
Synthetic $TlV_3(SO_4)_2(OH)_6$ *a* = 7.283 (±0.003) *c* = 17.772 (±0.001)				Synthetic $(H_3O)V_3(SO_4)_2(OH)_6$ *a* = 7.320 (±0.011) *c* = 16.968 (±0.001)				Synthetic $Pb_{0.5}V_3(SO_4)_2(OH)_6$ *a* = 7.293 (±0.003) *c* = 17.041 (±0.001)			
101	5.982	5.949	69	101	5.938	5.946	5	011	5.922	5.888	33
110	3.669	3.639	35	003	5.656	5.658	28	003	5.680	5.651	4
113	3.115	3.101	100	012	5.078	5.083	100	012	5.074	5.048	14
202	2.991	2.968	18	110	3.660	3.662	7	110	3.646	3.632	18
204	2.581	2.570	20	104	3.525	3.524	18	112	3.352	3.334	2
205	2.364	2.356	19	021	3.116	3.117	93	201	3.105	3.092	22
212	2.318	2.302	12	113	3.073	3.072	79	113	3.068	3.056	100
214	2.111	2.099	6	015	2.992	2.989	8	105	2.999	2.986	3
215	1.987	1.980	28	006	2.828	2.828	9	202	2.961	2.952	10
221	1.825	1.820	20	024	2.539	2.537	12	006	2.840	2.829	23
217	1.741	1.736	6	211	2.372	2.369	3	024	2.537	2.529	19
306	1.720	1.713	2	122	2.306	2.310	3	211	2.364	2.356	5
315	1.578	1.569	5	107	2.264	2.265	17	212	2.298	2.291	6
226	1.558	1.550	14	303	1.979	1.979	28	107	2.271	2.265	38
227	1.484	1.485	4	027	1.925	1.925	8	033	1.974	1.969	25
309	1.441	1.439	6	009	1.885	1.887	5	215	1.955	1.950	3
318	1.378	1.376	2	220	1.830	1.830	24	207	1.928	1.923	3
407	1.345	1.340	8	223	1.741	1.741	7	009	1.893	1.889	2
502	1.258	1.256	3	312	1.721	1.722	6	220	1.823	1.819	21
0.2.13	1.251	1.248	2	119	1.676	1.670	2	028	1.766	1.762	6
1.3.10	1.248	1.245	2	134	1.624	1.624	7	127	1.704	1.701	4
147	1.216	1.213	2	128	1.588	1.585	6	224	1.676	1.677	3
422	1.190	1.189	3	042	1.558	1.558	5	315	1.558	1.555	4
3.1.11	1.188	1.186	2	226	1.536	1.535	10	402	1.552	1.550	5
1.2.13	1.184	1.181	2	0.2.10	1.496	1.496	8	226	1.534	1.531	11
0.0.15	1.179	1.178	2	404	1.484	1.489	7	0.2.10	1.499	1.497	13
335	1.156	1.151	3	045	1.436	1.435	6	404	1.480	1.478	4
				2.0.11	1.387	1.387	2	321	1.443	1.441	2
				413	1.343	1.344	6	137	1.422	1.419	3
				407	1.326	1.325	3				
				229	1.313	1.310	3				

$CuK_{\alpha 1}$ radiation: λ = 1.54056 Å : Rigaku rotating anode diffractometer

TABLE 7. CALCULATED AND MEASURED DENSITIES OF THE V^{3+} ANALOGUES OF JAROSITE-GROUP MINERALS

Species	Calculated*	Calculated	Measured
$(H_3O)V_3(SO_4)_2(OH)_6$	–	2.930	2.94
$NaV_3(SO_4)_2(OH)_6$	3.022	3.007	2.71
$KV_3(SO_4)_2(OH)_6$	3.037	3.057	2.66
$RbV_3(SO_4)_2(OH)_6$	3.239	3.280	2.87
$TlV_3(SO_4)_2(OH)_6$	3.941	3.930	3.18
$(NH_4)V_3(SO_4)_2(OH)_6$	–	2.862	2.55
$Pb_{0.5}V_3(SO_4)_2(OH)_6$	–	3.491	3.23

* Grohol & Nocera (2002), Table 1, based on end-member compositions. The values of density are expressed in g/cm³.

GROHOL, D. & NOCERA, D.G. (2002): Hydrothermal oxidation-reduction methods for the preparation of pure and single crystalline alunites: synthesis and characterization of a new series of vanadium jarosites. *J. Am. Chem. Soc.* **124**, 2640-2646.

________, PAPOUTSAKIS, D. & NOCERA, D.G. (2001): $NaV_3(OH)_6(SO_4)_2$: a Kagomé-type compound with strong interlayer interactions. *Angew. Chemie Int. Ed.* **40**, 1519-1521.

JAMBOR, J.L. (1999): Nomenclature of the alunite supergroup. *Can. Mineral.* **37**, 1323-1341.

KOLITSCH, U. & PRING, A. (2001): Crystal chemistry of the crandallite, beudantite and alunite groups: a review and evaluation of the suitability as storage materials for toxic metals. *J. Mineral. Petrol. Sci.* **96**, 67-78.

________, TAYLOR, M.R., FALLON, G.D. & PRING, A. (1999): $BaV_3(PO_4)_2(OH,H_2O)_6$, a new member of the crandallite group, from the Spring Creek mine, South Australia: the first natural V^{3+}-member of the alunite family and its crystal structure. *Neues Jahrb. Mineral., Monatsh.*, 529-544.

KUBISZ, J. (1964): A study on minerals of the alunite–jarosite group. *Polska Akad. Nauk, Prace Geol.* **22**, 1-93.

LENGAUER, C.L., GIESTER, G. & IRRAN, E. (1994): $KCr_3(SO_4)_2(OH)_6$: synthesis, characterization, powder diffraction data and structural refinement by the Rietveld technique and a compilation of alunite-type compounds. *Powder Diffraction* **9**, 265-271.

PAPOUTSAKIS, D., GROHOL, D. & NOCERA, D.G. (2002): Magnetic properties of a homologous series of vanadium jarosite compounds. *J. Am. Chem. Soc.* **124**, 2647-2656.

RIPMEESTER, J.A., RATCLIFFE, C.I., DUTRIZAC, J.E. & JAMBOR, J.L. (1986): Hydronium ion in the alunite–jarosite group. *Can. Mineral.* **24**, 435-447.

SCHINDLER, M., HAWTHORNE, F.C. & BAUR, W.H. (2000): Crystal chemical aspects of vanadium: polyhedral geometrics, characteristic bond valences, and polymerization of (VO_n) polyhedra. *Chem. Mater.* **12**, 1248-1259.

STOFFREGEN, R.E., ALPERS, C.N. & JAMBOR, J.L. (2001): Alunite–jarosite crystallography, thermodynamics and geochronology. *In* Sulfate Minerals – Crystallography, Geochemistry, and Environmental Significance (C.N. Alpers, J.L. Jambor & D.K. Nordstrom, eds.). *Rev. Mineral. Geochem.* **40**, 453-479.

TUDO, J. & LAPLACE, G. (1977): Les sulfates double de vanadium et d'ammonium. 1. Sur la schoenite de vanadium II et d'ammonium. *Bull. Soc. Chim. Fr.* (7–8), 653-655.

________, ________, TACHEZ, M. & THEOBALD, F. (1973): Sur l'hydroxysulfate $VOHSO_4$. *C.R. Acad. Sci. Paris* **C277**, 767-770.

Received November 8, 2002, revised manuscript accepted February 23, 2003.