Grandviewite, $Cu_3Al_9(SO_4)_2(OH)_{29}$, a new mineral from the Grandview Mine, Arizona, USA

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ABSTRACT

Grandviewite, $Cu_3Al_9(SO_4)_2(OH)_{29}$, (IMA 2007-004), is a new mineral from the Grandview mine, Grand Canyon, Arizona, USA. The name is given for the locality. The mineral forms radiating sprays of extremely acicular laths, up to 0.5 mm in length and about 2 μm thick. Individual crystals are of the order of 0.1 μm thick. Laths are elongated parallel to [100] or [001] and flattened on {001} or {100}. Grandviewite is most frequently perched on botryoidal crusts of chalcoalumite, which in turn lies on masses of cyanotrichite intermixed with minor carbonatecyanotrichite. The mineral is monoclinic, space group P2, $P2_1$, Pm, P2/m or $P2_1/m$, with $a = 10.908(2)$, $b = 6.393(3)$, $c = 10.118(2)$ Å, $\beta = 107.47(2)°$, $V = 673.0(1)$ Å^3, $Z = 1$, $D_{calc} = 2.72$ g cm^{-3}. The ten strongest lines in the X-ray powder diffraction pattern [d in Å(I)(hkl)] are 6.208(100)(101), 3.949(79)(102), 5.287(35)(20-1)), 9.667(33)(001), 2.816(14)(30-3), 3.625(10)(30-1), 2.990 (9)(12-1), 2.413(9)(004), 2.721(8)(220), 2.019(8)(20-5, 420). Analyses of Cu (AAS), Al (colorimetric), SO_3 and H_2O (TGA) gave CuO, 21.4; Al_2O_3, 40.7; SO_3, 14.5, H_2O, 23.3, total 99.9 wt%. The empirical formula (based on two sulfate ions pfu) is: $Cu_{2.97}Al_{8.82}(SO_4)_2(OH)_{28.55}$. The simplified formula is $Cu_3Al_9(SO_4)_2(OH)_{29}$, which requires CuO, 21.33; Al_2O_3, 41.01; SO_3, 14.31, H_2O, 23.35 wt%. Color is greenish blue with a very pale blue streak; luster is vitreous; Mohs' hardness is 2 and the mineral is sectile. Cleavage is perfect on {100} or {001}. Grandviewite is biaxial (–), with $\alpha = 1.590(4)$, $\beta = 1.625(4)$, $\gamma = 1.645(4)$ (white light), 2V (calc.) = 72(3)°. Pleochroism is distinct, Z = pale blue-green, Y = very pale yellow, X = very pale yellow, and is strong when concordant stacks of elongated plates are viewed perpendicular to the stacking direction.

INTRODUCTION

The Grandview mine (also known as the Last Chance mine) is situated at Cape Royal, Horseshoe Mesa, Grand Canyon National Park, Coconino County, Arizona, USA; 36°1'3"N , 111°58'26"W. It is famous for its superb specimens of cyanotrichite. Associated minerals include cyanotrichite, carbonatecyanotrichite, chalcoalumite, antlerite, brochantite, langite, devilline, chalcanthite, aurichalcite, malachite, azurite, adamite, zeunerite, metazeunerite, olivenite, parnauite, scorodite, smithsonite, cerussite, chalcocite, hemimorphite, barite, gypsum, illite and kaolinite (Leicht, 1971; Anthony *et al.*, 1995). Leicht (1971) has published the definitive work on the mineralogy of the deposit and noted the presence of three unidentified species; brief descriptions and characteristic powder X-ray data were provided. Unknowns #6a and #6b, copper-iron arsenate–sulfates, were subsequently identified as being parnauite (Anthony *et al.*, 1995). Unknown #5 was described as a Cu–Al–sulfate.

Recently, a number of small specimens from the Grandview mine were provided by Dr Ray Grant for identification.

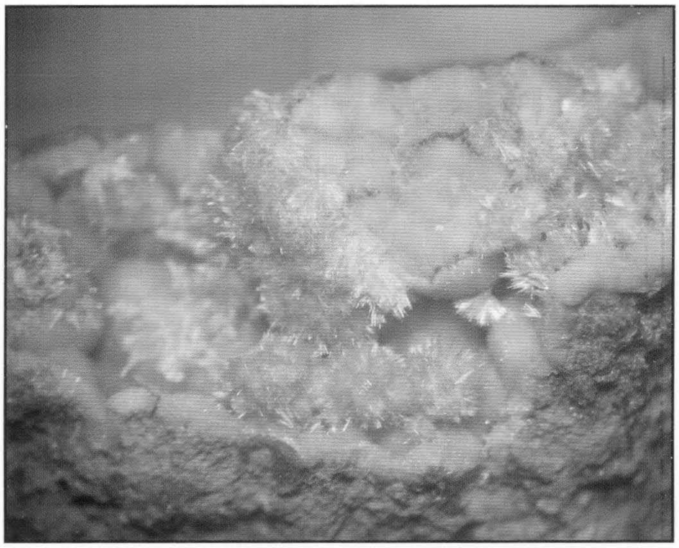

Figure 1: Radiating clusters of acicular grandviewite crystals (pale greenish blue) up to 1 mm across perched on a layer of chalcoalumite (white). The latter forms a crust on cyanotrichite containing minor amounts of carbonatecyanotrichite.

Several contained extremely acicular, greenish blue laths lining vughs in goethite-rich gossan. They were mostly perched on botryoidal crusts of chalcoalumite overlying masses of felted and radiating crystals of cyanotrichite (Figure 1). Powder X-ray measurements established the identity of the greenish blue material with unknown #5 and this has now been characterised as the new mineral grandviewite, $Cu_3Al_9(SO_4)_2(OH)_{29}$. The new mineral and the mineral name were approved by the Commission on New Minerals and Mineral Names, IMA (IMA 2007-004). The holotype is housed in the collection of Museum Victoria, specimen number M50490 (Geosciences Department, Museum Victoria, PO Box 666, Melbourne, VIC 3001, Australia). The mineral is named for the locality.

OCCURRENCE

The general mode of occurrence of grandviewite is as noted above. Sometimes it has grown directly on the goethite matrix. In a few cases it is overgrown by cyanotrichite. The cyanotrichite was established by powder X-ray measurements as hosting small amounts of visually indistinguishable crystals of carbonatecyanotrichite. Brochantite is also present in the samples examined, together with minor malachite. Grandviewite is a secondary mineral formed by the oxidation of Cu-bearing sulfides. Sulfide minerals are rather scarce in the deposit, but Leicht (1971) reported the presence of pyrite, chalcopyrite and bornite, and possibly chalcocite.

PHYSICAL AND OPTICAL PROPERTIES

The mineral forms radiating sprays of extremely acicular laths, up to 0.5 mm in length (Figure 2). The laths are about 2 µm in width and individual crystals are of the order of 0.1 µm thick. Terminations of individual crystals are nearly always rounded, but some show chisel-like forms. The laths are elongated parallel to [100] or [001] and flattened on {001} or {100}. Forms are {010}, and {100} or {001}, but we have not been able to unambiguously distinguish [100] and [001] with respect to crystal morphology (Figure 1). No twinning was observed.Grandviewite is transparent and greenish blue with a very pale blue streak. It has a vitreous luster and is non-fluorescent. Mohs' hardness is 2 and crystals are sectile. Cleavage is perfect on {100} or {001}, fracture is uneven. The calculated density is 2.721 g cm^{-3}, using the empirical formula and derived unit cell. The measured density is 2.81 g cm^{-3} (by flotation in brominated hydrocarbons). The mineral is soluble in dilute mineral acids without effervescence and gives microchemical tests for Cu, Al and sulfate. With moderate heating the mineral gives off water and blackens. TGA/DSC measurements show that grandviewite begins to lose water at 100°C in a pure argon stream. Some 4.5% total weight is lost by 160° (endothermic peak at 127°), with the remainder being lost between 200 and 500°C (endothermic peak at 248°). SO_3 is lost between 620 and 680°C (two endothermic peaks at 660 and 675°C). FT-IR spectra show absorptions at 3568 (sharp) and 3354 cm^{-1}. The latter is broad, as found for gibbsite (Gadsden, 1975), and is attributed to stretching of OH coordinated to Al. Sulfate modes are observed at 1105 and 1063 cm^{-1} (tentatively attributed to ν_3), 970 and 915 cm^{-1} (tentatively attributed to ν_1) and 670 ((tentatively attributed to ν_4). A band at 773 cm^{-1} is unassigned and that at 615 cm^{-1} is ascribed to OH libration. Some of the above bands in the 950-1100 cm-1 region may be overlapped with AlOH bending modes.

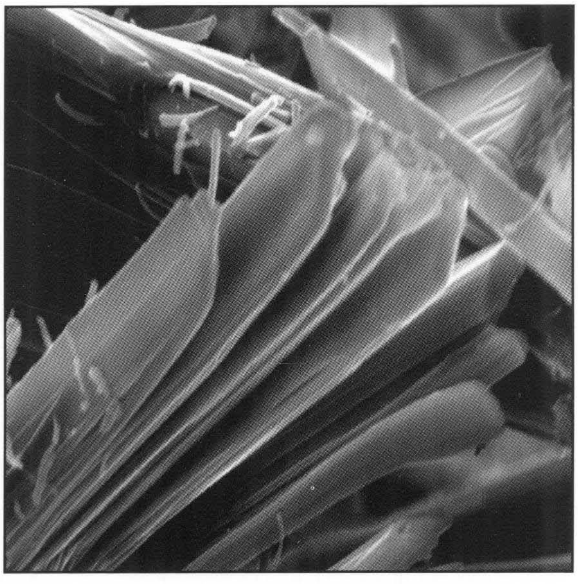

Figure 2: SEM image of grandviewite. The flattened, acicular crystals, some showing curvature, are up to 0.5 mm long, but only up to 2 µm thick. It is clearly evident that individual crystals are extremely thin. Note the perfect cleavage parallel to the axis of elongation.

Grandviewite is biaxial (–), with $\alpha = 1.590(4)$, $\beta = 1.625(4)$, $\gamma = 1.645(4)$ (white light); 2V(calc.) = 72(3)°. Leicht (1971) reported $\beta = 1.625$, $\gamma = 1.645$ without errors and our measurements confirm these values, within the errors quoted. Individual crystals were too small for a conoscopic figure to be observed and hence determine dispersion. Crystals exhibit straight extinction and the orientation is Y = *b*, with Z approximately parallel to the needle axis. Pleochroism is distinct with Z = pale blue-green, Y = very pale yellow, X = very pale yellow. Pleochroism is strong when concordant stacks of elongated plates are viewed perpendicular to the stacking direction under the microscope. Leicht (1971) reported that the mineral is strongly pleochroic, but no scheme was given. Compatibility, $1 - (K_p/K_c) = 0.051$, is good, using the empirical formula and calculated density (Mandarino, 1981).

CHEMICAL COMPOSITION

Electron microprobe (JEOL 8600) examination qualitatively showed the presence of Cu, Al and S with trace amounts of Zn, but wet-chemical analysis (AAS) gave less than 0.05% ZnO. Crystals are unstable in the microprobe beam and are observed to curl up and fracture. Probe analysis was thus not possible and the physical behaviour of crystals in the

Table 1: Analytical data (wt%) for grandviewite (five analyses for Cu and Al, two for SO_3 and H_2O).

	Average	Range	SD
CuO	21.4	21.3 – 21.5	0.1
Al_2O_3	40.7	40.6 – 40.9	0.1
SO_3	14.5	14.3 and 14.7	
H_2O	23.3	23.1 and 23.5	
Total	99.9		

Table 2: X-ray powder-diffraction data for grandviewite. The ten strongest lines are marked in bold face.

I	d_{meas} Å	d_{calc} Å	*h k l*	I^a	d_{meas} Å^a
6	10.392	10.405	1 0 0		
33	**9.667**	**9.651**	**0 0 1**	8	9.60
100	**6.208**	**6.207**	**1 0 1**	10	6.22
35	**5.287**	**5.291**	**2 0 -1**	8	5.26
5	4.992	4.986	1 0 -2		
6	4.828	4.825	0 0 2		
5	4.225	4.227	2 0 -2		
5	4.092	4.095	2 0 1		
79	**3.949**	**3.948**	**1 0 2**	10	3.95
10	**3.625**	**3.629**	**3 0 -1**	2	3.62
5	3.467	3.468	3 0 0		
7	3.332	3.330	3 0 -2		
6	3.193	3.196	0 2 0		
6	3.104	3.104	2 0 2		
9	**2.990**	**2.990**	**1 2 -1**		
14	**2.816**	**2.818**	**3 0 -3**	6	2.81
8	**2.721**	**2.723**	**2 2 0**		
4	2.522	2.523	1 0 -4		
6	2.493	2.493	2 0 -4		
9	**2.413**	**2.413**	**0 0 4**	7	2.37
5	2.336	2.337	3 0 -4		
3	2.208	2.209	1 0 4		
5	2.076	2.074	4 2 -1		
8	**2.019**	**2.018**	**2 0 -5**	3	2.01
	2.018		4 2 0		
4	1.974	1.974	2 0 4		
5	1.805	1.804	6 0 -1		
3	1.776	1.777	0 3 3		
3	1.750	1.750	3 0 4		
4	1.668	1.667	3 2 -5		
6	1.622	1.620	5 2 -4		
	1.620		2 3 -4		
3	1.537	1.536	7 0 -3		
3	1.493	1.494	7 1 -3		
2	1.421	1.421	2 0 6		
	1.421		2 4 2		
	1.355		8 0 -3		
3	1.354	1.354	6 2 2		
	1.322		2 3 -6		
2	1.321	1.322	5 1 -7		
	1.320		4 4 1		
2	1.296	1.295	8 1 -4		
	1.295		1 4 4		
	1.215		7 2 2		
3	1.215	1.215	7 3 -4		
	1.215		4 0 6		

[a] Eight most intense lines reported for Unknown # 5 by Leicht (1971); photographic data (Debye-Scherrer camera).

beam rendered determination of Cu:Al:S ratios unreliable. Cu was analysed using AAS (Perkin Elmer Aanalyst 100AAS spectrophotometer) and Al by colorimetry (Tiron) for hand-picked samples. Thermogravimetric analyses of SO_3 and H_2O and differential scanning calorimetry (DSC) data were obtained using a Netzsch STA 449C Jupiter simultaneous DSC-TGA thermoanalyzer. Two samples with masses of 1.67 and 0.95 mg, respectively, were loaded in PtRh crucibles without lids and measured at a heating rate of 5 deg min^{-1} to 1000°C using ultra high purity argon (99.999%) at a flow rate of 25 ml min^{-1}. Volatile compounds formed during pyrolysis were transferred to an FT-IR cell and identified using a Bruker VERTEX 70 spectrometer with an external mercury-cadmium-telluride (MCT) detector. No CO_2 gas was detected during either run. Analytical results are given in Table 1. The empirical formula (based on two sulfate ions *pfu*) is: $Cu_{2.97}Al_{8.82}(SO_4)_2(OH)_{28.55}$. The simplified formula is $Cu_3Al_9(SO_4)_2(OH)_{29}$, which requires CuO, 21.33; Al_2O_3, 41.01; SO_3, 14.31, H_2O, 23.35, total 100.00 wt.%. It is both unusual and noteworthy that water of crystallization is absent in the derived stoichiometry.

CRYSTALLOGRAPHY

Single-crystal X-ray studies could not be carried out because of the size of the crystals available, especially with respect to their thinness. X-ray diffraction data were recorded using a Philips PW1925-20 powder diffractometer (Ni-filtered Cu *K*α radiation with pure Si as internal standard; λ = 1.5406 Å), and are listed in Table 2. A search for a possible unit cell was undertaken using DICVOL91 (Boultif and Louer, 1991) for the 20 strongest reflections. Possible cells were obtained only for the monoclinic system. The cell with the best figure of merit obtained was selected and the complete possible reflection record calculated using PowderCell (Kraus and Nolze, 1996a,b). All observed reflections were able to be indexed and unit-cell parameters were then refined using LAPOD (Langford, 1973). Other potential monoclinic cells generated by DICVOL91could not be used to index all reflections with the same precision. Grandviewite is monoclinic with a = 10.908(2), b = 6.393(3), c = 10.118(2) Å, β = 107.47(2)°, V = 673.0(1) Å^3, Z = 1. The a:b:c ratio calculated from the unit-cell parameters is: 1.7062:1:1.5827. An inspection of the indexed X-ray powder-diffraction pattern (Table 2) shows that the unit cell is primitive and that no glide-plane symmetry is present. Because an appropriate number of 0*k*0 reflections was not observed, the existence or otherwise of a 2_1 screw axis could not be determined unambiguously. Possible space groups are $P2$, $P2_1$, Pm, $P2/m$ or $P2_1/m$.

RELATIONSHIPS WITH OTHER SPECIES

Grandviewite belongs to Strunz and Nickel (2001) classification 7.BB. Several basic Cu-Al sulfates of different composition are known. Most display an acicular habit. They may be conveniently distinguished by X-ray powder-diffraction measurements and chemical analyses. Table 3 lists characteristic diffraction data for these phases.

Table 3: Characteristic X-ray powder-diffraction data (*d*-spacings, Å) for the basic Cu-Al sulfates and some related species with relative intensities given in parentheses (Anthony *et al.*, 2003; Chukanov *et al.*, 1999; this work)[a].

1	2	3	4	5	6	7	8
9.667(33)	8.502(100)	10.2(100)	10.13(93)	5.62(50)	10.29(80)	8.9(100)	10.5(100)
6.208(100)	7.898(22)	5.47(50)	5.03(60)	5.160(90)	5.589(90)	4.47(90)	5.26(17)
5.287(35)	5.100(13)	5.26(80)	4.21(100)	4.276(100)	4.232(100)	2.65(30)	3.50(6)
3.949(79)	4.786(22)	3.88(90)	3.33(58)	3.565(40)	2.828(90)	2.55(60)	2.60(5)
3.625(10)	4.250(91)	3.38(35)	2.51(52)	2.380(35)	2.362(100)	2.28(50)	2.46(2)
2.990(9)	4.178(23)	3.04(40)	2.01(53)	2.326(35)	1.871(80)	1.98(30)	2.23(2)
2.77(45)	2.520(11)	2.392(35)		2.137(30)	1.817(80)	1.53(30)	1.524(4)
2.816(14)							
2.721(8)							
2.413(9)							
2.019(8)							

[a] 1: Grandviewite, $Cu_3Al_9(SO_4)_2(OH)_{29}$; 2: chalcoalumite, $CuAl_4SO_4(OH)_{12}\cdot 3H_2O$; 3: cyanotrichite, $Cu_4Al_2SO_4(OH)_{12}\cdot 2H_2O$; 4: carbonate-cyanotrichite, $Cu_4Al_2(CO_3,SO_4)(OH)_{12}\cdot 2H_2O$; 5: camerolaite, $Cu_4Al_2(HSbO_4,SO_4)(CO_3)(OH)_{10}\cdot 2H_2O$; 6: khaidarkanite[a], $Cu_4Al_3(OH)_{14}F_3\cdot 2H_2O$; 7: woodwardite, $Cu_4Al_2SO_4(OH)_{12}\cdot 2\text{-}4H_2O$(?); 8: hydrowoodwardite, $Cu_2Al_2SO_4(OH)_8\cdot nH_2O$. [b]Khairdarkanite is structurally related to cyanotrichite and camerolaite (Rastsvetaeva *et al.*, 1998).

NOTES FOR COLLECTORS

Many collectors will have acquired specimens of cyanotrichite from the Grandview mine. It should be noted that the "cyanotrichite" is invariably a mixture of cyanotrichite and lesser but variable amounts of carbonatecyanotrichite. These are visually indistinguishable. A few specimens have been recovered from the deposit that consist of extremely acicular, dark reddish brown to black crystals perched on blue cyanotrichite. This reddish brown mineral is Co-rich and is subject to a continuing study. In all specimens of grandviewite that have been sighted, the mineral presents a consistent habit of radiating clusters of needles perched on white to very pale sky blue chalcoalumite (Figure 1) or on cyanotrichite crusts. The characteristic greenish blue colour of grandviewite makes it simple to distinguish the mineral from its associates in the Grandview deposit. Specimens of cyanotrichite should be checked for the presence of grandviewite and the Co-rich material mentioned above.

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