

A reexamination of the turquoise group: the mineral aheylite, planerite (redefined), turquoise and coeruleolactite

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ABSTRACT

The turquoise group has the general formula: $A_{0-1}B_6(PO_4)_{4-x}(PO_3OH)_x(OH)_8 \cdot 4H_2O$, where $x = 0-2$, and consists of six members: planerite, turquoise, faustite, aheylite, chalcociderite and an unnamed $Fe^{2+}-Fe^{3+}$ analogue. The existence of 'coeruleolactite' is doubtful. Planerite is revalidated as a species and is characterized by a dominant *A*-site vacancy. Aheylite is established as a new member of the group, and is characterized by having Fe^{2+} dominant in the *A*-site.

Chemical analyses of 15 pure samples of microcrystalline planerite, turquoise, and aheylite show that a maximum of two of the (PO_4) groups are protonated (PO_3OH) in planerite. Complete solid solution exists between planerite and turquoise. Other members of the group show variable *A*-site vacancy as well. Most samples of 'turquoise' are cation-deficient or are planerite. Direct determination of water indicates that there are 4 molecules of water.

Planerite, ideally $\square Al_6(PO_4)_2(PO_3OH)_2(OH)_8 \cdot 4H_2O$, is white, pale blue or pale green, and occurs as mamillary, botryoidal crusts as much as several mm thick; may also be massive; microcrystalline, crystals typically 2–4 micrometres, luster chalky to earthy, *H*. 5, somewhat brittle, no cleavage observed, splintery fracture, D_m 2.68(2), D_c 2.71, not magnetic, not fluorescent, mean RI about 1.60. *a* 7.505(2), *b* 9.723(3), *c* 7.814(2) Å, α 111.43°, β 115.56°, γ 68.69°, *V* 464.2(1) Å³, *Z* = 1.

Aheylite, ideally $Fe^{2+}Al_6(PO_4)_4(OH)_8 \cdot 4H_2O$, is pale blue or green, and occurs as isolated and aggregate clumps of hemispherical or spherical, radiating to interlocked masses of crystals that average 3 micrometres in maximum dimension; porcelaneous-subvitreous luster, moderate to brittle tenacity, no cleavage observed, hackly to splintery fracture, not magnetic, not fluorescent, biax. (+), mean RI is about 1.63, D_m 2.84(2), D_c 2.90. *a* 7.400(1), *b* 9.896(1), *c* 7.627(1) Å, α 110.87°, β 115.00°, γ 69.96°, *V* 460.62(9) Å³, *Z* = 1.

KEYWORDS: turquoise group, planerite, aheylite, 'coeruleolactite', X-ray diffraction data.

Introduction

MINERALS of the turquoise group have been known since antiquity and have been valued for their use as gems. Pogue (1915) summarized what was known about turquoise in his monograph. However, the structure and chemistry of members of the group (Table 1) were not clear until

relatively recently (Cid-Dresner, 1964, 1965; Cid-Dresner and Villarroel, 1972; and Guthrie and Bish, 1991, for turquoise; Giuseppeti *et al.*, 1989, for chalcociderite; Foord and Taggart, 1986, for planerite and aheylite). This paper presents new complete chemical analyses of 15 pure samples and summarizes the elemental site occupancies of the various sites for the members

TABLE 1. Members of the turquoise group: general-formula: $A_{0-1}B_6(PO_4)_{4-x}(PO_3OH)_x(OH)_6 \cdot 4H_2O$ where $x = 0-2$

A-site	B-site	$(PO_4)_{4-x}$	$(PO_3OH)_x$	Mineral name
□	Al	2	2	Planerite
Cu	Al	4	0	Turquoise
Zn	Al	4	0	Faustite
Fe ²⁺	Al	4	0	Aheylite
Ca?	Al	4	0	Coeruleolactite
□	Fe ³⁺	2	2	unknown as yet
Cu	Fe ³⁺	4	0	Chalcosiderite
Zn	Fe ³⁺	4	0	unknown as yet
Fe ²⁺	Fe ³⁺	4	0	(unnamed)*
Ca?	Fe ³⁺	4	0	unknown as yet

* First reported by Mücke (1981) from Hagendorf, but without supporting chemical and structural data. Mücke (personal communication (1983) provided the authors with full data for the mineral, as submitted to the CNMMN IMA. The mineral was approved, but the proposed name was not.

of the turquoise group. It also presents results of an examination of two specimens of blue to blue-green 'coeruleolactite' from the type locality.

Turquoise and other members of the group do not contain 5 molecules of water as has been shown by some authors to the present time, but only 4 molecules. The crystal structure determinations (Cid-Dresdner, 1964, 1965; Giuseppeti, *et al.*, 1989; Guthrie and Bish, 1991) for turquoise and chalcosiderite also indicate four molecules to be present. As vacancy becomes dominant in the A-site, then the amount of protonation, to a maximum of two of the phosphate groups, increases. Charge balance is maintained by the development of (PO_3OH) groups as the A-site occupancy decreases. The two sites for H are what principally caused the number of molecules of molecular water to previously be reported as 4 or 5. Some minor H_2O for OH substitution may also occur. Alteration processes such as those described by Van Wambeke (1971) do not account for the A-site cation deficiency in turquoise group minerals.

A chemical, X-ray and Mössbauer examination of a turquoise from Greece (Sklavounos *et al.*, 1992) showed 9.09 wt.% CuO, 0.26 wt.% BaO, Al_2O_3 35.7, Fe_2O_3 1.27, As_2O_5 0.14, P_2O_5 34.00 and 19.41 wt.% H_2O (by difference). This is clearly a high Cu-containing turquoise with essentially no A-site vacancy. The 19.41 wt.% H_2O , assigned by difference, is substantially more than the ideal amount of 17.72 wt.% H_2O . P_2O_5 is

about 1 wt.% low from that for theoretical turquoise. It is unfortunate that a direct determination for water was not done.

In the case of the 'cuprofaustite' described by Kunov *et al.* (1982), this mineral is clearly a cation-deficient (A-site deficient) faustite. The turquoise from the Kelly Bank mine, Rockbridge Co., VA (Mitchell and Freeland, 1978; Barwood and Zelazny, 1982) has been shown to be planerite (this study). The mineral described by Ivanov (1979) is best described as a cation-deficient aluminian chalcosiderite. Similarly, the turquoise described from Paikhoy, Russia (Belyaev and Ievlev, 1990) is best characterized as a Cu-Fe bearing planerite. The turquoises (microprobe analyses with no direct determination of water) described by Silaev *et al.* (1995) from Paikhoy and other locations in the Ural Mountains are turquoise-planerite.

Analytical methods

Cations (Cu, Zn, Fe, Al, P) were determined on small, hand picked samples ranging from 4 to 12 mg using the ICP technique described in Lichte *et al.* (1983, 1987). Early in this work samples were digested with KOH fusion at 500°C. Later in this technique the digestion was improved and 1 mg of sample was digested per ml of high purity 6 N HCl (prepared by gaseous transfer of HCl from concentrated hydrochloric acid over to double distilled water) using small

volumetric tubes, a stirring hot plate at 80° C, and a micro-magnetic stir bar.

H_2O^- was determined gravimetrically after drying at 105°C for four days. After drying, the sample was then analysed for water at 900°C by Karl Fisher titration using the technique of Jackson *et al.* (1985, 1987) and the results were then reported as H_2O^+

Samples examined

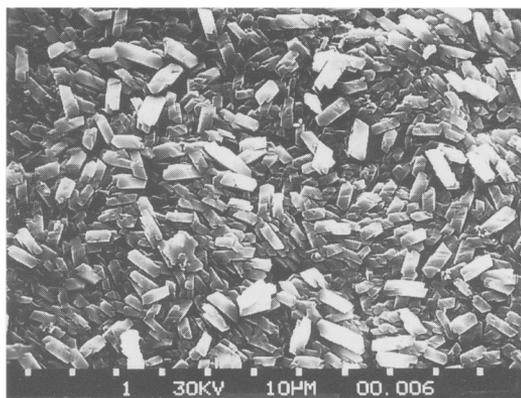
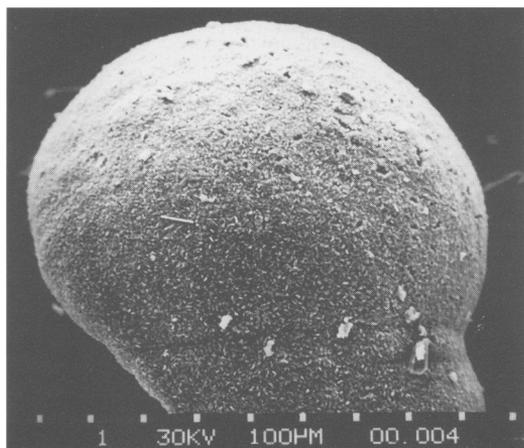
Analyses for a total of 15 samples of planerite, aheylite, and turquoise, many with their museum catalogue numbers, ideal compositions for turquoise, planerite and aheylite, along with one unpublished analysis of planerite from Arkansas, are given in Table 2. Every effort was made to obtain early specimens of 'type' planerite from the Gumeshevsk copper mine, Urals, Russia, so that the mineral could be properly revalidated. True type samples were not preserved as such in the mid-19th century. One specimen of planerite was obtained from The Natural History Museum, London (specimen no. BM 36020, acquired about 1864), along with one specimen (dated 1869) from Harvard University (specimen 62121, Liebener collection). Two old specimens were obtained from the USNM (nos. R5524 and R9710). Additional specimens of planerite were obtained from Charles University (Prague) (12389), and (unnumbered) from the Mining Institute of Leningrad (Gorny Institute). Specimens of planerite were also obtained from

the Bryn Mawr College collection (Rand Collection #8520). We also obtained some turquoise (USNM # 97340) from the Bishop mine, Lynch Station, VA that had been studied by Schaller (1912). Five samples of aheylite were provided by Mr Richard A. Kosnar, and one by Mr Anthony Jones. Many attempts were made to find, for analysis, specimens of white and blue varieties of 'coeruleolactite' from the Rindsberg mine, Katzenelnbogen (also spelled Katzenellenbogen), Hesse (formerly Nassau), Germany, but only two specimens (of the blue to blue-green variety) were able to be obtained through the courtesy of Mr Forrest Cureton (one specimen), and H.J. and I.A. Wilke (given to Mr David Garske who gave the second specimen to Mr Forrest Cureton).

SEM-EDS studies

A Cambridge Stereoscan 250 Mk-1 instrument with attached Tracor Northern EDS system was used for examination, chemical characterization, and photomicrographs of all turquoise group minerals examined.

Most specimens of members of the turquoise group are microcrystalline and appear as earthy, fine-grained, variable density materials. However, the specimens of aheylite and planerite examined in this study along with some turquoise samples are micro-crystalline to macrocrystalline. SEM photos (Figs 1–8) show the complex and excellent crystallinity of these minerals. It



FIGS 1 and 2. FIG. 1 (*left*). SEM photo of a sphere of aheylite crystals from Huanuni, Bolivia. FIG. 2 (*right*). SEM photo at intermediate power showing diamond-shaped crystals making up the sphere shown in Fig. 1.

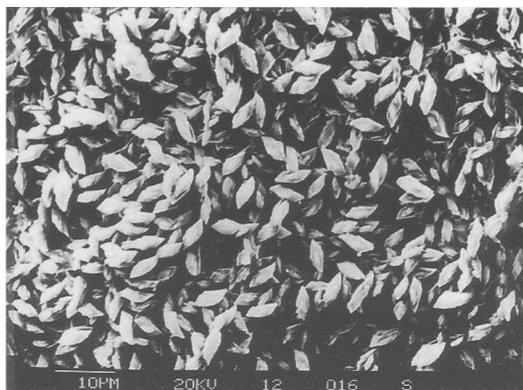
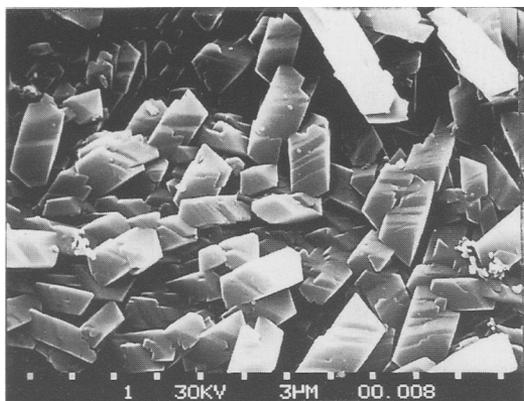
TABLE 2. Chemical analyses of members of the turquoise group including the unpublished analysis by M.D. Foster of planerite from Arkansas

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	
CuO	—	—	—	—	—	—	—	—	3.92	3.93	9.78	9.00	8.81	3.41	2.33	3.10	0.99	0.40	0.23	—	—	—	
ZnO	3.39	4.48	4.18	—	4.02	2.52	1.54	—	0.66	0.91	—	—	0.14	0.19	0.14	0.74	0.15	0.07	0.03	—	—	—	—
FeO	4.14	4.23	4.06	—	4.14	4.91	3.22	8.92	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Fe ₂ O ₃	—	—	—	—	—	—	—	—	—	—	—	0.21	0.28	0.49	0.87	0.46	0.44	0.21	0.00	0.8	0.86	—	—
Al ₂ O ₃	39.5	38.0	36.9	—	38.1	38.1	38.9	37.96	38.2	37.5	37.60	36.50	37.7	38.2	—	—	—	39.9	39.5	40.1	37.75	40.68	
P ₂ O ₅	34.3	36.0	35.8	—	35.4	36.1	36.7	35.23	36.4	35.9	34.90	34.13	34.5	36.3	—	—	—	38.2	37.3	37.1	35.75	37.76	
H ₂ O ⁺	—	—	—	—	18.5	18.5	19.5	17.89	19.0	19.0*	17.72	—	18.2	19.7	19.5	17.7	19.4	21.0	20.8	20.4	21.21	21.56	
H ₂ O _{total}	—	—	—	—	18.6	—	—	—	—	—	—	20.12	—	—	—	—	—	—	—	21.1	—	—	
H ₂ O ⁻	—	—	—	—	0.08	0.08	0.10	0.00	0.00	3.27	0.00	—	0.45	1.60	—	—	—	0.84	1.23	0.87	.12	0.00	
Total	—	—	—	—	100.24	100.13	101.06	100.00	101.45	100.51	100.00	99.96	100.08	99.89	—	—	—	100.62	99.09	99.27	100.10	100.00	

TABLE 2 (cont'd.)

- Atheylite, Huanuni Mine, District of Oruro, Bolivia, ICP analysis of KOH fusion at 500°C, 8.08 mg. Sample from R.A. Kosnar.
- Atheylite, Huanuni Mine, District of Oruro, Bolivia, ICP analysis of KOH fusion at 500°C, 8.84 mg. Sample from R.A. Kosnar.
- Atheylite, Huanuni Mine, District of Oruro, Bolivia, ICP analysis of KOH fusion at 500°C, 9.96 mg. Sample from R.A. Kosnar.
- Atheylite, Huanuni Mine, District of Oruro, Bolivia, H₂O⁻ gravimetrically, H₂O⁺ by Karl Fisher titration. Sample from R.A. Kosnar.
- Atheylite, Huanuni Mine, District of Oruro, Bolivia, average of 1, 2, 3, and 4. Samples from R. A. Kosnar.
(FeZn_{0.40}□_{0.10})Al₆(PO₄)_{3.72}(PO₃OH)_{0.28}(OH)₈ · 4.10 H₂O
- Atheylite, Huanuni Mine, District of Oruro, Bolivia, ICP analysis 7.49 mg sample. H₂O⁻ gravimetrically, H₂O⁺ by Karl Fisher titration, 8.59 mg sample. Samples from A. Jones, Duarte, California.
(FeZn_{0.25}□_{0.20})Al₆(PO₄)_{3.68}(PO₃OH)_{0.40}(OH)₈ · 4.00 H₂O
- *Half empty' theylite-planerite, Huanuni Mine, District of Oruro, Bolivia, ICP analysis 4.76 mg sample. H₂O⁻ gravimetrically, and H₂O⁺ by Karl Fisher titration, 5.828 mg sample.
(□_{0.50}Fe₃Zn_{0.15})Al₆(PO₄)_{3.07}(PO₃OH)_{1.00}(OH)₈ · 4.01 H₂O
- Ideal theylite.
Fe²⁺Al₆(PO₄)₄(OH)₈-4 H₂O
- *Half empty' planerite-turquoise, General Trimble's Mine, Pennsylvania, Bryn Mawr College, Rand collection #8520, ICP analysis 10.39 mg sample. H₂O⁻ gravimetrically, H₂O⁺ by Karl Fisher titration, 10.4 mg sample.
(□_{0.54}Cu_{0.40}Zn_{0.06})Al₆(PO₄)_{3.03}(PO₃OH)_{1.08}(OH)₈-3.91 H₂O
- *Half empty' planerite-turquoise, General Trimble's Mine, Penn., Bryn Mawr College, Rand collection #8520, ICP analysis 7.57 mg sample. *Water from determination reported in analysis #9.
(□_{0.51}Cu_{0.40}Zn_{0.09})Al₆(PO₄)_{3.11}(PO₃OH)_{1.02}(OH)₈-4.09 H₂O
- Ideal turquoise.
Cu Al₆(PO₄)₄(OH)₈-4 H₂O
- Turquoise, Lynch Station, Virginia. Analysis by Schaller (1912) American Journal of Science, 33, p. 35. Schaller performed a Penfield analysis for total water.
(Cu_{0.95}□_{0.05})Al_{5.98}Fe_{0.02}(PO₄)_{3.91}(PO₃OH)_{0.10}(OH)₈-5.27 H₂O
- Turquoise, Lynch Station, Virginia. New analysis of Schaller's U.S.N.M. 97340 sample. ICP analysis of 5.617 mg. Iron determined as total iron and expressed as Fe₂O₃. H₂O⁻ gravimetrically, H₂O⁺ by Karl Fisher titration, 5.780 mg sample. 1.86% insoluble residue (quartz) 'normalized out'.
(Cu_{0.89}□_{0.10}Zn_{0.01})Al_{5.97}Fe_{0.03}(PO₄)_{3.73}(PO₃OH)_{0.20}(OH)₈-4.06 H₂O
- Planerite, Mt. Tschernov, Gumeshevsk, Urals, U.S.S.R. Harvard #62121, L. Lieberer Collection (1869) ICP analysis of 11.877 mg sample. H₂O⁻ gravimetrically, H₂O⁺ by Karl Fisher titration, 13.055 mg sample.
(□_{0.64}Cu_{0.34}Zn_{0.02})Al_{5.95}Fe_{0.05}(PO₄)_{2.78}(PO₃OH)_{1.28}(OH)₈-4.04 H₂O
- Planerite Gumeshevsk, Urals, U.S.S.R., sample from D.P. Gregoryev, Mining Institute of Leningrad. ICP analysis of 4.773 mg sample. Separate sample dried at 105°C, then H₂O⁺ by Karl Fisher titration.
- Planerite, Urals, U.S.S.R. British Museum BM 36020 entered into the collection in 1864. ICP analysis of 6.090 mg sample. Separate sample dried at 105°C, then H₂O⁺ by Karl Fischer titration.
- Planerite, Urals, U.S.S.R. Charles University, Prague, Czechoslovakia, #12389. ICP analysis of 5.355 mg sample. Separate sample dried at 105°C, then H₂O⁻ by Karl Fischer titration.
- Planerite, Syssert District, Urals, U.S.S.R., U.S.N.M. R5524. Average of duplicate ICP analyses of 8.876 and 9.283 mg samples. H₂O⁻ gravimetrically, H₂O⁺ by Karl Fisher titration, 5.376 mg sample.
(□_{0.95}Cu_{0.04}Zn_{0.01})Al_{5.98}Fe_{0.02}(PO₄)_{2.21}(PO₃OH)_{1.90}(OH)₈-3.96 H₂O
- Planerite, Gumeshevsk, Urals, U.S.S.R., U.S.N.M. R9710. ICP analysis of 10.544 mg sample. H₂O⁻ gravimetrically, H₂O⁺ by Karl Fisher titration, 14.892 mg sample.
(□_{0.98}Cu_{0.02}Zn_{0.003})Al₆(PO₄)_{2.11}(PO₃OH)_{1.96}(OH)₈-3.96 H₂O
- Planerite, Mauldin Mountain quarry, Mt. Ida, Montgomery Co. Arkansas. Microprobe analysis and total water (Penfield) by P.J. Dunn. H₂O⁻ gravimetrically, H₂O⁺ by Karl Fisher titration.
□_{1.00}(Al_{5.92}Fe_{0.08})Al₆(PO₄)_{1.92}(PO₃OH)_{2.00}(OH)₈-4.07 H₂O
- Planerite-turquoise, Dug Hill, Arkansas, collected by W.T. Schaller in 1937, analysis by Margaret Foster, August 29, 1951, using classical methods. TiO₂ 0.67%, Cr₂O₃ 0.19%, V₂O₅ 0.20%, K₂O 0.03%, Na₂O 0.01
(□_{0.87}Cu_{0.31}Fe₂(Al_{5.89}Fe_{0.09}Cr_{0.02})PO₄)_{2.72}(PO₃OH)_{1.29}(OH)₈-4.73 H₂O
- Ideal planerite.
□_{1.00}Al₆(PO₄)₂(PO₃OH)₂(OH)₈-4 H₂O

Note: Structural formulas calculated on the basis of the following assumptions: B site occupancy (Al, Fe³⁺, Cr) equaling 6.0; H was distributed in the following sequence: H₂O⁻ was not used, H₂O⁺ was distributed to (OH)₈ based on assumed stoichiometry; the number of PO₃OH molecules was determined by calculating charge balance, and the remainder of the H placed in the molecular water site (H₂O).



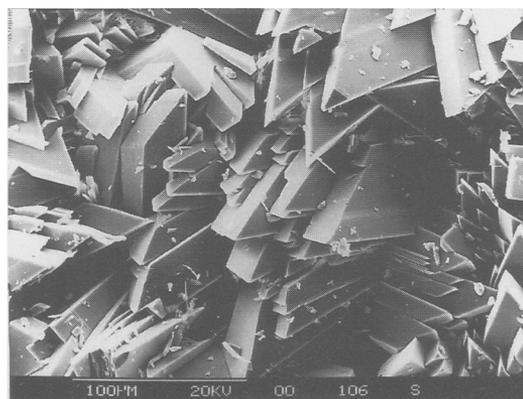
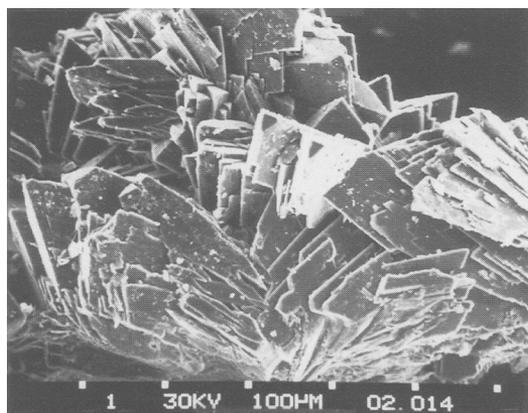
FIGS 3 and 4. FIG. 3 (*left*). SEM photo at high power showing individual crystals of aheylite shown in Figs 2 and 3. FIG. 4 (*right*). SEM photo of planerite crystals (R9710) from Gumeshevsk, Urals, Russia.

should be pointed out that many crystalline samples of turquoise group members are chemically zoned and this chemical zonation often correlates with colour zonation of various samples. For example darker green zones contain more iron, darker blue zones contain more copper, and rarely other elements such as Cr, V, and Zn show up as well.

TGA and Mössbauer data

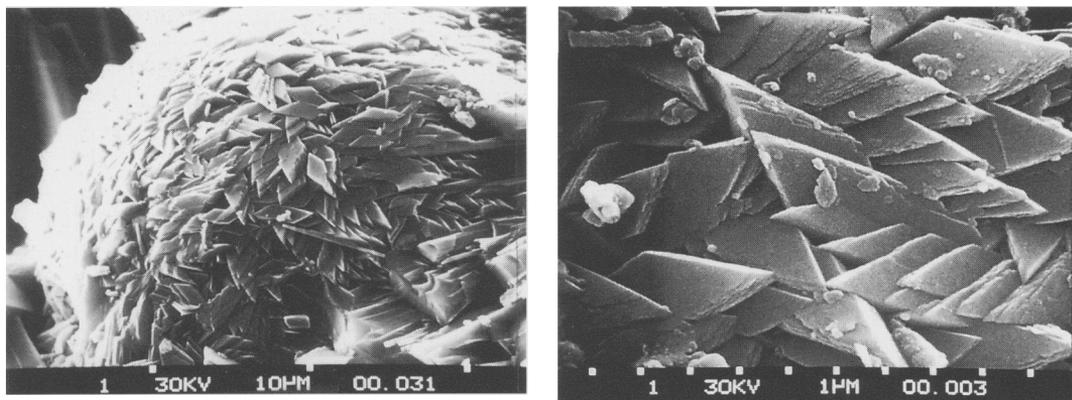
TGA studies were done in the laboratory of C. Gene Whitney (USGS). Both his assistance and that of Kenneth J. Esposito, enabled us to do this important aspect of characterization of the

members of the turquoise group. Instrumentation used was a Perkin-Elmer TGA 300 system. Mössbauer data were collected through the courtesy of D.L. Williamson (Colo. School of Mines). TGA data for two planerites (R9710 and R5524) indicate three discrete weight loss events: 1. 170–200°C (H₂O), 2. 280–300°C (OH) and 3. 340°C (PO₃OH) (Fig. 9). Turquoise from Lynch Station, VA (9% vacancy) shows only one weight loss event at 420°C (Fig. 10). Similar results for Lynch Station turquoise were obtained by Mr. Henry Barwood (Indiana Geological Survey). The molecular water in fully or nearly completely *A*-site filled turquoise is tightly bound and is released together with (OH). To check the



FIGS 5 and 6. FIG. 5 (*left*). SEM photo of Lynch Station, VA, turquoise crystals (USNM #97340). FIG. 6 (*right*). SEM photo of turquoise crystals from Itatiaiuçu iron mine, Minas Gerais, Brazil.

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FIGS 7 and 8. FIG. 7 (*left*). SEM photo of a sphere of planerite-turquoise ('coeruleolactite') from General Trimble's mine, Chester Co. PA. FIG. 8 (*right*). SEM photo showing a close-up view of the planerite-turquoise shown in Fig 7.

accuracy of the TGA apparatus, reference samples of wavellite, paravauxite and vivianite were also analysed. The total weight loss for each mineral agreed well with the ideal total water content. Wavellite loses molecular water at 225°C, and OH at 335°C; paravauxite loses water at 150°C, and OH at 270°C; vivianite loses most of its water at 180°C.

Mössbauer spectroscopy (by D.L. Williamson, CSM) study of four planerites (one from the BMNH, dated 1864, and probably provided by Hermann (1862*a,b*) himself) from Gumeshevsk indicates that all of the iron present is ferric and not ferrous as stated by Hermann (1862*a*). The other three specimens analysed are: USNM #R5524, D.P. Grigoryev (#15, table 2), and Charles Univ. #12389. One sample of aheylite from Huanuni, Bolivia was determined to have a maximum $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of 0.05 thus indicating that virtually all of the iron present is ferrous.

A detailed EPR, Mössbauer, absorption and chemical study was done (Zang and Lin, 1984) for a sequence of turquoise samples containing varying amounts of iron. As is well known the blue to green coloration in turquoise is due to the Cu/Fe ratio and the relative amounts of Fe^{2+} and Fe^{3+} present. Pure blue samples have little or no Fe^{3+} present (e.g., Khorassani and Abedini, 1976). Coloration in turquoise was also addressed by Nikolskaya *et al.* (1976). An increase in the amount of Fe^{3+} is particularly effective in producing a green coloration. Aheylite contains appreciable Fe^{2+} but is only very faintly coloured blue to blue green.

X-ray diffraction studies

Automated X-ray powder diffractometer scans were made using a Norelco-Philips diffractometer with the following analytical conditions: 40 kV and 30 mA, 1/2°/min. and 1/2 inch/min. scan speed. Scans were made from 4° to 76° 2θ in both directions using graphite-monochromatized $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.54059 \text{ \AA}$). Averages of peak positions and intensities were taken from the two scans. Scans were made of planerite, aheylite and a planerite-turquoise. Quartz was used as an internal standard for the Gumeshevsk planerite and the Huanuni aheylite. Annealed CaF_2 was used as an internal standard for the planerite-turquoise from General Trimble's mine. Cell-dimensions for turquoise from Lynch Station, VA were determined using monochromatized $\text{Cu-K}\alpha_1$ radiation with a Haag-Guinier camera, and NBS 540a silicon as an internal standard. The X-ray data are given in Table 3. The similarities can readily be seen between these three species, but there are some significant intensity differences of certain reflections: e.g. $d(010)$ at about 9.0 Å. In true planerite, the *A*-site is empty and there is no $d(010)$ diffraction line present. Turquoise on the other hand, with a filled *A*-site, shows a well-defined $d(010)$ peak. The diffraction pattern for planerite contains less than half of the number of diffraction maxima observed for turquoise. Peak intensities and observed reflections for planerite are substantially different from those of turquoise. For example the $2\bar{1}1$ reflection is the most intense maximum for planerite and is not observed in

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1.666	1.665	2
1.607	1.608	3
1.601	1.602	5
1.592	1.592	3
1.580	1.580	30
1.574	1.574	4
1.566	1.566	25
1.548	1.548	8
1.527	1.528	5
1.506	1.506	35
1.490	1.490	35

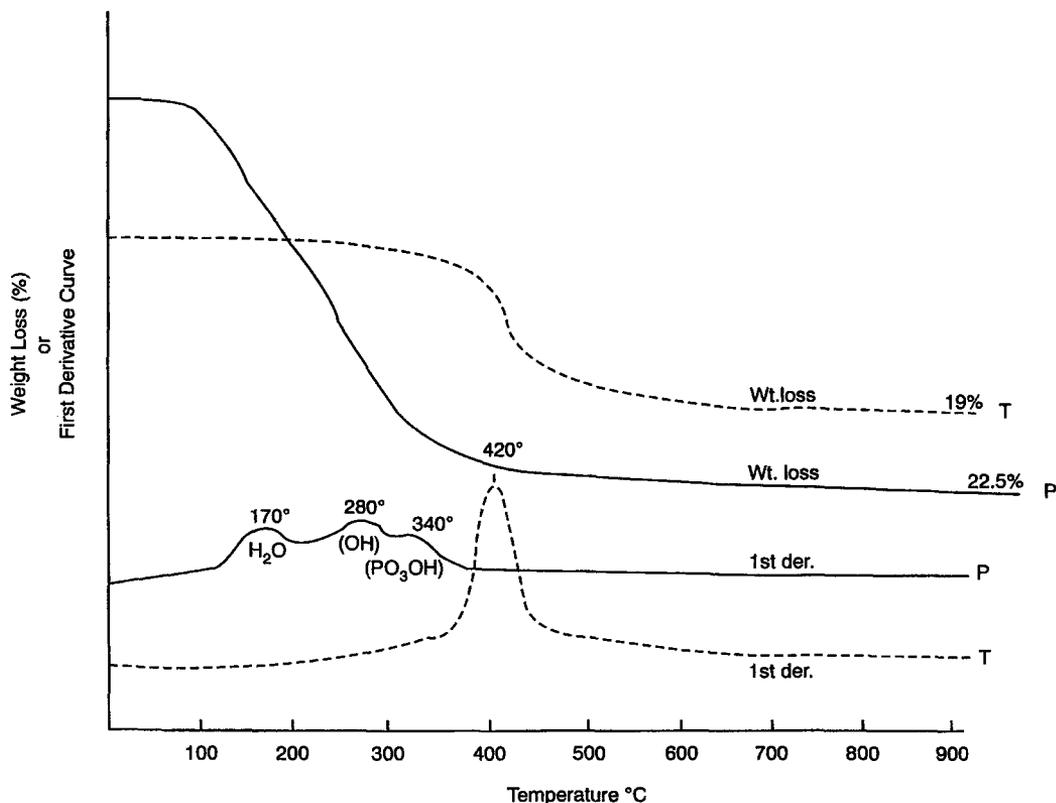


Fig. 9. TGA curves for planerite (P) from Gumeshevsk and for turquoise (T) from Lynch Station, VA.

turquoise. Another major difference is the presence of the $1\bar{1}1$ reflection in planerite that is not observed for turquoise. Unit cell dimensions for members of the turquoise group are compared in Table 4. Chalcosiderite and the $\text{Fe}^{2+}\text{-Fe}^{3+}$ analogue of turquoise both have similar volumes of about 502 \AA^3 while all of the other members of the group have volumes of about 460 \AA^3 . Unit-cell dimensions for the turquoise from Greece (Sklavounos *et al.*, 1992) were: a 7.52, b 10.24, c 7.70 \AA , α 111.30°, β 115.12°, γ 69.32°. These cell dimensions are slightly larger than reported for turquoise (ICDD 6-214). A turquoise (0.88 A site occupancy) from Altar, Chile had: a 7.4100(2), b 7.6356(2), c 9.9052(3) \AA , α 68.652(1)°, β 69.639(1)°, γ 65.034(1)°, V 460.50 \AA^3 , $Z = 1$, $D_{\text{calc}} = 2.91$ (Guthrie and Bish, 1991). These dimensions and cell volume agree closely with our determined cell data for Lynch Station, VA turquoise, viz. a 7.409(1), b

9.914(2), c 7.635(1) \AA , α 111.356°, β 114.973°, γ 69.532°, V 460.64(9) \AA^3 , $Z = 1$.

Planerite

Planerite, first described in 1862 by Hermann (1862*a,b*), was approved by the IMA CNMMN as a revalidated mineral in 1984 along with the new species aheylite. The ideal formula for the mineral is $\square_1\text{Al}_6(\text{PO}_4)_2(\text{PO}_3\text{OH})_2(\text{OH})_8\cdot 4\text{H}_2\text{O}$. The mineral generally appears as white to pale blue or pale green, mamillary, botryoidal crusts as much as several mm thick on substrates ranging from quartz to other Al-phosphate minerals. It is microcrystalline with an individual grain size of 2–3 micrometres and sometimes larger (Fig. 4). The luster is chalky to earthy, fair transparency on thin fragments, no fluorescence in SW or LW UV light, $H. = 5$, moderate to brittle, no cleavage observed,

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TABLE 4. Unit-cell dimensions for members of the turquoise group utilizing data from this work as well as from the literature

	Turquoise	Faustite	Fe ²⁺ -Fe ³⁺ member	Turquoise- planerite	Chalcosiderite	Planerite	Aheylite
<i>a</i>	7.410 Å	7.44 Å	7.67 Å	7.526 Å	7.672 Å	7.505 Å	7.400 Å
<i>b</i>	7.636	9.89	10.25	9.946	10.199	9.723	9.896
<i>c</i>	9.905	7.67	7.87	7.779	7.885	7.814	7.627
α	68.65°	110.72°	112.3°	112.42°	67.52°	111.43°	110.87°
β	69.64	115.65	115.7	116.56	69.17	115.56	115.00
γ	65.03	69.65	69.3	68.54	64.88	68.69	69.96
<i>V</i>	460.5 Å ³	463.0 Å ³	502.4 Å ³	467.8 Å ³	502.21 Å ³	464.2 Å ³	460.6 Å ³
<i>Z</i>	1	1	1	1	1	1	1
	Guthrie and Bish (1991)	ICDD 6-216	Mücke, 1983 (pers. comm.)	this paper	ICDD 37-446	this paper	this paper

Note: data for turquoise and chalcosiderite are shown using an all acute cell.

splintery fracture, D_m 2.68(5) and D_c 2.71(5). Not magnetic. Individual refractive indices were not able to be determined because of small grain size, but the mean RI is about 1.60(1). The unit-cell parameters determined from a least-squares refinement are: *a* 7.505(2), *b* 9.723(3), *c* 7.814(2) Å, α 111.43°, β 115.56°, γ 68.69°, *V* 464.2(1)³, *Z* = 1. Indexed X-ray powder diffraction data are given in Table 3.

A sample of small green spherulites of planerite from Dug Hill, near Avant, Garland Co., Arkansas (Smith, 1985), collected in 1937 by W.T. Schaller was completely analysed by M.D. Foster in 1951. This analysis has not been published in the literature previously, and is included (analysis 21) in Table 2. It can be seen that this planerite has about two-thirds of the A site vacant. It contains 0.2 wt.% each of Cr₂O₃ and V₂O₅, both elements of which are responsible for the characteristic green colour of Arkansas wavellite.

A sample (analysis no. 20, Table 2) of planerite from the Mauldin Mountain Quarry, Mt. Ida, Montgomery Co., Arkansas, is virtually end-member planerite as is one of the samples from Gumeshevsk (analysis no. 19, Table 2).

Six-step emission spectrographic analysis (by N.M. Conklin, U.S.G.S.) of two samples of planerite from General Trimble's Mine, East Whiteland Township, Chester Co., PA, yielded: 1. (pale blue, Rand Coll. 8520): Fe 0.07%, Mg 0.003%, Ca 0.005%, Ti 0.0015%, Si 0.03%, Al major, P major, Na <0.01%, K <0.01%, Mn 50 ppm, Ba 1500 ppm, Cr 15 ppm, Cu 3%, V 15

ppm, Y 20 ppm, Zn 3000 ppm. All other elements not detected at respective limits of detection. 2. (white, Rand Coll. 8520): Fe 0.15%, Mg 0.01%, Ca 0.015%, Ti 0.07%, Si 1.5%, Al major, Na <0.01%, K <0.01%, P major, Mn 30 ppm, Ba 150 ppm, Cr 15 ppm, Cu 500 ppm, V 15 ppm, Y 70 ppm, Zn 300 ppm, and Zr 70 ppm. All other elements not detected at respective limits of detection.

Planerite was described from Ponikla, Bohemia by Čech *et al.* (1961). Planerite has also been described from Japan (Matsubara *et al.*, 1987, 1988). ICDD 42-1318 lists indexed powder diffraction data for a Cu-bearing (2.42 wt.%) planerite from Toyoda, Kochi City, Shikoku, but these data are not as complete as the data presented here for virtually end-member planerite from the type locality.

Aheylite

Aheylite was approved as a new mineral, and member of the turquoise group, by the IMA CNMMN in 1984. The mineral occurs with variscite-type L, sphalerite, pyrite, quartz, vivianite, wavellite and cassiterite. The type locality is the Miraflores mine, District of Huanuni, Dept. of Oruro, Bolivia. The variscite-type L, aheylite, and sphalerite are very late in the paragenetic sequence and form botryoidal, microcrystalline masses on earlier formed minerals. Individual spheres of the aheylite may be as much as 1 mm or more across but the other two species are much

smaller. The three minerals are late hydrothermal crystallization products.

The aheylite occurs as isolated and aggregate clumps of hemispherical to spherical, radiating to interlocked very pale blue or blue-green felted and matted aggregates of crystals which average 3 microns in maximum dimension (see Figs 1–3). The mineral is very pale blue or blue green, white streak, porcelaneous-semivitreous luster, transparent in thin flakes, not fluorescent, H. 5–5.5, moderate to brittle tenacity, no cleavage observed, hackly to splintery fracture, D_m 2.84, D_c 2.90. Not magnetic. The mineral is biaxial positive, non-pleochroic, but individual indices could not be determined because of the exceedingly small grain size, mean R.I. is about 1.63.

Chemical analyses for aheylite are given in Table 2 (nos. 1–8). This mineral may be best thought of as the ferroan analogue of turquoise and faustite (Erd *et al.*, 1953). It should be noted that the mineral is zincian and in some samples $Zn(\text{atomic}) \approx Fe(\text{atomic})$. Some *A*-site vacancy is also present. Only one sample has Fe^{2+} greatly in excess of Zn or vacancy. Emission-spectrographic analysis revealed the following trace elements: Mg 0.001%, Ca 0.007%, Ti - none, Mn 7 ppm, Ba 15 ppm, Be 15 ppm, Co 15 ppm, Cr 7 ppm, Cu 2 ppm, Ni 7 ppm, Sn 20 ppm, V 200 ppm.

Unit-cell dimensions, calculated from least-squares refinement of powder diffraction data are: a 7.400Å(1), b 9.896(1), c 7.627(1) Å, α 110.87°, β 115.00°, γ 69.96°, V 460.62(9) Å³, $Z = 1$. See Table 3 for indexed X-ray powder diffraction data for planerite, aheylite, and turquoise.

The mineral is named for Allen V. Heyl (1918–) (U.S. Geological Survey, retired) in particular recognition of his work on Mississippi-Valley type ore deposits, as well as ore deposits in general.

Discussion

Only relatively few bulk samples of members of the turquoise group are pure or nearly so. Numerous references exist in the literature that contain analyses of impure material. Recent such papers include those of: Boriskin and Kuzmina (1976), Turesebekov *et al.*, 1979; and Yakontova *et al.* (1989). The most common impurity element is Si, although in some cases, small amounts of Si may substitute for P. Impurities have been shown by other authors as well as by the present authors to be many different things: amorphous silica, quartz, kaolinite, montmorillonite, allophane,

other phosphate minerals, etc. We made every effort in this study to analyse only pure materials and with a direct determination of the water content. By so doing, we are able to show definitively that turquoise group members have only 4 molecules of water and that additional water is accounted for by protonation of a maximum of two of the four PO_4 groups forming (PO_3OH) groups to form planerite. Some H_2O for (OH) substitution may also take place (Fig. 10). Excess amounts of water in turquoise, chalcociderite, and faustite, are due to solid solution towards planerite, or additional impurity phases containing significant amounts of water. Light blue or blue-green 'turquoise' from many world-wide localities is actually planerite rather than turquoise. Pure or nearly pure turquoise is quite rare as well, and the mineral from the Bishop mine, Lynch Station, Campbell Co., VA, is the best high-purity, well-crystallized, highly Cu-substituted turquoise (e.g. Schaller, 1912) that we examined. A re-determination of the density of the turquoise that was analysed by Schaller (1912) was made using methylene iodide diluted with acetone: $D_{obs} = 2.86(1)$; $D_{calc} = 2.91$. Some material from Lynch Station is intermediate between turquoise and chalcociderite, and a few samples of chalcociderite were found as well in a batch of assorted samples from the mine (J. Nelen microprobe data, 1984, pers. comm.).

Thus, planerite is characterized as the member of the turquoise group with the *A*-site predominantly to completely vacant. A complete gradation (solid-solution) series exists between planerite and turquoise based on the number of available analyses from this paper and from the literature (e.g. Matsubara *et al.*, 1987, 1988). Much of the material described as turquoise in the literature is actually planerite. However, the name turquoise should be retained for gemological and historical uses. There appears to be significant solid-solution between chalcociderite and turquoise based on available reliable analyses, and there should be a complete solid solution series between faustite and turquoise, but the number of known faustite occurrences is quite small. Aheylite shows substitution with both planerite and faustite components.

Crystals of turquoise and other members of the group for that matter, larger than about 0.1 mm are rare. As noted by Braithwaite (1981), as of 1981 only the Bishop mine, Lynch Station, VA, and Otré, near Vielsalm, Ardennes, Belgium were known localities for well crystallized

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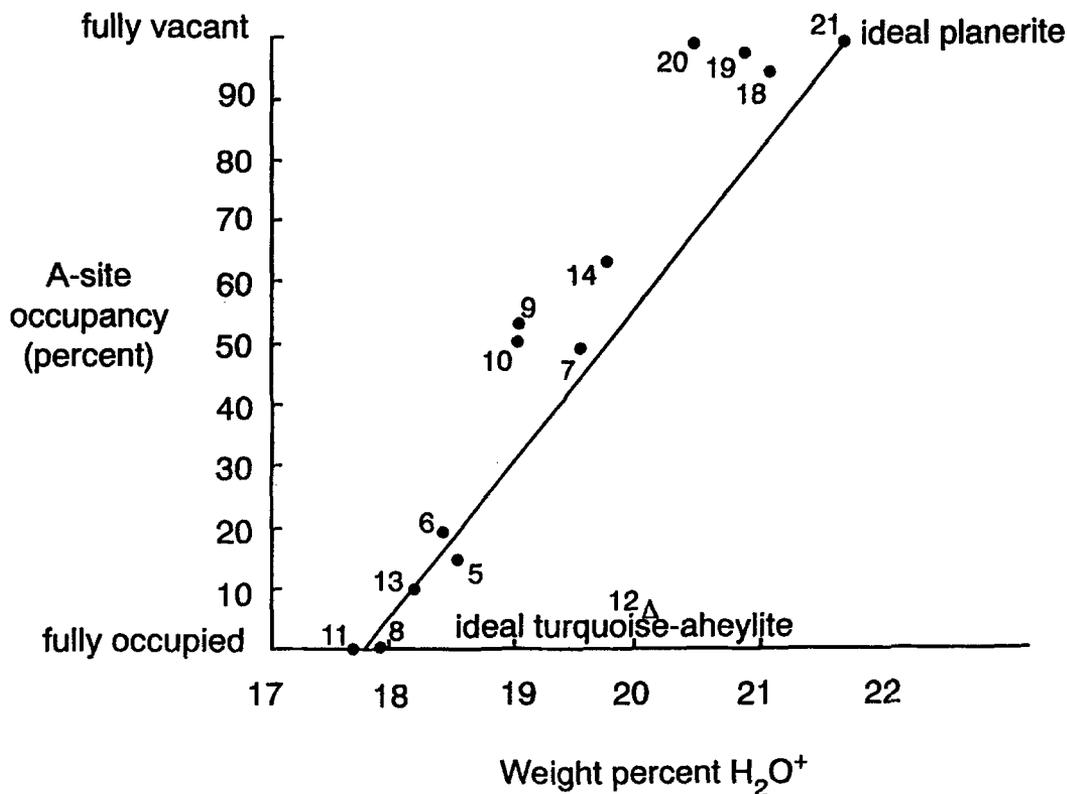


FIG. 10. Plot of wt.% H₂O vs percentage occupancy of the A-site (going from ideal turquoise and aheylite to planerite). Solid dots represent analyses from this work or ideal compositions of end-members. Open triangle represents analysis from Schaller (1912).

turquoise. Braithwaite added three British occurrences: Hensbarrow and Wheal Remfry china clay pits, on St. Austell Moor, and Wheal Phoenix (Stowe's Mine), Linkinhorne, all in Cornwall. Turquoise crystals also occur at the Narooma mine, NSW, Australia (Braithwaite, 1981; Price, 1981). Well-crystallized turquoise associated with quartz and dickite occurs at the Itatiaçu iron mine, southwest of Belo Horizonte, Minas Gerais, Brazil (Fig. 6). Chalcosiderite, it should be noted, is a rare mineral, known from only a few localities including: Cole and Shattuck shafts, Bisbee, Cochise Co., AZ; Wheal Phoenix, Linkinhorne; Gunheath Pit, St. Austell, Cornwall, England, UK; four localities in Germany: Herdorf, Siegerland, Hagendorf Süd, Bavaria; Schneckenstein, Saxony; and Siegen, Westphalia. It has also been found at the Lake Boga quarry, Victoria, Australia.

Of all of the known members of the turquoise group, faustite (from two localities: Nevada and Neyschapur, Iran); the unnamed Fe²⁺-Fe³⁺ member (one locality: Rotläufsch, Waldgirmes, Saxony, Germany) (Mücke, pers. comm., 1983) and aheylite (one locality: Bolivia), are the rarest. A Zn-bearing (to 2.6 wt.% Zn) turquoise from Burkantau region (central Kyzylkum), Russia was described by Boriskin (1974).

Varietal names such as cuprofaustite or alumoalchalcosiderite (Ivanov, 1979; Kunov *et al.*, 1982, 1986) should not be used, rather they would be termed cuprian faustite or aluminian chalcosiderite according to the current nomenclature rules of the IMA CNMMN. Further, some nomenclatural errors have been made in calling two samples of planerite from Tras Pahang, Malaysia (Murthy, 1989) 'turquoise' and 'faustite' respectively.

Studies on coeruleolactite

Valid specimens of 'coeruleolactite', the supposed Ca-dominant (*A*-site) member of the turquoise group, originally described by Peterson (1871), were sought for. Peterson (1871) described his material as being bluish milk-white in colour. Many different collectors and museums were asked if they had material from the type locality for 'coeruleolactite': Rindsberg, Katzenelnbogen, Nassau, Saxony, Germany. None could be obtained, even by visitation of the locality by Roland Dietrich and six other people (Roland Dietrich, pers. comm., 1985). A former mineral dealer, Mr Forrest Cureton (Grass Valley, CA) had a piece of 'coeruleolactite' labelled 'coeruleolactine' from Katzenelnbogen. The handwritten label appears to be about 80–90 years old. The specimen was obtained from Scott Williams Mineral Co., of Scottsdale, AZ, who had labelled it: "coeruleolactite — rich blue massive on limonite. Ausgebrannte Eisensteingrube, Katzenelnbogen, Nassau, Germany". This specimen shows light-medium coerulean blue material, with sprays of colourless wavellite, on a limonite matrix. X-ray diffraction analysis showed the presence of a member of the turquoise group with appreciable (20–30%) wavellite and variscite as well. SEM-EDS study confirmed that the mineral was a heterogeneous mixture of at least three different minerals. An ICP-AES analysis (P.H. Briggs, USGS) of the X-ray diffraction split showed (in wt.%): Al₂O₃ 35.9, CaO 0.15, FeO 0.18, P₂O₅ 36.7, BaO 0.02, CuO 2.75, Na₂O 0.04 K₂O 0.05 MnO 0.02, ZnO 0.20, total 76.01. Allowing for the admixed variscite and wavellite, it is clear that this specimen is a cuprian planerite.

A second specimen of light blue-green 'coeruleolactite' was also obtained from Mr Forrest Cureton, who obtained the specimen from another mineral dealer, Mr David Garske. Mr Garske obtained the specimen from Hans J. Wilke and Ilse A. Wilke who in turn obtained the specimen (a dump sample) in Germany. A semi-quantitative analysis (ICP-AES) showed only 0.3 wt.% CaO, approximately 3 wt.% Fe₂O₃ (all Fe as ferric iron), and about 5.0 wt.% CuO. This specimen is a turquoise-planerite. X-ray diffraction studies confirmed that the material was pure, as did SEM-EDS studies. Minor colourless wavellite (younger than the turquoise-planerite) is also present. A few areas (SEM-EDS study) contained appreciable amounts of CaO (more than

5 or 10 wt.%) and X-ray diffraction studies of one of these areas showed the presence of crandallite.

The ionic radius of Ca²⁺ is 0.99, significantly larger than the 0.69 for Cu²⁺, 0.76 for Fe²⁺, and 0.74 for Zn²⁺. It can be clearly seen that the ionic radius of Ca²⁺ is much larger (>20%) than any of the other cations found in the *A*-site of turquoise. Fischer (1958) presented an analysis of a white variety of 'coeruleolactite' from the Rindsberg mine, Nassau, Germany, and based on the 5.09 wt.% CaO content and an X-ray diffraction pattern that matched those for other members of the turquoise group, 'coeruleolactite' was stated to be a valid species. However, close examination of the other components determined: H₂O 23.4 wt.%, P₂O₅ 30.1, Al₂O₃ 40.3, MgO 0.4, CuO 0.24 indicates clearly that this 'coeruleolactite' is a mixture and not one mineral; likely containing crandallite and some wavellite and/or variscite as was found in the specimens that we examined. Fischer (1958) presented Debye-Scherrer X-ray diffraction data for both white and coerulean-blue varieties of 'coeruleolactite'. He did not indicate that contaminant mineral phases were also found. Dietrich (1978, 1982) identified what he thought was 'coeruleolactite' from the Rotläufchen mine in Waldgirmes near Wetzlar, Germany. However, the material does not have any Ca in it, and, while nicely microcrystalline, and apple green in colour, is a planerite containing some Fe and Cu.

'Coeruleolactite' was reported from the Cruzeiro pegmatite, Governador Valadares district, Brazil, by Proctor (1985) who obtained this information from an article in the *Mineralogical Record* by Cassedanne and Sauer (1980). This material was identified on the basis of X-ray powder diffraction data only.

Material from General Trimble's Mine, East Whiteland Township, Chester Co., PA was originally stated to be 'coeruleolactite' by Genth (1875) and later workers. McConnell (1942) correctly pointed out that the material was not 'coeruleolactite' but erred in calling it turquoise based only on X-ray examination and without chemical analysis. We obtained specimens of 'coeruleolactite' (Figs 7–8) from General Trimble's Mine from the Rand Collection at Bryn Mawr College, and based on our X-ray and complete chemical studies (Tables 2 and 3) have shown the mineral to be essentially half-empty turquoise but with vacancy dominating the *A*-site, thus dictating the proper name cuprian planerite. Unpublished X-ray studies by F. A. Hildebrand for W. Schaller (1952, internal USGS report) were

made for samples of planerite from Gumeshevsk, Syssert, Urals, Russia, and for 'coeruleolactite' from General Trimble's mine, East Whiteland Twp., Chester Co., PA. The same sample of planerite, USNM R5524 and one additional sample R5523 (from the same locality) were examined by X-ray powder diffraction methods by Hildebrand and both identified as planerite. The sample of 'coeruleolactite' (USNM R5610) was termed coeruleolactite with some admixed variscite.

Two samples of conchoidally fracturing dark olive green to blue green 'coeruleolactite' from the Royston District, Lyon County, NV (from Wards Natural Science Establishment) were studied and found to consist of material intermediate between planerite and chalcocyanite and about 15% admixed quartz. Less than 0.3 wt.% CaO was detected.

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