

Redgillite, $\text{Cu}_6(\text{OH})_{10}(\text{SO}_4)\cdot\text{H}_2\text{O}$, a new mineral from Caldbeck Fells, Cumbria, England: description and crystal structure

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ABSTRACT

Redgillite, $\text{Cu}_6(\text{OH})_{10}(\text{SO}_4)\cdot\text{H}_2\text{O}$, space group $P2_1/c$, a 3.155(3) Å, b 10.441(8) Å, c 19.436(16) Å, β 90.089(13)°, $V = 640.2(9)$ Å³, $Z = 2$, is a new mineral from Silver Gill, Caldbeck Fells, Cumbria, England. The strongest six lines of the X-ray powder-diffraction pattern [d in Å, (hkl)] are: 9.72 (90) (002), 7.11 (100) (012), 4.60 (30) (022), 4.068 (20) (023), 2.880 (30) (112,11 $\bar{2}$), 2.318 (50) (131,13 $\bar{1}$). It occurs as translucent to transparent grass-green bladed crystals up to 0.15 mm long with squared-off or tapering terminations; usually in radiating groups. Forms observed are {001} prominent, {010} as composite stepped faces, and {100} irregular. Redgillite has white streak, vitreous lustre and Mohs hardness of ~2. Blades are slightly flexible with irregular fracture and exhibit a perfect {001} cleavage and good {100} and {010} cleavages. The measured density (by sink-float) is 3.45(5) g/cm³; the calculated density is 3.450 g/cm³. The mineral dissolves slowly in dilute HCl. Redgillite is biaxial-negative with $\alpha = 1.693(2)$, $\beta = 1.721(2)$, $\gamma = 1.723(2)$, $2V = 30(2)^\circ$ (meas.) and 30° (calc.); dispersion is $r > v$, medium; pleochroism: Y blue-green > X blue-green > Z yellow-green; orientation: $X \approx c$, $Y = b$, $Z \approx a$. Electron microprobe analyses yielded CuO 68.9, SO₃ 11.6, total 80.5. With water inferred from the structure analysis, the empirical formula is: $\text{Cu}_{5.995}(\text{OH})_{9.991}(\text{SO}_4)_{1.003}\cdot\text{H}_2\text{O}$. Redgillite is typically found in thin fractures in partly oxidized sulphides where it is commonly associated with langite and more rarely with malachite, cuprite, connellite and brochantite. The name is for the Red Gill mine, from which the mineral is best known. The crystal structure of redgillite was determined and refined to $R = 0.090$ for 1529 observed reflections [$I > 2\sigma(I)$]. The redgillite structure consists of Jahn-Teller distorted CuO₆ octahedra and SO₄ tetrahedra. The octahedra share edges to form sheets that are zig-zag in cross section. The SO₄ tetrahedra share an oxygen with the Cu layer and link the layers by hydrogen bonds to OH groups. The crystal structures of wroewolfeite, langite, posnjakite, spangolite and schulenbergitte are similar to redgillite. They all contain edge sharing CuO₆ layers connected to SO₄ groups with the layers bridged via hydrogen bonds.

KEYWORDS: redgillite, new mineral, copper sulphate hydrate, Lake District, England.

Introduction

COOPER and Stanley (1990, p. 133) reported an “unknown copper sulphate hydrate” found by Peter Braithwaite on the No. 2 Level (Old Dutch Level) mine dump at the Red Gill mine, Caldbeck

Fells, Cumbria, England. It was shown by X-ray diffraction (XRD) analysis to be identical to a mineral previously found at the Esgair Hir mine, Talybont, Wales. Colour photographs of the mineral also appear in that publication. Subsequently, the mineral was found at other localities in the British Isles including: the Silver Gill vein, Caldbeck Fells, Cumbria and the Penberthy Croft mine, St. Hilary, Cornwall,

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DOI: 10.1180/0026461056960302

England (Betterton, 2000); the Sheefry mine, Co. Mayo, Ireland; and numerous mines in central Wales, including the Frongoch mine, Devil's Bridge; the Bwlchrhennaid mine, Goginan; the Nant y cagle (or Eaglebrook) mine, Talybont; the Darren mine, Talybont; and the Llechweddhelyg mine, Bontgoch.

A description of the mining history, the mines, the geology and the mineralogy of the Caldbeck Fells, Cumbria, England was given by Cooper and Stanley (1991). Since that report, the name 'redgillite' has come into relatively common usage for this mineral, despite the fact that it had not been approved by the Commission on New Minerals and Mineral Names (CNMMN) of the IMA. Because the crystals of the mineral from the Red Gill mine were not of sufficient quality to describe the species adequately, better crystals collected underground in the nearby Silver Gill vein have been used in this characterization of the species and in its crystal-structure determination. Silver Gill and the Silver Gill vein specifically, should therefore be considered the type locality for the mineral, although the name 'redgillite' is retained for the species in recognition of its best known occurrence and to avoid possible confusion. The mineral and name have been approved by the CNMMN. The holotype is deposited in the Manchester Museum, The University of Manchester, UK (catalogue number MANCH:18024).

Occurrence

The crystals of redgillite used in this study are from a specimen collected by Peter Braithwaite. This specimen, designated as the holotype, was collected underground on the Golden Hugh level of the Silver Gill vein, Caldbeck Fells, Cumbria, England. In the UK grid reference system, this site is located at NY 2987 3405 (Note that the Red Gill mine is located less than 1 km away at NY 2950 3478).

Silver Gill is a steep-sided ravine that runs for about 750 m from the moorland plateau east of Great Sca Fell to Dale Beck (NY 2978 3397 to NY 3018 3469). The Silver Gill vein crosses Silver Gill beck in its upper reaches (NY 2987 3404) and is conspicuous as a quartz rib on both sides of the valley. The vein was mapped by the British Geological Survey (1997) as a NE–SW trending mineralized normal fault structure between NY 308 357 and NY 297 339. Most of the mine workings in the gill are driven from the

stream bed as crosscuts into the Silver Gill vein. There are at least five adit levels and the Golden Hugh level is the uppermost and was driven directly on the vein. The Golden Hugh level was open in the early 1980s and gave access to several small stopes, but it is now covered over.

The Silver Gill vein contains lead-zinc-copper mineralization, historically the most important style of mineralization in the Caldbeck Fells. The major primary minerals present are chalcopyrite and galena, with lesser sphalerite, covellite and pyrite. Quartz is the dominant gangue mineral with minor baryte and the carbonates calcite and dolomite. The mineralization is thought to be early Carboniferous in age (Cooper and Stanley, 1990). Oxidation processes, presumably in the Tertiary, produced the suite of supergene minerals for which the mines at Caldbeck Fells are famous.

Redgillite is typically found in thin fractures in partly oxidized sulphides where it is commonly associated with langite and more rarely with malachite, cuprite, connellite and brochantite. Other supergene minerals from the Silver Gill vein include: anglesite, aurichalcite, bechererite, caledonite, cerussite, copper, covellite, fraipontite, goethite, hemimorphite, hydrocerussite, lanarkite, leadhillite, linarite, posnjakite, pyromorphite, ramsbeckite, rosasite, schulenbergite, smithsonite, sulphur, susannite, wroewolfeite and wulfenite. At the other localities where redgillite occurs, it appears to be a dump oxidation product and, therefore, is probably post-mining in origin.

Physical and optical properties

Redgillite typically occurs as grass-green bladed crystals with squared-off or tapering terminations; usually in radiating groups (Fig. 1). On the type specimen, blades are up to 0.15 mm long with typical dimensions: $0.100 \times 0.020 \times 0.005$ mm ($x \times y \times z$). Forms observed were {001} prominent (the only form giving good signal on the reflecting goniometer), {010} under high magnification seen as composite stepped faces, and {100} irregular. No twinning was observed, though twinning on {001} may be the cause of the anomalous interference figure observed for one crystal studied.

The streak of redgillite is white. Crystals are translucent to transparent and exhibit vitreous lustre. The mineral is non-fluorescent. The hardness could not be measured accurately, but it is very soft, probably having a Mohs hardness of ~2. Crystals are brittle, and slightly flexible, but

not elastic. They exhibit perfect cleavage on {001} and good cleavage on {100} and {010}. The fracture is uneven. The mineral dissolves slowly in dilute HCl. The density measured by sink-float in Clerici solution is 3.45(5) g/cm³. The calculated density is 3.450 g/cm³.

Crystals are optically biaxial-negative. Indices of refraction measured in Na light (589 nm) are α 1.693(2), β 1.721(2), γ 1.723(2). The measured 2V angle is 30(2)^o and the calculated 2V is 30^o. The dispersion is $r > v$, medium. The optical orientation is $X \approx c$, $Y = b$, $Z \approx a$. Pleochroism is pronounced: Y blue-green > X blue-green > Z yellow-green.

Chemistry

Chemical analyses of redgillite were performed using a Cameca SX50 electron microprobe, first by surveying the crystal's composition by EDS and then in WDS mode (15 kV, 10 nA, beam diameter 10 μ m). The WDS results of seven analyses on a polished surface of crystalline fragments mounted in epoxy using Cu metal and BaSO₄ standards provided the following averages (ranges): CuO 68.9(66.8–70.7), SO₃ 11.6(11.0–12.4), total 80.5(77.8–82.5). No other elements were detected.

The small amount of material available precluded the determination of H₂O by direct measurement so the amount of water present is inferred from the structure analysis. The empirical formula (based on 15 oxygen atoms) is: Cu_{5.995}(OH)_{9.991}(SO₄)_{1.003}·H₂O. The simplified formula is Cu₆(OH)₁₀(SO₄)·H₂O. The Gladstone-Dale compatibility index [$1 - (K_p/K_C)$] is -0.040 (good; nearly excellent).

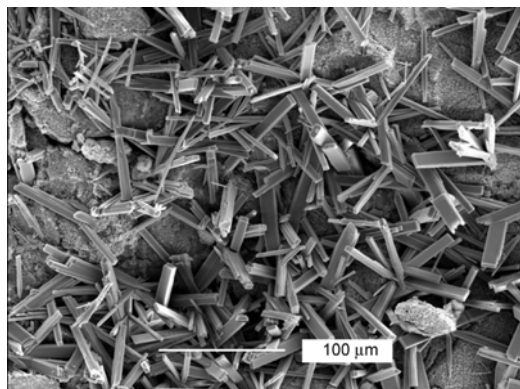


FIG. 1. Electron micrograph of redgillite crystals.

X-ray crystallography and structure determination

X-ray powder diffraction data (Table 1) were obtained using a Gandolfi camera (114.6 mm diameter, Ni-filtered Cu-K α radiation). The data show good agreement with the pattern calculated from the structure. For structure data collection, a crystal of redgillite from the type specimen was mounted on the tip of a glass fibre tapered to

TABLE 1. X-ray powder data for redgillite¹.

| I_{obs} | d_{obs} | d_{calc} | I_{calc} | hkl |
|------------------|------------------|-------------------|-------------------|---------------|
| 90 | 9.72 | 9.718 | 82 | 0 0 2 |
| — | — | 9.198 | 16 | 0 1 1 |
| 100 | 7.11 | 7.114 | 100 | 0 1 2 |
| <5 | 5.22 | 5.221 | 3 | 0 2 0 |
| 30 | 4.60 | 4.599 | 39 | 0 2 2 |
| 5 | 4.41 | 4.405 | 7 | 0 1 4 |
| 20 | 4.068 | 4.065 | 26 | 0 2 3 |
| 10 | 3.555 | 3.557 | 9 | 0 2 4 |
| 5 | 3.232 | 3.239 | 4 | 0 0 6 |
| 10 | 3.069 | 3.066 | 12 | 0 3 3 |
| 30 | 2.880 | { 2.885 | 12 | 1 1 $\bar{2}$ |
| | | { 2.883 | 18 | 1 1 2 |
| 5 | 2.751 | 2.753 | 8 | 0 2 6 |
| 10 | 2.648 | { 2.648 | 6 | 1 0 $\bar{4}$ |
| | | { 2.644 | 5 | 1 0 4 |
| 10 | 2.596 | 2.593 | 9 | 0 3 5 |
| 15 | 2.426 | 2.430 | 8 | 0 0 8 |
| 10 | 2.362 | 2.366 | 14 | 0 1 8 |
| — | — | 2.338 | 12 | 1 3 0 |
| 50 | 2.318 | { 2.321 | 28 | 1 3 $\bar{1}$ |
| | | { 2.321 | 14 | 1 3 1 |
| 10 | 2.259 | { 2.262 | 7 | 1 0 $\bar{6}$ |
| | | { 2.258 | 3 | 1 0 6 |
| 5 | 2.206 | { 2.211 | 2 | 1 1 $\bar{6}$ |
| | | { 2.207 | 3 | 1 1 6 |
| 15 | 2.000 | { 2.001 | 3 | 1 4 $\bar{1}$ |
| | | { 2.000 | 10 | 1 4 1 |
| 15 | 1.941 | 1.944 | 12 | 0 0 10 |
| 5 | 1.732 | 1.733 | 7 | 0 6 1 |
| 10 | 1.681 | { 1.684 | 2 | 1 3 8 |
| | | { 1.682 | 3 | 1 5 $\bar{3}$ |
| | | { 1.681 | 4 | 1 5 3 |
| 10 | 1.629 | { 1.630 | 2 | 1 4 7 |
| | | { 1.628 | 3 | 1 4 7 |
| 15 | 1.583 | { 1.587 | 5 | 1 3 9 |
| | | { 1.585 | 9 | 1 3 9 |
| | | { 1.578 | 5 | 2 0 0 |

¹ Ni-filtered Cu-K α radiation, 116.4 mm diameter Gandolfi camera, I_{obs} estimated visually, and all calculated d spacings with $I_{\text{calc}} \geq 10$ are listed.

10 μm . Data were collected at GSECARS and ChemMatCARS (CARS = Consortium for Advanced Radiation Sources) sectors 13 and 15 at the Advanced Photon Source, Argonne, Illinois. The data set used in the refinement was collected using radiation of wavelength 0.6888 \AA monochromated by a water-cooled (111) diamond crystal. Higher harmonics were removed using vertical Pt-coated Si mirrors and apertures to produce a $200 \times 200 \mu\text{m}$ beam. Data were recorded using a Bruker 6000 SMART CCD (charge-coupled device) detector at a fixed 2θ angle of 31° and scanning ϕ in 0.5° steps with 1 s counting per frame. The CCD detector was mounted on a Huber 4-circle diffractometer with the ω axis of the diffractometer in the plane of the synchrotron ring. A full rotation of the ϕ axis yielded 720 frames with $\chi = 0^\circ$. Unit-cell dimensions were refined by least squares using 738 reflections and are given in Table 2. Data were integrated and corrected for Lorentz, polarization, and background effects using Bruker software (SAINTPLUS). Systematic errors, such as beam decay and absorption, were corrected with the program SADABS on the basis of the intensities of equivalent reflections. The crystal structure was solved and refined using *SHELXTL*, Sheldrick (1997).

The high R value (0.090) was the result of the poor crystal quality, but this was the best crystal found. The crystal consisted of several single crystals with one major component contributing most of the intensity. The spots on some CCD frames were distributed in arcs of constant 2θ . The crystal was refined using the twin law (1,0,0/0, $\bar{1}$,0/0,0, $\bar{1}$) which reduced the R from 0.115 to 0.090.

The occupancy of the S atom refined to 0.5 and was fixed. A peak $\sim 1.5 \text{\AA}$ from S was split into two atoms O8 and O9 and refined to positions 0.8 \AA apart. These atoms are two of the four oxygen atoms forming the SO_4 group. No hydrogen positions were located from the structure determination, but OH and H_2O groups were assigned using a bond-valence calculation.

Table 2 gives the details of the data collection and structure refinement, Table 3 – the final fractional coordinates and isotropic displacement parameters, Table 4 – interatomic distances and angles, and Table 5 – the bond valences calculated using *Valist* (Willis and Brown 1999). Table 6, anisotropic displacement parameters, and Table 7, a listing of the calculated and observed structure factors, have been deposited with the Principal Editor of *Mineralogical Magazine* and can be obtained

TABLE 2. Data collection and structure refinement details for redgillite.

| | |
|--|--|
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a | 3.155(3) \AA |
| b | 10.441(8) \AA |
| c | 19.436(16) \AA |
| β | 90.089(13) $^\circ$ |
| V | 640.2(9) \AA^3 |
| Z | 2 |
| Crystal size | $70 \times 20 \times 6 \mu\text{m}$ |
| Temperature | 293(2) K |
| Wavelength | 0.6888 \AA |
| Absorption coefficient | 10.03 mm^{-1} |
| $F(000)$ | 644 |
| θ range for data collection | 1.89 to 30.92° |
| h, k, l ranges | $-2 \rightarrow 2, -15 \rightarrow 15, -28 \rightarrow 28$ |
| Reflections collected | 5120 |
| Independent reflections | 1529 [$R(\text{int}) = 0.0397$] |
| Completeness to $\theta = 30.92^\circ$ | 68.3% |
| Absorption correction | None |
| Refinement method | Full-matrix least-squares on F^2 |
| Data/restraints/parameters | 1529/0/109 |
| Goodness-of-fit on F^2 | 1.105 |
| Final R indices [$I > 2\sigma(I)$] | $R1 = 0.0896, wR2 = 0.2375$ |
| R indices (all data) | $R1 = 0.1047, wR2 = 0.2468$ |
| Largest diffraction peak and hole | 4.2 and $-2.0 \text{ e}\text{\AA}^{-3}$, near Cu atoms |

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TABLE 3. Positional and isotropic displacement parameters $\times 10^4$ for redgillite.

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} |
|-----------------|-----------|----------|----------|------------------------|
| Cu1 | 2782(10) | 6411(2) | 2998(1) | 17(1) |
| Cu2 | 7220(10) | 4638(2) | 2043(1) | 18(1) |
| Cu3 | 7913(10) | 8083(2) | 4117(1) | 22(1) |
| S ¹ | 8147(50) | 7026(7) | 5699(4) | 31(3) |
| O1 | 2880(50) | 5966(10) | 2013(5) | 19(3) |
| O2 | 7250(60) | 5085(10) | 3030(5) | 23(3) |
| O3 | 2950(60) | 6843(9) | 3999(5) | 23(3) |
| O4 | 7160(60) | 4274(10) | 1026(5) | 21(3) |
| O5 | 0450(50) | 3021(10) | 2158(6) | 22(3) |
| O6 | 7990(80) | 8283(13) | 5274(7) | 45(5) |
| O7 ¹ | 7870(180) | 5890(30) | 5276(18) | 54(10) |
| O8 ¹ | 4720(170) | 7010(40) | 6200(20) | 51(9) |
| O9 ¹ | 2370(180) | 7030(30) | 6034(17) | 45(8) |

¹ the occupancies of the S, O7, O8 and O9 sites are 0.5 and O8 and O9 are 0.8 Å apart and cannot be occupied simultaneously.

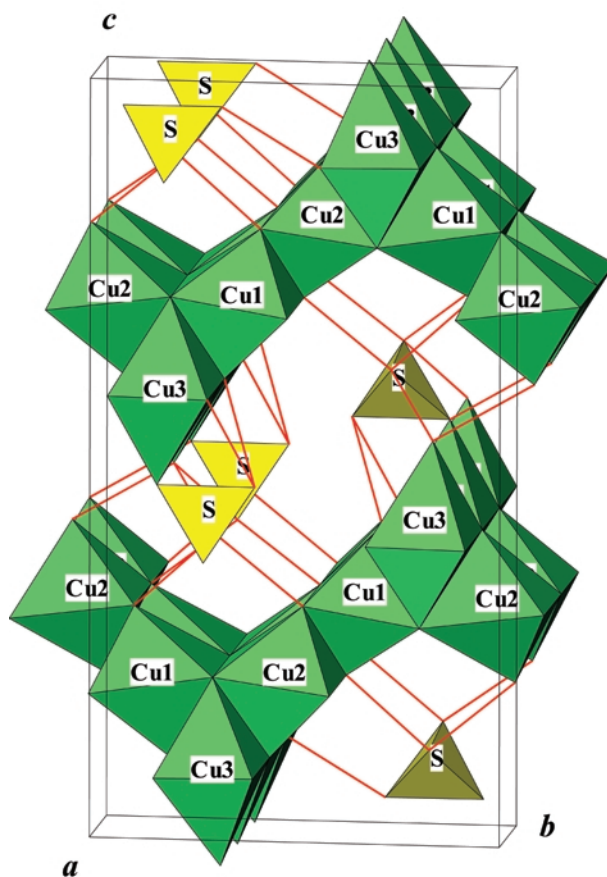


FIG. 2. Redgillite, looking down the *a* axis. CuO₆ octahedra (green) share an oxygen with SO₄ tetrahedra (yellow). Cu layers are linked through SO₄ groups by hydrogen bonds to the next layer (shown as red lines).

TABLE 4. Bond distances (Å) and angles (°) for redgillite.

| Cu1 octahedron | | Cu2 octahedron | | Cu3 octahedron | | SO ₄ tetrahedron | |
|----------------|-----------|----------------|-----------|----------------|-----------|-------------------------------|---------|
| Cu1–O1 | 1.971(10) | Cu2–O1 | 1.948(13) | Cu3–O4 | 2.010(16) | S–O7 | 1.44(3) |
| Cu1–O2 | 1.977(16) | Cu2–O2 | 1.976(10) | Cu3–O4 | 2.045(15) | S–O8 | 1.45(5) |
| Cu1–O5 | 1.988(13) | Cu2–O5 | 1.984(12) | Cu3–O3 | 2.046(16) | S–O9 | 1.48(6) |
| Cu1–O3 | 1.996(11) | Cu2–O4 | 2.012(10) | Cu3–O3 | 2.062(15) | S–O6 | 1.55(2) |
| Cu1–O2 | 2.230(15) | Cu2–O1 | 2.262(16) | Cu3–O6 | 2.257(14) | O7–S–O8 | 109(3) |
| Cu1–O5 | 2.736(15) | Cu2–O5 | 2.733(15) | Cu3–O5 | 2.534(12) | O7–S–O9 | 108(3) |
| | | | | | | O8–S–O9 | 112(2) |
| O1–Cu1–O2 | 81.5(5) | O1–Cu2–O2 | 82.1(6) | O4–Cu3–O4 | 102.1(5) | O7–S–O6 | 112(2) |
| O1–Cu1–O5 | 93.5(5) | O1–Cu2–O5 | 165.7(6) | O4–Cu3–O3 | 165.5(4) | O8–S–O6 | 110(2) |
| O2–Cu1–O5 | 164.2(6) | O2–Cu2–O5 | 95.1(5) | O4–Cu3–O3 | 76.7(6) | O9–S–O6 | 105(2) |
| O1–Cu1–O3 | 177.5(7) | O1–Cu2–O4 | 95.7(5) | O4–Cu3–O3 | 77.1(5) | | |
| O2–Cu1–O3 | 96.3(5) | O2–Cu2–O4 | 177.2(4) | O4–Cu3–O3 | 165.7(4) | SO ₄ hydrogen bond | |
| O5–Cu1–O3 | 88.3(5) | O5–Cu2–O4 | 87.4(5) | O3–Cu3–O3 | 100.4(4) | O6–O8 | 3.08(5) |
| O1–Cu1–O2 | 83.9(5) | O1–Cu2–O1 | 96.8(5) | O4–Cu3–O6 | 94.3(6) | O6–O9 | 2.65(5) |
| O2–Cu1–O2 | 97.0(4) | O2–Cu2–O1 | 83.0(5) | O4–Cu3–O6 | 94.9(6) | O6–O4 | 2.95(2) |
| O5–Cu1–O2 | 97.4(6) | O5–Cu2–O1 | 96.8(6) | O3–Cu3–O6 | 100.2(7) | O7–O3 | 3.10(4) |
| O3–Cu1–O2 | 97.6(5) | O4–Cu2–O1 | 95.6(5) | O3–Cu3–O6 | 99.4(6) | O7–O3 | 3.12(4) |
| O1–Cu1–O5 | 91.3(5) | O1–Cu2–O5 | 83.8(5) | O4–Cu3–O5 | 73.8(4) | O8–O1 | 2.70(4) |
| O2–Cu1–O5 | 83.0(5) | O2–Cu2–O5 | 93.9(5) | O4–Cu3–O5 | 92.5(4) | O8–O2 | 2.72(4) |
| O5–Cu1–O5 | 82.2(4) | O5–Cu2–O5 | 82.3(4) | O3–Cu3–O5 | 91.8(4) | O9–O1 | 2.83(4) |
| O3–Cu1–O5 | 87.2(5) | O4–Cu2–O5 | 87.6(5) | O3–Cu3–O5 | 73.5(4) | O9–O2 | 2.86(4) |
| O2–Cu1–O5 | 175.2(4) | O1–Cu2–O5 | 176.7(4) | O6–Cu3–O5 | 167.1(7) | O8–O6–O9 | 86(2) |
| | | | | | | Cu3–O6–O8 | 123(1) |
| | | | | | | Cu3–O6–O9 | 120(1) |
| | | | | | | Cu3–O6–O4 | 113(1) |
| | | | | | | S–O7–O3 | 103(2) |
| | | | | | | S–O7–O3 | 99(2) |
| | | | | | | S–O8–O1 | 122(2) |
| | | | | | | S–O8–O2 | 123(2) |
| | | | | | | S–O9–O1 | 110(2) |
| | | | | | | S–O9–O2 | 108(2) |

from the authors or from the Mineralogical Society website: www.minersoc.org/pages/e_journals/dep_mat.html.

Description of the structure

The redgillite structure consists of CuO₆ octahedra and SO₄ tetrahedra. The octahedra share edges to form sheets that are zig-zag in cross section when viewed down the *a* axis and are stacked perpendicular to the *c* axis (Fig. 2). Each leg of the zig-zag is four octahedra long and repeats after every six octahedra. SO₄ tetrahedra which reside in the space between the Cu layers, form columns parallel to the *a* axis. The S site is only half occupied, implying that only every second site in the column is filled. One O in SO₄ is shared with Cu and the remaining three, bonded

only to Cu, occupy the space between Cu layers. The oxygen atoms link Cu layers via hydrogen bonds to other oxygen atoms (see red lines in Fig. 2). There are three different Cu sites: Cu1 and Cu2 are Cu(OH)₆ octahedra whereas Cu3 is Cu(OH)₅·H₂O or Cu(OH)₅O (O-SO₃) depending on the identity of the O6 atom (see below).

A bond valence calculation (see Table 5) gives bond valences for oxygen atoms. Rows H_{don} and H_{acc} are included in the table even though these hydrogen atoms were not determined experimentally. The value of H_{don} for O5 is probably >0.80 because it does not form hydrogen bonds. The values in the row H_{acc} have been estimated using bond distances listed in the 'SO₄ hydrogen bond' section of Table 4. Note that O8 and O9 accept hydrogen bonds from 3 OH groups, but distances for O8 are long, so a value of 0.40 rather than 0.60

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TABLE 5. Bond valences (VU) in redgillite

| | O1 | O2 | O3 | O4 | O5 | O6 ¹ | O6 ² | O7 | O8 | O9 | Total |
|---------------------|--------------|--------------|--------------|--------------|--------------|-----------------|-----------------|------|------|------|-------|
| Cu1 | 0.45 | 0.45 0.23 | 0.43 | | 0.43 0.06 | | | | | | 2.05 |
| Cu2 | 0.48 0.21 | 0.45 | | 0.41 | 0.44 0.06 | | | | | | 2.05 |
| Cu3 | | | 0.37 0.36 | 0.41 0.37 | 0.10 | 0.21 | 0.21 | | | | 1.82 |
| S | | | | | | 1.21 | | 1.64 | 1.60 | 1.48 | 5.93 |
| H(don) ³ | 0.80 | 0.80 | 0.80 | 0.80 | 0.80 | | 1.60 | | | | |
| H(acc) ⁴ | | | | | | 0.20 | 0.20 | 0.40 | 0.40 | 0.60 | |
| Total | 1.94 | 1.93 | 1.96 | 1.99 | 1.89 | 1.62 | 2.01 | 2.04 | 2.00 | 2.08 | |

¹ O6 bonded to Cu and S

² O6 bonded only to Cu

³ hydrogen-donating H-bonds

⁴ hydrogen-accepting H-bond

was listed. The valence sums for O1 to O5 range from 1.89 to 1.96, if it is assumed that hydrogen atoms donating hydrogen bonds are attached. These oxygen atoms must therefore be OH groups. There are two environments around O6 because the SO₄ site is only half occupied. When SO₄ is present, O6 is bonded to Cu and to S. It can also accept a hydrogen bond from O4. The total valence sum is 1.62, less than the expected value of 2.00, but O6 is disordered and uncertainty in the distances between Cu3 and S could increase its value. When the SO₄ site is unoccupied, O6 is bonded only to Cu3. The addition of two hydrogen atoms to form H₂O achieves valence balance. The hydrogen atoms of the water molecule have the correct geometry to hydrogen bond to SO₄ groups (see Fig. 3, red lines). This produces a chain of alternating SO₄ groups and H₂O molecules running perpendicular to *a*. The bond valences of the remaining oxygen, forming SO₄ (O7, O8 and O9), calculated assuming that they are accepting hydrogen bonds, (2.01–2.08) are close to the expected value of 2.00.

The three unique CuO₆ octahedra have four short distances of ~2.0 Å and two longer ranging from ~2.2 to 2.7 Å. This distortion results from the Jahn-Teller effect (see Table 4 for details). The S–O distances in the SO₄ anions range from 1.44 to 1.55 Å. The longer distance is associated with the O6 oxygen atom that can be bonded to either Cu and S or Cu and two H atoms.

Discussion

The crystal structures of wroewolfeite (Hawthorne and Groat, 1985), langite (Gentsch and Weber, 1984), posnjakite (Mellini and Merlino, 1979), spangolite (Hawthorne *et al.*, 1993), and schulenbergite (Mumme *et al.*, 1994) are similar to redgillite in that they contain layers of edge-sharing Cu octahedra connected to SO₄ groups. The layers are bridged by hydrogen bonds. The octahedral layer in redgillite is unique, since it is corrugated (zig-zag) and not flat. The octahedral layers in these structures can have the SO₄ groups attached in two ways. All SO₄ groups can be attached to either one or both sides of the octahedral sheet. The sulphate decoration of the layer surfaces in redgillite is two-sided as in schulenbergite (Hawthorne *et al.*, 2000). A Mg₆SO₂(OH)₁₄ structure (Hamada *et al.*, 1996) has a similar, but not identical, layer with a ~3.0 Å cell repeat. It also contains chains of alternating H₂O and SO₄ groups like those in redgillite.

Acknowledgements

This work was performed at GeoSoilEnviroCARS (GSECARS), Sector 13, and ChemMatCARS, Sector 15, Advanced Photon Source at Argonne National Laboratory. GSECARS and ChemMatCARS are supported by the National Science Foundation, Department of Energy, and

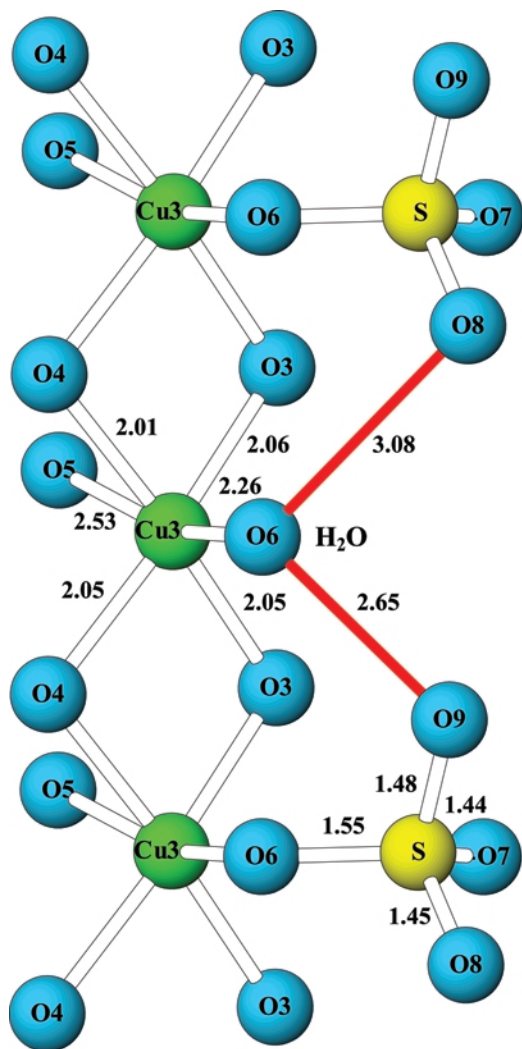


FIG. 3. Redgillite structure showing the alternation of SO_4 groups and H_2O molecules O6. Hydrogen bonds (red lines) between O6 and O8 and O9 form chains of alternating SO_4 and H_2O molecules parallel to a .

W.M. Keck Foundation. Use of the Advanced Photon Source was supported by the US Department of Energy, Basic Energy Sciences, Office of Energy Research, under Contract No. W-31-109-Eng-38. J.J.P. thanks the Materials Research Science and Engineering Center at The University of Chicago for support. We would also like to thank Peter Braithwaite of Derbyshire, UK, for kindly provided the sample of redgillite used in this study and John Betterton for his interest.

The structure drawings were produced using *ATOMS*, by Shape Software.

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[Manuscript received 13 April 2005; revised 4 November 2005]