

Renierite, $\text{Cu}_{10}\text{ZnGe}_2\text{Fe}_4\text{S}_{16}$ – $\text{Cu}_{11}\text{GeAsFe}_4\text{S}_{16}$: a coupled solid solution series

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Abstract

The composition of renierite is found to be $\text{Cu}_{10}(\text{Zn}_{1-x}\text{Cu})\text{Ge}_{2-x}\text{As}_x\text{Fe}_4\text{S}_{16}$ ($0 \leq x \leq 1$), with continuous solid solution between the zincian and arsenian endmembers, $\text{Cu}_{10}\text{ZnGe}_2\text{Fe}_4\text{S}_{16}$ and $\text{Cu}_{11}\text{GeAsFe}_4\text{S}_{16}$, through the coupled substitution $\text{Zn(II)} + \text{Ge(IV)} = \text{Cu(I)} + \text{As(V)}$. This is the first reported example of extensive coupled solid solution in a sulfide mineral. The renierite structure is a tetragonal, pseudoisometric derivative of the sphalerite structure type, with space group $P4_2m$. There are two of the above formula units per unit cell, which has dimensions $a = 10.622(1) \text{ \AA}$ and $c = 10.551(1) \text{ \AA}$ for zincian renierite, and $a = 10.60(1) \text{ \AA}$ and $c = 10.45(1) \text{ \AA}$ for arsenian renierite. Mössbauer spectroscopy indicates magnetically ordered Fe(III) in three distinct sites. The presence of bulk magnetism, together with magnetic susceptibility data, indicate that the magnetic ordering is anisotropic and is slightly uncompensated antiferromagnetic (weakly ferrimagnetic). Electrical measurements show that renierite is a p-type semiconductor.

Arsenian renierite, not previously characterized, is similar to zincian renierite in polished section, with a slightly redder color and lower anisotropy. It is reddish-orange with relief very similar to that of bornite, though it is harder ($VH_{25} = 286$) and does not tarnish in air. It is slightly birefractive, with colors varying from orange-yellow to reddish-orange in nearly crossed polarizers. The strongest powder X-ray diffraction lines are $(d(I/I_0)(hkl))$: $3.042(100)(222)$, $1.861(29)(044)$, $1.869(16)(440)$, $1.594(11)(622)$, and $1.017(10)(10.2.2)$. The calculated density is 4.50 g/cm^3 . Specimens have been found at the Ruby Creek copper deposit, Alaska, where zincian renierite also occurs, and at the Inexco #1 mine, Jamestown, Colorado. At Ruby Creek, arsenian renierite occurs as sparse grains $20\text{--}50 \mu\text{m}$ across together with bornite, chalcopyrite, pyrite, tennantite-tetrahedrite, chalcocite, and germanite. In the ore at Jamestown it occurs as rounded grains up to $75 \mu\text{m}$ across associated with galena, chalcopyrite, sphalerite, bornite, tennantite, fluorite, geocronite, and possibly germanite.

Renierite is of widespread occurrence in Cu-Zn-Pb ores throughout the world and is particularly characteristic of dolomite-hosted Cu-Zn-Pb sulfide deposits. Small grains of what appears to be bornite or "orange bornite" in sulfide ores should be carefully examined to determine if they are in fact renierite.

Introduction

Renierite was first described as a distinct mineral from the Cu-Pb-Zn deposit at Kipushi, Zaire, where it had formerly been called "orange bornite" (Vaes, 1948). It has subsequently been found at Tsumeb, Namibia, and at numerous Cu-Pb-Zn deposits throughout the world. The present study was begun when renierite was found by the author during investigations of samples from the Ruby Creek copper deposit, southern Brooks Range, Alaska. Due to its close resemblance to bornite in the reflecting microscope, renierite is easily overlooked and appears to be a widespread mineral in copper-rich sulfide ore deposits.

The composition of renierite has remained in dispute since the discovery of the mineral. Some of the proposed

chemical formulas are shown in Table 1. An apparent deficiency of sulfur was often reported when a metal-to-sulfur ratio of one was assumed. The role of the small amounts of As and Zn found in the analyses was not known. Powder X-ray diffraction data were found to be very similar to those of chalcopyrite and stannite, and a similar sphalerite-derivative structure was presumed, either isometric or tetragonal (Murdoch, 1953; Lambot, 1950; Lévy and Prouvost, 1957; Viaene and Moreau, 1968).

During the course of this investigation it became apparent that various renierite compositions reflect significant solid solution, particularly towards a high-As, high-Cu, low-Zn and low-Ge endmember. The discovery of grains having compositions close to this new endmember

Table 1. Proposed chemical formulas for renierite

| | |
|--|-------------------------|
| $(\text{Cu, Fe, Ge, Zn, As, Sn})_5$ | Vaes, 1948 |
| $(\text{Cu, Fe})_3(\text{Fe, Ge, Zn, Sn})(\text{S, As})_4$ | Lambot, 1950 |
| $\text{Cu}_6\text{Fe}_3\text{GeS}_{10}$ | Viaene and Moreau, 1968 |
| $(\text{Cu, Ge, Ga, As, Fe, Zn})_{0.95}\text{S}$ | Springer, 1969 |
| $\text{Cu}_3(\text{Fe, Ge, Zn})(\text{S, As})_4$ | Fleischer, 1983 |

(arsenian renierite) from Ruby Creek, and particularly from Jamestown, Colorado, confirmed its existence. The composition of renierite can be expressed as $\text{Cu}_{10}(\text{Zn}_{1-x}\text{Cu}_x)(\text{Ge}_{2-x}\text{As}_x)\text{Fe}_4\text{S}_{16}$, where $0 \leq x \leq 0.5$ for zincian renierite and $0.5 < x \leq 1$ for arsenian renierite.

Table 2. Occurrences of renierite

| Country | State or Province | Locality | Host Rock | Deposit Description | Ge, Ga Sulfide Minerals | Associated Minerals | References |
|----------|--------------------|----------------------------------|--|---|-------------------------|---|---------------------------------------|
| Bulgaria | Pazardzhik | Radka deposit | andesite-dacite volcaniclastics and dikes | Cu-Zn-Pb-As sulfides in large veins, stockworks, and beds | arn, rn, ge, bri, gl | py, en, cp, bn, cv, col, tn, id, dg, cc, st, Au, Ag, bt, ra, be, sy, td, fl | Tzonev, 1982 |
| Bulgaria | Sofiya | Chelopech deposit | andesite-dacite | ? | rn, gl | en, luz, tn, py, fm, col, ist, hmu, cp, bn, cv, dg, Au | Terziyev, 1965; 1966 |
| Congo | | M'Passa, 150 km W of Brazzaville | Late Precambrian calcareous dolomite | Cu-Zn-Pb mineralization in faults and fractures | rn, ge | cp, bn, tn, cc, gn, sp, py | Picot <i>et al.</i> , 1963 |
| Cuba | Pinar del Rio | NW part of province | Jurassic schists | ore in faulted, brecciated zones | rn, ge, gl | cp, sp, py, tn, cc, asp, carb | Tvalchrelidze and Holmgren, 1971 |
| Italy | Sardinia | San Giovanni Pb-Zn mine | Cambrian dolomite, ls; Silurian schist | ore in carbonates at contact with schist | rn | sp, gn; lesser ba, py | Lauzac, 1965 |
| Japan | Akita | Shakanai mine | Miocene dacite-basalt volcaniclastics & dikes | Kuroko-type stratiform | arn | cp, py, sp, gn, bn, dg, cv, el, str, fu | Miyazaki <i>et al.</i> , 1978 |
| Namibia | | Tsumeb mine | Late Precambrian dolomite, breccia, "pseudoaplite" | large, irregular pipe; see text | ge, rn, bri, gl | cp, bn, sp, tn, cc, gn | Söhngge, 1963; Sclar and Geier, 1957 |
| USA | Alaska | Ruby Creek deposit, Bornite | Devonian dolomite, dolomitic breccia | Cu-rich sulfide ore in dolomite breccia; see text | rn, arn, ge | cp, bn, py, tn, cc, dg, car | this study |
| USA | Colorado | Inexco #1 mine, Jamestown | granitic rocks, gneiss, schist, migmatite | pipe-like sulfide body; see text | arn, ge(?) | gn, sp, cp, tn, td, bn, cc, gc, fl | Lowe, 1975; Jenkins, 1979; this study |
| USSR | Arkhangelsk, RSFSR | Vaygach | carbonates (?) | ? | rn, ge, arg | sp, bn, py, cp, gn, ba, fl | Silaev, 1980 |
| USSR | Armenian SSR | Akhtala | ? | ? | rn | tn, gn, bn, sp, cp | Kodzhoian, 1962 |
| USSR | Caucasus region | Urup deposit | volcanics within sedimentary sequence | hydrothermal, epigenetic | rn | py, cp, bn, sp, gn, tn, luz | Kachalovskaya <i>et al.</i> , 1975 |
| USSR | Kazakhstan | ? | carbonates | hydrothermal (?) | rn, ge | sp, bn, tn, cc, gn, py, en, fm, luz, ba | Yakovlev and Smirnov, 1963 |
| USSR | Uzbekistan | ? | carbonates | ? | rn | py, mc, gn, sp, cp, sp | Chebotarev <i>et al.</i> , 1975 |
| Zaire | Shaba | Prince Leopold mine, Kipushi | Late Precambrian dolomite, dolomitic shale and breccia | highly irregular pipe along fault; see text | rn, ge, bri, gl | cp, bn, tn, py, cc, sp, car | Intiomale and Oosterbosch, 1974 |

Mineral abbreviations: Ag-silver; arg-argyrodite; arn-arsenian renierite; asp-arsenopyrite; Au-gold; ba-barite; be-beegerite; bn-bornite; bri-briartite; bt-betekhtinite; car-carrollite; cc-chalcocite; col-colusite; cp-chalcopyrite; cv-covellite; el-electrum; fm-famatinite; fu-furtoite; gc-geocronite; ge-germanite; gl-gallite; gn-galena; hmu-hemusite; id-idaite; ist-isostannite; luz-luzonite; mc-marcasite; py-pyrite; ra-rathite; rn-renierite; sp-sphalerite; st-stannite; str-stromeyerite; sy-sylvanite; td-tetrahedrite; tn-tennantite

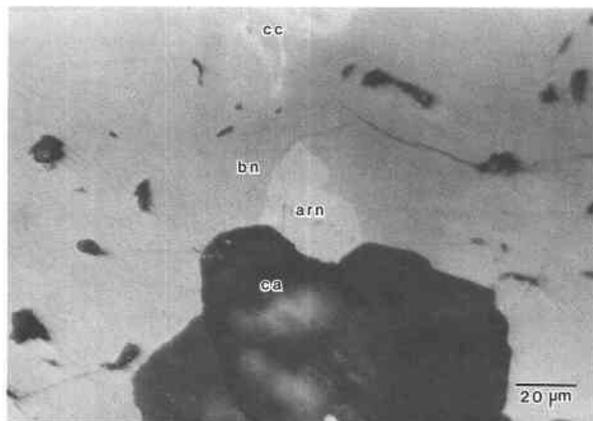


Fig. 1. Arsenian renierite (arn) from Ruby Creek, Alaska. Associated minerals are bornite (bn), chalcocite-digenite intergrowth (cc), and calcite (ca). Plane polarized reflected light.

In this study, the composition, properties, and structure of renierite were investigated using electron microprobe analyses, Mössbauer spectroscopy, powder X-ray diffraction, single-crystal electron diffraction, reflectance spectroscopy, and electrical and magnetic measurements.

Occurrences and associations

The known occurrences of renierite are summarized in Table 2; other occurrences of "orange bornite" may turn out to be renierite as well. The localities from which renierite was obtained for this study are described in more detail below.

Renierite is found most abundantly at Kipushi, Zaire and Tsumeb, Namibia. The Zn-Cu-Pb orebody at Kipushi occurs at the faulted boundary between brecciated dolomitic shale and a marine dolomite sequence. The sulfide ore forms a highly irregular subvertical pipe, with sulfide replacement zones extending along bedding planes and fracture zones in the wall rocks (Intiomale and Oosterbosch, 1974; De Vos et al., 1974). Renierite is locally abundant at this deposit, together with bornite, tennantite, chal-

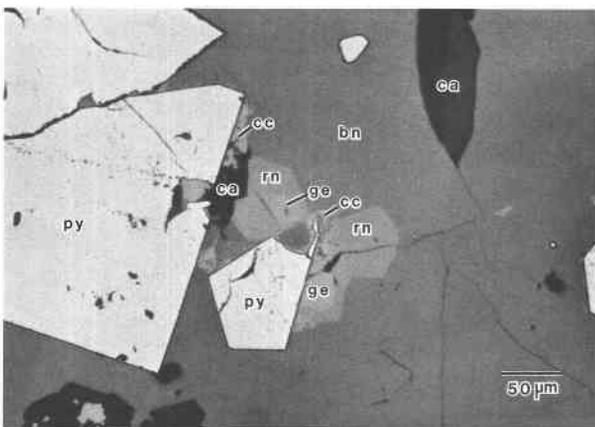


Fig. 2. Zincian renierite (rn) from Ruby Creek, Alaska. Associated minerals are bornite (bn), pyrite (py), germanite (ge), chalcocite (cc), and calcite (ca). Plane polarized reflected light.

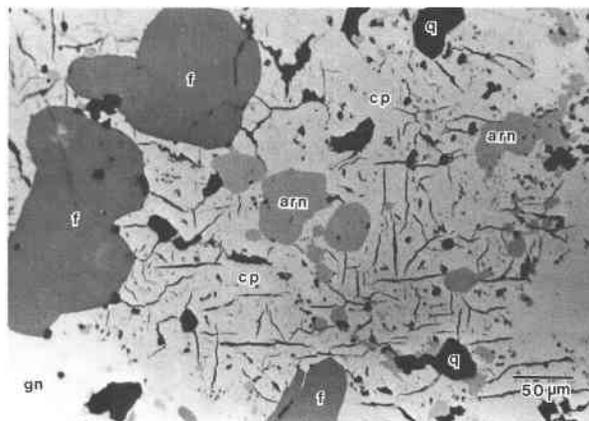


Fig. 3. Rounded grains of arsenian renierite (arn) from the Inexco #1 mine, Jamestown, Colorado. Associated minerals include "crackled" chalcopyrite (cp), fluorite (f), galena (gn), and quartz (q). Plane polarized reflected light.

copyrite, sphalerite, galena, briartite, and gallite. It generally occurs as small (<75 μm) inclusions in the other sulfides or as fine-grained masses up to at least several centimeters across.

The Pb-Zn-Cu deposit at Tsumeb consists of an irregular pipe-like intrusive within a late-Precambrian dolomite sequence. The pipe contains massive sulfide ore together with breccia, kersanite, diabase dikes, and an enigmatic quartz-feldspar rock termed "pseudoaplite" (Söhnge, 1964). A summary and bibliography of this deposit is given by Wilson (1977). Renierite occurs as microscopic intergrowths throughout the hypogene ore. It is highly concentrated in Ge-rich zones found within high-grade hypogene copper ore at various levels in the mine (Sclar and Geier, 1957). The Ge-rich ore zones contain large amounts of germanite (masses weighing up to 28 tons have been found (Söhnge, 1964)), together with smaller amounts of the Ge minerals renierite and briartite, and the Ga mineral gallite. The renierite occurs as fine-grained inclusions within germanite, which it sometimes appears to have replaced, and as fine-grained masses up to several centimeters across associated with tennantite, chalcopyrite, bornite, sphalerite, germanite, gallite, galena, enargite, digenite, and pyrite. Stringers of germanite and renierite are also occasionally found in the dolomitic wallrock (Söhnge, 1964).

The Ruby Creek copper deposit, in the southwestern Brooks Range near Bornite, Alaska, consists of sulfide-rich dolomite breccia zones within a Middle Devonian marine carbonate sequence. The copper mineralization appears to be superimposed upon carbonate rock rich in framboidal, diagenetic pyrite. Ruby Creek is structurally complex, with numerous fault blocks truncating and displacing bodies of sulfide ore. The deposit has been described by Bernstein and Cox (1986), Hitzman (1983), and Runnells (1963, 1969). Both zincian and arsenian renierite occur at Ruby Creek, as small (<50 μm) inclusions in bornite and chalcocite, associated with chalcopyrite, tennantite-tetrahedrite, pyrite (some cobaltiferous), sphalerite, carrollite, and rare tiny grains of germanite (Figs. 1 and 2).

Arsenian renierite from the Inexco #1 mine, Jamestown, Colorado was also investigated in this study. The Inexco #1 deposit consists of stockwork veins and breccia pipes within Precambrian granite, gneiss, and schist, adjacent to a Cretaceous porphyritic granodiorite stock and a Tertiary quartz-monzonite to syenite stock (Lowe, 1975; Jenkins, 1979). The veins and breccia pipes

Table 3. Electron microprobe analyses of renierite

| | 1 | 2 | 3 | 4L* | 5 | 6 | 7 | 8L | 9L | 10 | 11 | 12 |
|----------------|--------|--------|--------|-------|-------|--------|-------|-------|--------|--------|--------|--------|
| Weight Percent | | | | | | | | | | | | |
| Cu | 40.16 | 41.54 | 41.38 | 39.50 | 40.92 | 41.26 | 41.12 | 41.60 | 41.90 | 43.37 | 43.77 | 44.16 |
| Zn | 4.13 | 2.98 | 2.98 | 2.90 | 2.94 | 3.09 | 2.50 | 2.70 | 2.10 | 1.25 | 0.65 | |
| Ge | 9.17 | 8.73 | 8.71 | 8.10 | 8.02 | 7.97 | 7.34 | 7.30 | 7.30 | 5.79 | 5.00 | 4.59 |
| W | | -- | -- | -- | 0.11 | 0.02 | 0.15 | -- | -- | 0.24 | 0.00 | |
| As | | 0.36 | 0.32 | 0.70 | 0.90 | 0.87 | 1.09 | 2.00 | 2.10 | 3.08 | 3.80 | 4.73 |
| Sb | | 0.00 | 0.01 | -- | 0.04 | 0.02 | 0.67 | -- | -- | 0.18 | 0.12 | |
| V | | -- | -- | -- | 0.06 | 0.06 | 0.07 | -- | -- | 0.03 | 0.01 | |
| Fe | 14.12 | 13.37 | 13.44 | 14.10 | 13.99 | 14.29 | 14.17 | 13.00 | 13.10 | 14.17 | 14.55 | 14.11 |
| Ga | | 0.60 | 0.63 | -- | 0.18 | 0.09 | 0.04 | 0.50 | 1.60 | 0.00 | 0.00 | |
| S | 32.42 | 32.50 | 32.62 | 31.40 | 32.19 | 32.40 | 32.42 | 32.60 | 32.70 | 32.20 | 32.59 | 32.41 |
| Total | 100.00 | 100.08 | 100.09 | 96.70 | 99.35 | 100.07 | 99.57 | 99.70 | 100.80 | 100.31 | 100.49 | 100.00 |
| Sum = 33 Atoms | | | | | | | | | | | | |
| Cu | 10.00 | 10.34 | 10.29 | 10.17 | 10.26 | 10.26 | 10.30 | 10.39 | 10.37 | 10.81 | 10.84 | 11.00 |
| Zn | 1.00 | 0.73 | 0.73 | 0.72 | 0.72 | 0.74 | 0.61 | 0.65 | 0.50 | 0.30 | 0.16 | |
| Ge | 2.00 | 1.90 | 1.90 | 1.83 | 1.77 | 1.74 | 1.61 | 1.60 | 1.59 | 1.27 | 1.09 | 1.00 |
| W | | -- | -- | -- | 0.01 | 0.00 | 0.01 | -- | -- | 0.02 | 0.00 | |
| As | | 0.08 | 0.06 | 0.15 | 0.19 | 0.19 | 0.24 | 0.43 | 0.44 | 0.65 | 0.80 | 1.00 |
| Sb | | 0.00 | 0.00 | -- | 0.00 | 0.00 | 0.08 | -- | -- | 0.03 | 0.02 | |
| V | | -- | -- | -- | 0.02 | 0.02 | 0.02 | -- | -- | 0.02 | 0.00 | |
| Fe | 4.00 | 3.78 | 3.81 | 4.12 | 3.98 | 4.05 | 4.04 | 3.70 | 3.70 | 4.02 | 4.11 | 4.00 |
| Ga | | 0.14 | 0.14 | -- | 0.05 | 0.02 | 0.02 | 0.11 | 0.36 | 0.00 | 0.00 | |
| S | 16.00 | 16.03 | 16.07 | 16.01 | 16.00 | 15.99 | 16.09 | 16.13 | 16.04 | 15.89 | 15.99 | 16.00 |

The symbol "--" indicates that the element was not looked for.

* The "L" indicates an analysis taken from the literature.

1. $\text{Cu}_{1.0}\text{ZnGe}_2\text{Fe}_4\text{S}_{16}$; 2,3. Renierite, Kipushi, Zaire; 4L. Renierite, Kipushi (Viaene and Moreau, 1968); 5. Renierite, Kipushi - USNM #115510; 6. Renierite, Tsumeb, Namibia - Stanford #28269; 7. Renierite, Ruby Creek, Alaska - RC34-19; 8L,9L. Renierite, Tsumeb (Springer, 1969); 10. Arsenian renierite, Ruby Creek, Alaska - RCU44-5; 11. Arsenian renierite, Jamestown, Colorado; 12. $\text{Cu}_{11}\text{GeAsFe}_4\text{S}_{16}$

contain abundant sulfides and sulfosalts, with significant concentrations of bismuth, tellurium, and gold. Fluorite is found throughout the deposit in varying quantities. Arsenian renierite is found in high-grade Pb-Cu-Ag-Zn ore within the "Humbolt pillar," a remnant of a pipe-like sulfide body that was left behind by previous mining operations (Lowe, 1975). The arsenian renierite occurs as highly rounded inclusions up to 75 μm across in chalcopyrite, galena and bornite, together with tennantite, chalcocite, fluorite, and quartz (Fig. 3). Lowe (1975) also reported bismuth, geocronite, gold, and possibly tiny amounts of germanite and briartite in the ore.

Chemical analyses corresponding to those of arsenian renierite also have been reported for sulfide grains from the Radka deposit, Bulgaria and the Shakanai deposit, Japan. At the volcanoclastic-hosted Radka Cu-Pb-Zn deposit, Tzonev (1982) described yellow-brown, anisotropic grains up to 0.1 mm across having an orange tint of what he called "renierite II," with the composition $\text{Cu}_{10.8}\text{Ge}_{1.0}\text{As}_{1.0}\text{Fe}_{4.2}\text{S}_{16.0}$. Miyazaki et al. (1978) reported weakly anisotropic grains up to 10 μm across of a renierite-like mineral from the Miocene Kuroko-type Shakanai deposit, having the composition $\text{Cu}_{11.0}\text{Zn}_{0.3}\text{Ge}_{1.0}\text{As}_{0.9}\text{Fe}_{3.7}\text{S}_{16.1}$ (based on a single electron microprobe analysis).

In polished section renierite appears to coexist in equilibrium with bornite, chalcopyrite, tennantite, chalcocite, galena, and sphalerite. It usually appears to replace germanite where the two are found together; this relationship was observed in specimens from Tsumeb, Kipushi, Ruby Creek, and possibly Jamestown. At M'Passa, Congo the apparent reverse relationship was re-

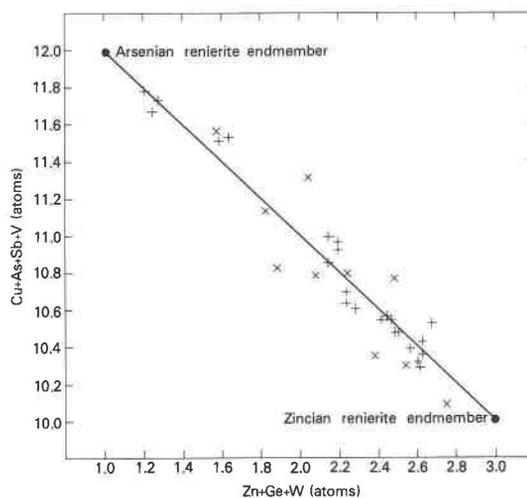


Fig. 4. Major chemical variations in renierite, showing the coupled substitution of Cu + As (plus lesser Sb and V) for Zn + Ge (plus lesser W). The "+" symbols represent electron microprobe analyses performed by the author; the "x" symbols represent analyses taken from the literature (references are given in Table 3). The straight line segment represents ideal, 1:1 substitution of Cu + As + Sb + V for Zn + Ge + W between arsenian (on the left) and zincian renierite (on the right) endmembers. The units are atoms, calculated by setting the sum of all atoms in the analysis at 33.

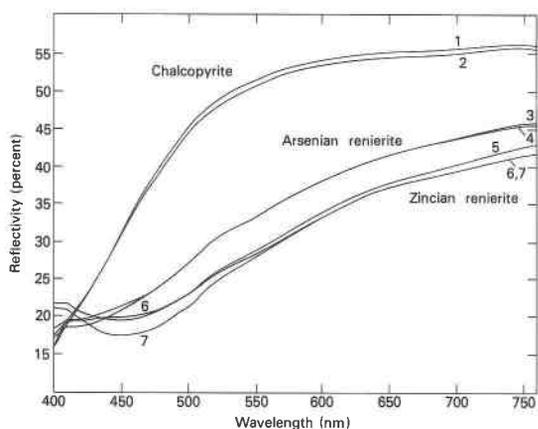


Fig. 5. Reflectivity spectra of renierite and chalcopyrite. Reflectivity values are relative to optical Al, in nonpolarized light. Samples: (1) chalcopyrite, Jamestown, Colorado; (2) chalcopyrite, Elmwood, Tennessee; (3, 4) arsenian renierite, Jamestown, Colorado; (5) arsenian renierite, Ruby Creek, Alaska; (6) zincian renierite, Kipushi, Zaire (USNM #115510); (7) zincian renierite, Ruby Creek, Alaska.

ported, with grains of renierite being rimmed by germanite (Picot et al., 1963).

Chemistry

Chemical analyses were performed on an ARL-SEM electron microprobe at the U.S. Geological Survey in Menlo Park, California. Standards used were synthetic crystals as follows: CuFeS_2 (chalcopyrite, for Cu, Fe, S); $\text{Zn}_{0.6}\text{Fe}_{0.4}\text{S}$ (sphalerite, for Zn); GaAs (for Ga); InAs (for In); Cu_3AsS_4 (enargite, for As); Cu_3SbS_4 (famatinite, for Sb); and Ge, V, and W metals. Wavelength scans were also run and other elements were not detected. The instrument was operated at 15 kV and 15 nA sample current, with a beam size of about 1 μm . Some representative analyses are given in Table 3, together with three analyses from the literature.

When the data are reduced such that the sum of the atoms equals 33 (Table 3), several chemical relationships become apparent (reducing the data such that $S = 16$ atoms gives nearly identical results, but puts too much weight on the quality of the S analysis). These chemical relationships are: (1) $S = 16 \pm 0.1$; (2) $10 < \text{Cu} < 11$ and $\text{Cu} + \text{Zn} = 11 \pm 0.1$; (3) $1 < \text{Ge} < 2$ and $\text{Ge} + \text{As} + \text{Sb} + \text{W} + \text{V} = 2 \pm 0.1$; (4) $0 < \text{Zn} < 1$, $0 < \text{As} < 1$, and $\text{Zn} + \text{As} + \text{Sb} + \text{V} = 1 \pm 0.2$; and (5) $\text{Fe} \approx 4$, and $\text{Fe} + \text{Ga} = 4 \pm 0.1$. The chemical formula can thus be given as $\text{Cu}_{10}(\text{Zn}_{1-x}\text{Cu}_x)(\text{Ge}, \pm \text{W})_{2-x}(\text{As}, \pm \text{Sb}, \pm \text{V})_x(\text{Fe}, \pm \text{Ga})_4\text{S}_{16}$, where $0 \leq x \leq 1$. The chemical variation is mainly between the endmembers $\text{Cu}_{10}\text{ZnGe}_2\text{Fe}_4\text{S}_{16}$ (zincian renierite), and $\text{Cu}_{11}\text{GeAsFe}_4\text{S}_{16}$ (arsenian renierite), with continuous solid solution apparently occurring between them. This chemical variation is graphically shown in Figure 4. Considerable Sb can substitute for As (up to 1 wt.% Sb has been found in renierite from Ruby Creek), and an Sb endmember may exist. Since Sb is a larger atom than the

Table 4. Reflectivity data for zincian and arsenian renierite

| Wavelength nm | Percent Reflectivity* Zincian Renierite | Percent Reflectivity* Arsenian renierite | Wavelength nm | Percent Reflectivity Zincian Renierite | Percent Reflectivity Arsenian renierite |
|------------------|---|--|------------------|--|---|
| 400 | 19.0 | 17.5 | 589 | 33.1 | 37.1 |
| 420 | 20.0 | 19.6 | 600 | 34.3 | 38.1 |
| 440 | 20.3 | 20.7 | 620 | 36.0 | 39.7 |
| 460 | 20.6 | 22.2 | 640 | 37.6 | 41.1 |
| 470 | 20.9 | 23.2 | 650 | 38.0 | 41.5 |
| 480 | 21.7 | 24.6 | 660 | 38.7 | 42.0 |
| 500 | 23.5 | 27.4 | 680 | 39.8 | 42.9 |
| 520 | 26.3 | 30.5 | 700 | 40.8 | 43.8 |
| 540 | 28.2 | 32.5 | 720 | 41.7 | 44.6 |
| 546 | 28.7 | 32.9 | 740 | 42.8 | 45.5 |
| 560 | 30.3 | 34.5 | 760 | 43.4 | 45.8 |
| 580 | 32.3 | 36.3 | | | |

* Reflectivity values are relative to optical-quality sputtered Al on polished Al. Samples: Zincian renierite, Kipushi, Zaire (USNM #115510); Arsenian renierite, Inexco #1 mine, Jamestown, Colorado.

major metals in renierite, the amount of isomorphous substitution may be limited.

Optical properties and reflection spectroscopy

Renierite is opaque with a metallic luster and polishes easily. In polished section it resembles bornite, though its color is more orange. Arsenian renierite is slightly redder than zincian renierite. The relief is nearly identical to that of bornite. A distinct difference from bornite is that renierite does not become noticeably tarnished in air, while the surface of bornite quickly oxidizes and darkens in color.

Zincian renierite is distinctly anisotropic, varying in color from yellow to reddish-orange. The colors are best observed with nearly crossed polarizers. Arsenian renierite shows weaker anisotropy than zincian renierite, with colors varying from orange-yellow to reddish-orange when observed with nearly crossed polarizers. Fine polysynthetic twinning is commonly observed in both varieties of renierite.

Reflectivity measurements were made on a NanoSpec/10 computerized microspectrophotometer manufactured by Nanometrics, Inc. of Sunnyvale, California. The instrument is attached to a reflecting microscope and consists of a quartz-halogen light source, a holographic grating monochromator, and a GaAs photodetector. These are connected to a spectral data processor having 2000 channels of memory that records and displays the data and compares it to a reference standard. The monochromator has a bandwidth of about 4 nm, and a square aperture of about 15 μm on a side was used. The reference standard (representing 100% reflectivity at all wavelengths) was optical-quality evaporated Al on polished Al. Reflectivity values were recorded every 10 nm between 390 and 760 nm, plus measurements at 546 and 589 nm. All measurements were made in air using a 40 \times objective (n.a. 0.65) and were taken during a single session. The results were all highly reproducible during this session.

Measurements were made on renierite samples from Kipushi, Ruby Creek, and Jamestown, and on chalcopyrite from Jamestown and from Elmwood, Tennessee. The spectra obtained from these samples are shown in Figure 5, and some of the numerical data in Table 4. These

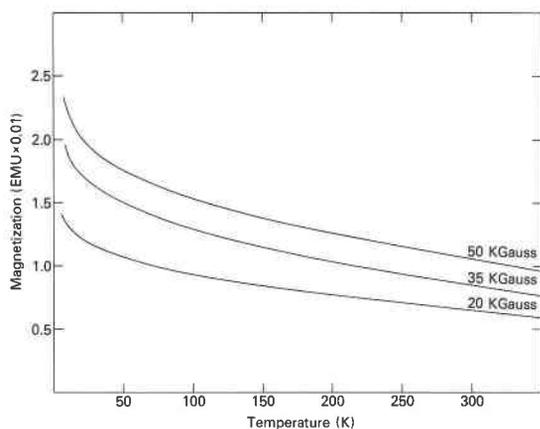


Fig. 6. Magnetic susceptibility data for zincian renierite from Tsumeb (Stanford #28269). Values were measured in a SQUID magnetometer at fluxes of 20, 35, and 50 kgauss on 0.02154 g of sample containing 14.0 wt. percent Fe.

results agree fairly well with previously published spectra of renierite and chalcopyrite (e.g., Lévy and Prouvost, 1957; Karapemyan, 1963; Francotte et al., 1965; Yarenskaya, 1971), though the present spectra show more detail and are over a broader spectral range. Arsenian renierite has slightly higher reflectivities at the longer wavelengths than does zincian renierite, accounting for its slightly redder color. Arsenian renierite from Ruby Creek contains a large amount of the zincian renierite endmember; its spectrum is intermediate between those of endmember zincian renierite and endmember arsenian renierite (Fig. 5, curve 5). The reflectivity peak at about 400 nm for both arsenian renierite and zincian renierite from Ruby Creek (curves 5 and 7) may reflect the presence of Sb, which is not present in significant amounts in the other samples (see Table 3). The general similarity in shape of the renierite spectra and those of chalcopyrite are due largely to the similarity in crystal structure and composition.

Physical and chemical properties

Zincian renierite has a Mohs hardness of about 3.5. Vickers microhardness measurements, using a load of 25 g, range from 340 to 363 (mean 351) for zincian renierite; and 274 to 302 (mean 286) for arsenian renierite. In polished section renierite appears slightly harder than chalcopyrite. No distinct cleavage or parting was observed, though a poor cleavage may exist parallel to {110}, as this was consistently a preferred orientation when renierite grains were observed in the TEM.

In polished section, renierite is not attacked by cold dilute HNO_3 or HCl . Vaes (1948) reported that renierite is etched by a mixture of $\text{HNO}_3 + \text{H}_2\text{O}$ (1:2) + $\text{HCl} + \text{HClO}_3$, and is dissolved by concentrated HNO_3 .

Zincian and arsenian renierite display bulk magnetism. In addition, samples of massive renierite from Kipushi, when brought near a magnetic compass, are found to have

strong magnetic polarity. This suggests high magnetic coersivity; the direction of remanent magnetism may indicate the ambient polarity at the time of renierite crystallization. Qualitatively, the degree of magnetism is less than that of magnetite or monoclinic pyrrhotite and similar to that of ilmenite.

The density of zincian renierite from Tsumeb (Stanford #28269) was determined on a Berman density balance using toluene at 24°C. This sample contains less than 2% of other minerals, mostly quartz, with minute amounts of chalcocite and tennantite (determined in the reflecting microscope, SEM, and electron microprobe). A grain weighing about 0.24 g was used for the measurement. The measured density was determined to be 4.38(1) g/cm³. The calculated density of this sample is 4.40(3) g/cm³ (using the measured unit cell volume of 1190 Å³, and based on an average of five chemical analyses; the error is due mainly to the uncertainty of these analyses). Insufficient material was available to measure the density of arsenian renierite. The calculated density for endmember zincian renierite is 4.414 g/cm³ assuming a cell volume of 1190 Å³, and for endmember arsenian renierite is 4.50 g/cm³ assuming a cell volume of 1174 Å³.

Quantitative magnetic and electrical measurements

As most sulfide minerals have a high degree of covalent bonding and are semiconductors (with some delocalization of the valence electrons into the conduction band), it is useful to study the magnetic and electrical properties that result. The magnetic susceptibility of renierite was measured on an S.H.E. Corporation model 868 variable temperature superconducting SQUID magnetometer at Lawrence Berkeley Laboratory, Berkeley, California. The sample consisted of 0.02154 g of zincian renierite from Tsumeb (Stanford #28269) packed in a Kel-F container. Measurements were made at 5 to 350 K at constant fields of 20, 35, and 50 kgauss. Susceptibility measurements of the container were subtracted out. Results are shown in Figure 6. Magnetic saturation was apparently not reached even at 50 kgauss, indicating great coersivity; this was also seen in the large hysteresis loops obtained at room temperature. A coersivity value of 10.0 kOe at ± 20 kgauss was obtained at 20°C for 0.0584 g of powdered sample packed in a Teflon container. The high coersivity indicates strong magnetic anisotropy, which could result from highly directional magnetic ordering, or the presence of small magnetic domains having relatively rigid boundaries. Plotting the data on graphs of magnetization versus inverse temperature, and of inverse magnetization versus temperature, indicates a weakly ferrimagnetic material. The change in slope of the curves in Figure 6 below about 30 K may indicate a change in magnetic ordering below this temperature. The magnetic properties will be discussed further in the section on Mössbauer spectroscopy.

Electrical resistivity measurements were made on lightly polished surfaces using a four-point probe having a spacing of 0.020" (0.0508 cm) between electrodes. Renierite samples used were: Stanford #28269, Tsumeb; USNM

Table 5. Powder X-ray diffraction data for zincian renierite

| hkl | d _{calc.} | d _{obs.} (G*) | d _{obs.} (D**) | I (G) | I/I ₀ (D) |
|--------|--------------------|---------------------------|----------------------------|----------|-------------------------|
| 110 | 7.51 | 7.52 | 7.52 | w | 1.0 |
| 200 | 5.31 | 5.31 | 5.29 | vw | 0.8 |
| 002 | 5.28 | 5.28 | | vw | |
| 112 | 4.32 | 4.32 | 4.33 | w | 2.3 |
| 022 | 3.743 | | 3.743 | | 0.6 |
| 310 | 3.359 | 3.356 | | vw | |
| 222 | 3.059 | 3.059 | 3.059 | vs | 100.0 |
| 312 | 2.833 | 2.832 | 2.832 | w | 2.3 |
| 400 | 2.656 | 2.657 | 2.656 | m | 7.5 |
| 004 | 2.638 | 2.638 | 2.636 | m | 3.8 |
| 330 | 2.504 | | 2.504 | | 0.2 |
| 114 | 2.489 | | 2.491 | | 0.3 |
| 332 | 2.262 | 2.259 | 2.259 | w | 1.2 |
| 440 | 1.878 | 1.878 | 1.878 | s | 16.0 |
| 044 | 1.871 | 1.871 | 1.871 | vs | 41.0 |
| 334 | 1.816 | 1.813 | 1.815 | w | 0.5 |
| 622 | 1.600 | 1.600 | 1.600 | m | 18.2 |
| 226 | 1.593 | 1.593 | 1.592 | m | 11.8 |
| 444 | 1.530 | 1.530 | 1.530 | w | 1.3 |
| 800 | 1.328 | 1.328 | 1.327 | m | 3.5 |
| 008 | 1.319 | 1.319 | 1.319 | w | 2.2 |
| 662 | 1.218 | 1.218 | 1.218 | m | 3.4 |
| 266 | 1.215 | 1.215 | 1.215 | m | 6.3 |
| 840 | 1.188 | | 1.188 | | 0.5 |
| 084 | 1.186 | | 1.186 | | 0.5 |
| 408 | 1.181 | | 1.181 | | 0.5 |
| 844 | 1.083 | 1.083 | 1.083 | s | 7.3 |
| 448 | 1.079 | 1.079 | 1.079 | vw | 4.5 |
| 10.2.2 | 1.022 | 1.022 | 1.022 | w | 3.3 |
| 2.2.10 | 1.016 | 1.016 | 1.016 | vw | 2.1 |
| 880 | 0.939 | | 0.939 | | 0.9 |
| 088 | 0.936 | | 0.936 | | 2.3 |
| 10.6.2 | 0.898 | | 0.898 | | 2.5 |
| 2.10.6 | 0.896 | | 0.896 | | 1.9 |
| 6.2.10 | 0.893 | | 0.893 | | 2.2 |

a_{calc.} = 10.622 Å; c_{calc.} = 10.551 Å
 Abbreviations: vw - very weak; w - weak; m - moderate; s - strong; vs - very strong
 *G = Guinier camera, CuKα₁ radiation, λ = 1.5405981 Å, calibrated with Si.
 **D = diffractometer, CuKα₁ radiation, λ = 1.5405981 Å, calibrated with Si.

Table 6. Powder X-ray diffraction data for arsenian renierite

| hkl | d _{calc.} | d _{obs.} (DS*) | d _{obs.} (DI**) | I (DS) | I/I ₀ (DI) |
|--------|--------------------|----------------------------|-----------------------------|-----------|--------------------------|
| 200 | 5.30 | | 5.33 | | 4 |
| 112 | 4.29 | 4.29 | 4.30 | vw*** | 4 |
| 310 | 3.35 | | 3.35 | | 5 |
| 222 | 3.045 | 3.046 | 3.042 | m | 100 |
| 400 | 2.650 | 2.683 | 2.653 | vw | 6 |
| 004 | 2.613 | 2.617 | 2.608 | vw | 3 |
| 033 | 2.481 | 2.484 | | vwv | |
| 440 | 1.874 | | 1.869 | | 16 |
| 044 | 1.860 | | 1.861 | vw | 29 |
| 622 | 1.596 | 1.595 | 1.594 | vw | 11 |
| 226 | 1.579 | | 1.588 | | 9 |
| 844 | 1.079 | 1.078 | | vw | |
| 10.2.2 | 1.019 | 1.017 | | w | |
| 880 | 0.937 | 0.939 | | w | |

a_{calc.} = 10.60 Å; c_{calc.} = 10.45 Å
 Abbreviations: vw - very, very weak; w - very weak; w - weak; m - moderate.
 *Debye - Scherrer camera, CuKα₁ radiation, λ = 1.54178 Å, using galena as internal calibration.
 **Diffractometer chart, CuKα₁ radiation, λ = 1.54178 Å, galena as internal calibration. Chart recorded in 1975 by B.V. Lowe.
 ***The sample contained considerable galena and sphalerite; none of the arsenian renierite lines are strong.

#115510, Kipushi; and USNM #R8814, Kipushi. Grains from Ruby Creek and Jamestown were too small for this measurement. A sliced single crystal of chalcopyrite from French Creek, Pennsylvania (Stanford #6696) was also measured for comparison. Renierite samples USNM #115510 and USNM #8814 contained inclusions of other sulfides; all the renierite samples were polycrystalline with crystals about 5 to 50 μm across. All the samples were at least 2.5 mm thick, effectively infinite for this measurement. A current of 5 mA was applied through the outer electrodes and the voltage drop measured across the inner electrodes. The resistivity, ρ, was calculated: $\rho = 2\pi a(\Delta V/I)$, where a is the electrode spacing, ΔV the measured voltage drop, and I the applied current. About 20 different readings were made for each specimen.

The measured resistivity of the purest and most homogeneous sample (Stanford #28269, Tsumeb) was consistently between 1.1 and 1.4 ohm cm, averaging 1.3 ohm cm. The other two, less homogeneous samples ranged from 1.3 to 5.7 ohm cm. These values are typical of fairly

high conductivity semiconductors. The values measured for the chalcopyrite were 5×10^{-2} to 8×10^{-2} ohm cm, averaging 6×10^{-2} ohm cm, in good agreement with previous measurements (Pridmore and Shuey, 1976).

A thermal probe was used to determine p or n primary carrier type. One electrode was placed on the sample and the other was heated above the ambient temperature and placed at another point on the sample, and the direction of current flow (Seebeck voltage) was measured on a voltmeter. The predominant carrier (electrons (n-type) or electron "holes" (p-type)) is presumed to have the greatest net mobility away from the heated area (Vaughan and Craig, 1978, p. 78-79). The results were compared to those for known p- and n-type silicon. This measurement was carried out on the same samples that had their resistivities measured (above).

The thermal probe measurements of all the renierite samples showed a strong p-type response, indicating a slight excess of electron acceptors or a deficiency of electron donors. The chalcopyrite gave an n-type response, typical of nearly all reported chalcopyrite (Shuey, 1975, p. 243-244).

X-ray and electron diffraction

Powder X-ray diffraction data were obtained for zincian renierite from Tsumeb (Stanford #28269) and for arsenian renierite from Jamestown, Colorado. Data from the Tsumeb renierite were first determined using a Guinier camera with monochromatic CuKα₁ radiation at 35 kV and 15 mA, calibrated with Si metal. The same sample was then run on a Rigaku computerized diffractometer operated at 35 kV and 15 mA. A step-scan was taken from 3° to 130° 2θ, with a step size of 0.02° at 20 seconds per step. Calibration of the values was made with Si metal.

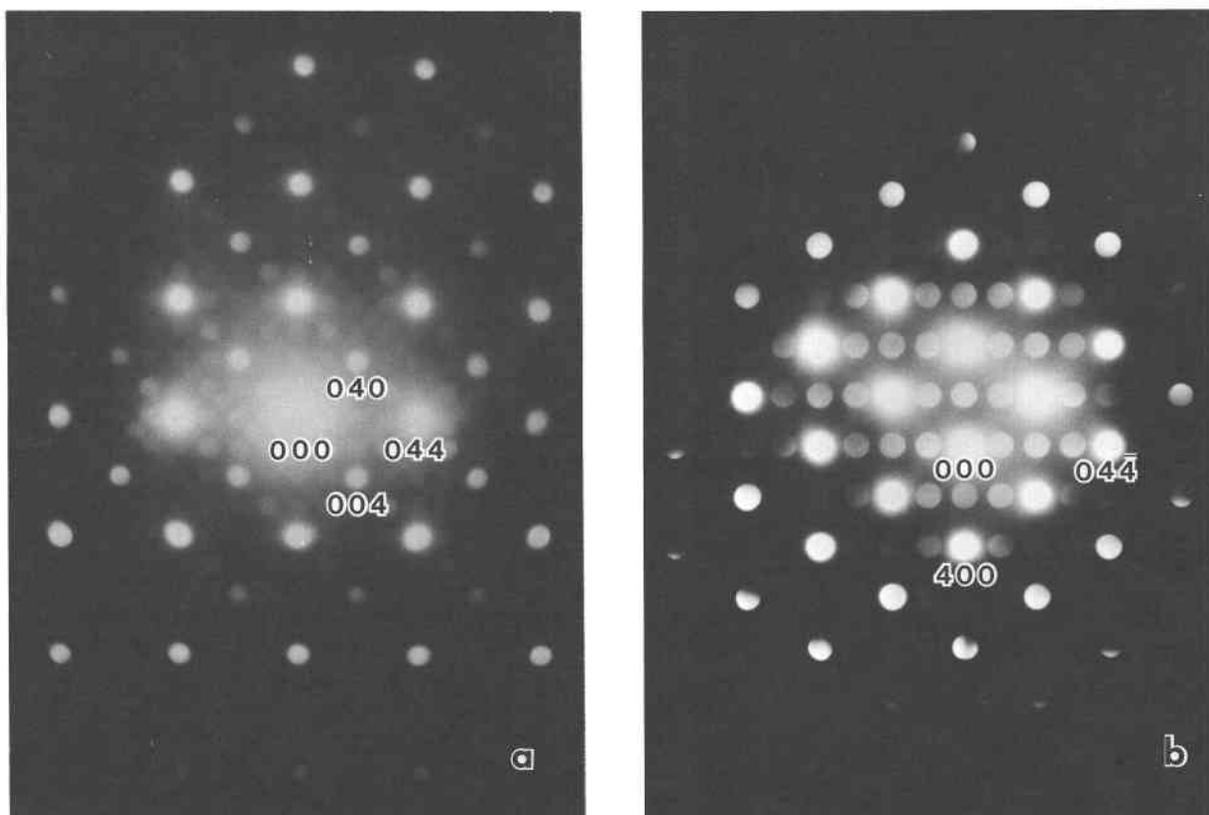


Fig. 7. Electron diffraction patterns for zincian renierite from Tsumeb (Stanford #28269) (see text for experimental methods). (a) Beam direction down a [100] axis. (b) Beam direction down a [110] axis.

The results of the two diffraction methods agree extremely well (Table 5). These data indicate that renierite is tetragonal, with a unit cell size of $a = 10.622(1)$, $c = 10.551(1)$ Å, $V = 1190$ Å³. The data are very similar to sphalerite and chalcopyrite and indicate a derivative structure, with a cell edge roughly twice that of sphalerite. Although carefully looked for, no reflections were observed where $h + k + l$ is odd, or with d -spacings greater than 7.5 Å. This suggests a body-centered or pseudo-body-centered unit cell that does not contain ordering beyond the determined unit-cell dimensions.

The sparseness and very small grain size of the arsenian renierite, combined with its intimate association with minerals having a similar structure (chalcopyrite and sphalerite), made X-ray diffraction data difficult to obtain. A very small amount of material was separated from a powdered ore sample with a magnet and was mounted in a Debye-Scherrer camera. Diffraction films indicated considerable contamination with galena and sphalerite, though the strongest arsenian renierite lines were observable. The results are shown in Table 6. B. V. Lowe (written comm., 1984) was able to magnetically separate enough material from a large amount of powdered ore to observe the strongest X-ray lines on a diffractometer. Several such diffractometer tracings, made in 1975 and run from 10–62° 2θ in Cu/Ni radiation, were provided to the author

for this study; these results are also shown in Table 6. The results suggest no large structural difference from zincian renierite, with a slightly smaller unit cell ($a = 10.60(1)$, $c = 10.45(1)$ Å), though the data are too poor to reach further conclusions. The substituting elements in arsenian and zincian renierite (Cu,Zn; Ge,As) are all nearly adjacent to each other in the periodic table, and little difference in unit cell size or structure would be expected from their coupled substitution.

Since suitably large single crystals could not be found for single-crystal X-ray diffraction studies, single-crystal electron diffraction was used in an attempt to further elucidate the crystal structure of renierite. A powdered sample of renierite from Tsumeb (Stanford #28269) was ultrasonically dispersed in a beaker of acetone and drops of the suspension were evaporated on Formvar-coated copper grids. The samples were examined in a Philips EM 400 TEM operated at 120 kV, using a double-tilt sample holder, at the Center for Materials Research, Stanford University. Energy dispersive X-ray analysis was used to confirm the identity of the grains being examined. To obtain bright images, convergent beam electron diffraction was used.

Electron diffraction images were readily obtained on the grains (examples are shown in Fig. 7). Grains of about 50 to 150 nm across were found to produce the best dif-

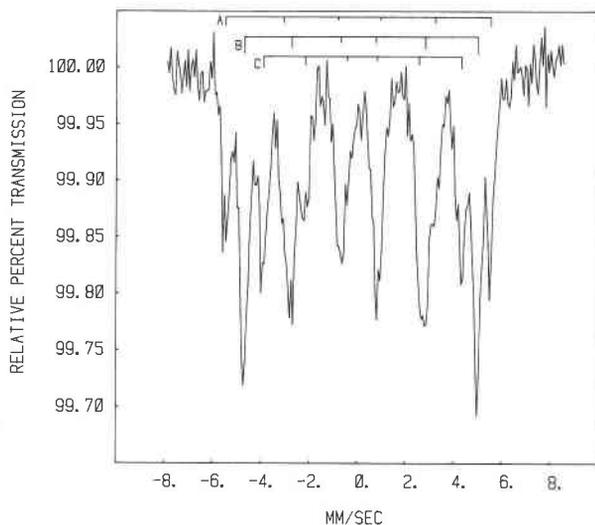


Fig. 8. Mössbauer spectrum of zincian renierite from Tsumeb (Stanford #28269). Positions and relative intensities of the three magnetic hyperfine spectra A, B, and C are also shown. Numerical data are given in Table 7. See text for experimental details.

fraction patterns. Diffraction images were obtained for beam directions down the axes [100], [110], [111], and [211]. Zero layer plane reflections were observed for all these directions, and first order Laue zone (folz) reflections were seen for the [111] and [211] directions. There is a pronounced sublattice pattern such that reflections having $h, k, l = 2n$ with $h + k, h + l = 4n$ are the only ones that are intense. These occur in patterns indicating a diamond-like subcell (Edington, 1976) with $a \approx 5.3 \text{ \AA}$, similar to sphalerite. The fainter reflections indicate a unit cell size of $a \approx 10.6 \text{ \AA}$. While there appear to be no systematically absent reflections, many reflections are very weak to absent, and most observed reflections are of the type $h + k + l = 2n$. Tilting experiments and calculations showed that the observed reflections are not due to double diffraction.

The symmetry of the patterns conforms to Laue group $4/mmm$ (tetragonal), point groups $\bar{4}2m$ and 422 . Only point group $\bar{4}2m$ is consistent with the tetrahedral coordination present in the observed subcell, and only space group $P\bar{4}2m$ is consistent with the lack of systematic absences. This differs from the body-centered cell suggested by the powder X-ray diffraction data; this could be because the additional reflections are too weak to be detected by the X-ray methods used, or it is possible that the sample becomes altered due to heating by the electron beam in the TEM. The latter possibility is considered unlikely in this case, since it is doubtful (though not impossible) that heating would produce a more ordered phase, suggested by a primitive lattice. The lattice appears to be pseudo-body-centered primitive.

Mössbauer spectroscopy

Mössbauer spectroscopy was done at the Center for Materials Research at Stanford University, using a ^{57}Co

Table 7. Mössbauer data for renierite

| Hyperfine spectrum | I.S. mm/sec | ϵ mm/sec | H_L kOe | fwhm mm/sec | I/I_0 |
|--------------------|-------------|-------------------|-----------|-------------|---------|
| A | 0.059 | -0.103 | 337 | 0.181 | 50 |
| B | 0.091 | +0.029 | 294 | 0.210 | 100 |
| C | 0.195 | +0.199 | 251 | 0.241 | 71 |

I.S. = isomer shift.

ϵ = difference between separation of two outermost right peaks and separation of two outermost left peaks, which, in approximation, is equal to the electric quadrupole shift: $e^2qQ/2(3\cos^2\theta-1)$. The angle θ is that between the magnetic field H_L and the electric field gradient eq , and Q is the nuclear electric quadrupole moment.

H_L = local magnetic field at the iron nucleus.

fwhm = full width at half maximum for peaks.

I/I_0 = relative areas under sets of peaks.

in Pd source at 25°C. The theory and practice of Mössbauer spectroscopy have been described well by several authors, including Wertheim (1964), Greenwood (1970), and Dyar (1984). The gamma-ray source was moved relative to the sample with a constant acceleration drive at $\pm 8 \text{ mm/sec}$. The count rate was measured with a gas-filled proportional counter and the data fed into a 512 channel multichannel analyzer, using a dwell time of 500 μsec per channel. The sample consisted of 400 mg of zincian renierite powder from Stanford sample #28269 (previously described), mixed with petroleum jelly and sandwiched between sheets of waxed paper, over a circular area of 5 cm^2 . This resulted in about 11 mg/cm^2 of Fe acting as the absorber. The experiment was run for 6 days, and about 4.8×10^6 counts per channel were obtained. The velocity distribution was calibrated with a laser interferometer built into the system. The velocity distribution was a symmetrical sawtooth waveform, with two cycles per the 512 channel sweep. This permitted the spectrum to be "folded" in half to improve the counting statistics and eliminate the sinusoidal variation in counts due to the varying absorber-source distance. The spectrum was computer fitted to 18 Lorentzian curves with a high degree of congruence (rms chi = 1.06; misfit = 0.0220). The standard deviations range from 0.003 to 0.008 mm/sec for the peak positions and from 0.010 to 0.014 mm/sec for the linewidths.

The Mössbauer spectrum obtained is shown in Figure 8, and the numerical data derived from it in Table 7. The spectrum is interpreted as consisting of three magnetic hyperfine sextets (as was found for pyrrhotite: Hafner and Kalvius, 1966; Levinson and Treves, 1968), only slightly, if at all, modified by electric quadrupole splitting. The measured electric quadrupole splitting parameters (ϵ) are not significantly different from zero. The absorption intensity of spectrum B is roughly twice that of A and 1.5 times that of C. The very small isomer shifts and electric quadrupole splitting parameters are characteristic of Fe(III) (see, for example, Greenwood, 1970). The three observed sextets show the presence of magnetically ordered Fe(III) in three structurally distinct sites, with one site being more numerous than the other two.

Discussion and conclusions

Chemistry

Renierite is the first sulfide mineral reported to show extensive coupled solid solution. The formula can be given as $\text{Cu}_{10}(\text{Zn}_{1-x}\text{Cu}_x)(\text{Ge}_{2-x}\text{As}_x)\text{Fe}_4\text{S}_{16}$, with $0 \leq x \leq 0.5$ for zincian renierite and $0.5 < x \leq 1$ for arsenian renierite. The As and Zn are essential constituents, and are not incidental minor elements. The substitutions that produce this solid-solution series are simply explained if the valence states of the metals are taken into account.

The Mössbauer results show that all the iron is present as Fe(III). Since metallic sulfides are highly covalently bonded (based on Pauling's electronegativity rules), the quantum-mechanically permissible directional bonding configurations for the atoms must be considered. In the regular or nearly regular tetrahedral sites present, Cu(I) would be highly favored over Cu(II), and Ge(IV) would be required rather than Ge(II) (Cotton and Wilkinson, 1962; Vaughan and Craig, 1978). These are also the valences that give charge balance with divalent sulfur and zinc, and charge balance also requires As(V). The coupled substitution between zincian and arsenian renierite can thus be expressed as $\text{Ge(IV)} + \text{Zn(II)} = \text{As(V)} + \text{Cu(I)}$. Similar substitutions are certainly present in other sulfides and sulfosalts.

The compositional variation is limited at the arsenian renierite endmember by the complete substitution of Cu(I) for Zn(II), so that further compensating substitution allowing for the substitution of As(V) for Ge(IV) is not possible. Similarly, the compositional variation is limited at the zincian renierite endmember by the complete substitution of Ge(IV) for As(V), so that no further substitution of Zn(II) for Cu(I) can occur.

Considerable Sb and lesser V can substitute for As, and an Sb endmember may exist (samples from Ruby Creek contain up to one weight percent Sb). Other simple substitutions noted are small amounts of Ga(III) for Fe(III), particularly at Kipushi, and W(IV) for Ge(IV), mainly at Tsumeb. A formula showing the known variations is thus $\text{Cu}_{10}(\text{Zn}_{1-x}\text{Cu}_x)(\text{Ge}, \pm \text{W})_{2-x}(\text{As}, \pm \text{Sb}, \pm \text{V})_x(\text{Fe}, \pm \text{Ga})_4\text{S}_{16}$, with $0 \leq x \leq 1$.

Markham and Lawrence (1965) stated that the Cu-Fe-Sn sulfide mawsonite is the tin analog of renierite. The present data show that this is not the case, since mawsonite has the composition $\text{Cu}_6\text{SnFe}_2\text{S}_8$, with no Zn or As reported (Springer, 1968; Petruk, 1973; Kovalenker et al., 1981). None of the reported tin sulfide minerals is an analog of renierite, although a tin analog may yet be found. Tin was not detected in any of the renierite samples analyzed in this study, although Terziyev (1965) reported a mineral resembling renierite from Bulgaria that semi-quantitative analysis showed to contain about one weight percent tin.

Crystal structure and physical properties

X-ray and electron diffraction data show that renierite has a structure that is a close derivative of the sphalerite

structure type. In the unit cell, metals could fill all the metal sites of a doubled sphalerite cell, with two left over. The chemical data above imply tetrahedral coordination for the metals, so that the remaining two atoms are probably in tetrahedral interstitial sites (bornite is an example of a sulfide having interstitial tetrahedral Cu(I) atoms in a sphalerite-derivative structure).

The Mössbauer data show the presence of Fe in three distinct magnetically ordered sites. The three magnetic spectra differ significantly from each other only in intensity, which is roughly proportional to the occupancy of each site, and in their local magnetic field strength (H_L). The three values of H_L are 251, 294, and 337 kOe, with 43 kOe separating the values. In chalcopyrite, where Fe(III) is antiferromagnetically ordered such that each Fe(III) atom is coupled to four next-nearest-neighbor Fe(III) atoms having opposite magnetic spin from itself (Donnay et al., 1958), H_L was found to be about 350 kOe (one magnetic hyperfine Mössbauer spectrum is produced). It is possible that renierite, with less Fe than chalcopyrite, has Fe(III) in sites having four, three, and two next-nearest-neighbor Fe(III) atoms with opposite magnetic spin, giving rise to H_L values of 337 (like chalcopyrite), 294, and 251 kOe. The intensities indicate that the Fe atoms proposed to have three next-nearest-neighbor Fe atoms are roughly twice as abundant as those with four and 1.5 times as abundant as those with two. This hypothesis will require a definitive crystal-structure analysis of renierite to be tested, but suggests the potential usefulness of the Mössbauer technique. The bulk magnetism of renierite may result from the net magnetic moments of the three types of iron atoms not entirely cancelling each other, resulting in slightly uncompensated antiferromagnetism (weak ferromagnetism).

The electrical data show renierite to be a p-type semiconductor. P-type conductivity, primarily by electron "holes," indicates an excess of electron acceptors (excess S), or a deficiency of electron donors (lack of metals; or excess Cu(I) for Zn(II), Ge(IV) for As(V), etc.). One simple explanation is that there is a slight deficiency of the interstitial metals in renierite due to the energy required to put atoms in the interstitial sites. In chalcopyrite, with no interstitial atoms essential to the structure, there may be a lower energy barrier to having a trace of interstitial metal atoms; nearly all chalcopyrite is found to be n-type (having a relative excess of electron donors, such as metal atoms).

Geological significance

Renierite is of widespread occurrence in Cu-Pb-Zn sulfide deposits. It is especially characteristic of dolomite-hosted Cu-Pb-Zn deposits, particularly those that have prominent breccia zones and that contain high concentrations of As. Such deposits include Kipushi, Tsumeb, and Ruby Creek. Many of these deposits contain early fine-grained pyrite, sometimes cobaltiferous, that predates the Cu-Pb-Zn mineralization. Organic matter is also often present. Renierite usually occurs in the most copper-rich parts of the ore. The mineral also appears characteristic

of Cu- and As-rich igneous-associated polymetallic deposits, such as the Chelopech and Radka deposits, Bulgaria; the Inexco #1 mine, Jamestown, Colorado; and the Shakanai mine, Japan. The widespread occurrence of renierite and other Ge-bearing sulfide minerals in epigenetic sulfide ore deposits, including those within silicate host rocks, indicates the predominantly chalcophile nature of Ge in hydrothermal processes.

Coupled solid solution such as found in renierite is probably widespread in sulfides, particularly in sphalerite-derivative minerals. The author has observed considerable substitution of Cu(I) + Ga(III) for 2Zn(II) in sphalerite from Tsumeb and elsewhere. The presence of Ag(I) and other monovalent elements in sphalerite may also be compensated by Ga(III), In(III) or possibly Fe(III). Such substitutions complicate the use of an Fe(II)/Zn(II) sphalerite geothermometer, but they present the possibility of numerous other geothermometers and geobarometers using sulfide minerals.

Renierite is easily overlooked due to its close resemblance to bornite. Small grains of what appears to be bornite or "orange bornite" in polished section should be carefully examined to see if they are actually renierite. The discovery of additional localities for this mineral would shed new light on the geochemistry of germanium and would contribute towards the characterization of ore deposits.

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