ZONED MICHENERITE-TESTIBIOPALLADITE FROM KAMBALDA, WESTERN AUSTRALIA

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ABSTRACT

Euhedral grains of michenerite-testibiopalladite occur as inclusions in altaite from a telluride-bearing quartz-carbonate vein that cuts nickel-iron sulfide ore at Lunnos Shoot, Kambalda. Grains vary in size from 50 to 200µm and consist of concentric compositional zones that show a progressive but step-like decrease in antimony and increase in bismuth from a core of testibiopalladite to a margin of michenerite. This is the first reported occurrence of testibiopalladite outside China. Electron microprobe analyses of three compositional zones show the variation from (Pd0.97Pt0.03Ni0.01)20.99-(Bi0.35Sb0.65Ag0.01)20.99Te1.04 to (Pd0.97Pt0.03Ni0.01)21.00(Bi0.35Sb0.65Ag0.01)20.99Te1.06 and to (Pd0.96Pt0.04Ni0.01)20.99-(Bi0.74Sb0.18Ag0.01)20.95Te1.08. Line scans demonstrate an almost complete range of compositions between previous data for michenerite and testibiopalladite. Hardness determinations give VHN 371 for testibiopalladite and 333 for michenerite. Other minerals in the vein are hessite, volynskite, rucklidgeite, melonite, galena, chalcopyrite and gold.

INTRODUCTION

Michenerite (PdBiTe) is a rare palladium mineral that occurs in association with Ni–Fe–Cu sulfide mineralization at Sudbury (Cabri et al. 1973, Cabri & Laflamme 1976), Monchegorsk and Oktyabrskoe, USSR (Genkin et al. 1963, 1972), Hitura, Finland (Häkki et al. 1976), Merensky Reef, South Africa (Vermaak & Hendriks 1976) and from localities in China (Huang et al. 1974). It is also present in the Witwatersrand gold ores (Feather 1976) and occurs with hydrothermal copper ores in Wyoming (McCullum et al. 1976).

The mineral was first described by Michener (1940) as PdBiAs, a 6.65Å, but was later named and redefined as PdBi by Hawley & Berry (1958). Studies by Genkin et al. (1963) showed that michenerite grains from Monchegorsk have...
compositions \( \text{Pd}_{0.44} \text{Pt}_{0.18} \text{Bi}_{0.81} \text{Te}_{1.18} \) and \( \text{Pd}_{0.72} \text{Pt}_{0.27} \text{Bi}_{0.08} \text{Te}_{1.08} \), with a “best” formula \( \text{Pd}_{0.72} \text{Pt}_{0.27} \text{BiTe} \). Genkin et al. (1972) also described michenerite from the Oktyabrskoe deposit having a formula \( \text{Pd}_{1.15} \text{(Bi}_{0.66} \text{Te}_{0.15})_{0.02} \). Cabri et al. (1973) analyzed a number of specimens from the Sudbury district and, as a result, redefined michenerite as PdBiTe.

Substitutions in michenerite can cause departures in composition from the defined formula; these are summarized as \((\text{Pd},\text{Pt},\text{Ni})(\text{Bi},\text{Sb},\text{Te}))\), or can be expressed as \((\text{Pd},\text{Pt},\text{Ni})(\text{Bi},\text{Sb},\text{Te}))\), as suggested by Genkin et al. (1972). Substitutions of Ag for Pd and Pb for Bi have also been reported but are of less certain status. The analyses of Sudbury material on which Cabri et al. (1973) based their redefinition of the mineral are all close to the ideal formula, but do show some substitution of Sb for Bi to give a range of calculated formulae from PdBiTe to Pd(\text{Bi}_{0.86} \text{Sb}_{0.14})\text{Te}_{1.01}.

In a subsequent study, Cabri & Laflamme (1976) delineated two compositional groups of michenerite on the basis of Pt content. The low-Pt group showed substitution of Ni for Pd and Sb for Bi up to \((\text{Pd}_{0.85} \text{Ni}_{0.15})(\text{Bi}_{0.86} \text{Sb}_{0.14})\text{Te})\). Grains of antimonian michenerite showed a substitution of Te for Bi to give calculated formulae with tellurium contents of up to \text{58.2}%. This substitution of Te for Bi, and to a lesser extent Bi for Te, had been predicted in experimental studies by Cabri et al. (1973) and Hoffman & MacLean (1976). Hoffman & MacLean consider the stability field of michenerite above 450°C to consist of a narrow solid solution in which Bi and Te may substitute to give compositions between \text{Te}_{2} \text{Bi}_{1} \text{Sb}_{0.66} \text{Te}_{0.34} \text{Bi}_{0.86} \text{Te}_{1.04} \text{Bi}_{1.11} \text{Te}_{0.04} \text{Bi}_{0.86} \text{Te}_{1.04}. A michenerite from China (Huang et al. 1974) has the formula PdBiTe to Pd(\text{Bi}_{0.86} \text{Sb}_{0.14})\text{Te}_{1.01}.

The platinian michenerites from Sudbury vary in composition between 2.1% to 13.9% Pt by weight, with an extreme composition of Pd_{0.86} \text{Pt}_{0.14} \text{Bi}_{0.05} \text{Te}_{0.08}. They are thus even more platinum-rich than those described by Genkin et al. (1963) from Monchegorsk (8.4 to 9.3 wt. % Pt). Hardness values for platinian michenerites do not differ from normal michenerites, though reflectance values are lower at the shorter wavelengths (Cabri & Laflamme 1976).

A silver content of 1.8 wt. % was reported in michenerite from Oktyabrskoe; silver was described as replacing palladium (Genkin et al. 1972). Cabri et al. (1973), however, point out the possibility of interference between PdL\(\beta\) and AgL\(\alpha\), not discussed by Genkin et al. Minor lead (1.9 wt. %) reported in michenerite from Oktyabrskoe (Kovalenker 1977) is assumed to substitute for bismuth. The analysis of michenerite from Hitura, Finland (Häkli et al. 1976) shows it to be close to ideal, with minor substitution of Ni for Pd and Sb for Bi. An antimony-rich michenerite, Pd_{1.05} \text{(Bi}_{0.86} \text{Sb}_{0.14})\text{Te}_{1.01}, was reported from the Witwatersrand (Feather 1976). It is of particular relevance to this study, as its composition is intermediate between michenerite and testibiopalladite.

Testibiopalladite (PdSbTe) is the antimony analogue of michenerite. The mineral was first described from two Cu–Ni sulfide deposits in China (P.M.M.R.G. 1974; summary in Fleischer et al. 1976). In southwestern China a mineralized serpentinite, emplaced into metamorphosed Permian rocks, contains testibiopalladite inclusions in an assemblage comprising gersdorffite, cobaltite, pyrrhotite, chalcopyrite and pentlandite. The other locality is in northeastern China where the mineral occurs as a relatively common constituent of a sulfide-bearing clinopyroxenite that intrudes Permian sandy shales and volcanic rocks. Electron microprobe analyses indicate the range of compositions \((\text{Pd}_{0.80-0.90} \text{Sb}_{0.00-0.20}) \text{Te}_{0.00-0.30})\) (Sbo.os-os Bio.os Tel.60-70).

Physical properties of previously described michenerite and testibiopalladite are compared in Table 1.

**DESCRIPTION OF THE KAMBALDA OCCURRENCE**

The Kambalda nickel deposits were discovered in 1966, and since then have been Australia’s principal nickel producers; they were described most recently by Ross & Hopkins (1975). Platinum-group elements occur in the ores (Keays...
TABLE 2. ELECTRON PROBE ANALYSES OF MICHENERITE-TESTIBIOPALLADITE

<table>
<thead>
<tr>
<th>TESTIBIOPALLADITE</th>
<th>CENTRE 2</th>
<th>MICHENERITE</th>
<th>RIM 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt.% At.%</td>
<td>Wt.% At.%</td>
<td>Wt.% At.%</td>
</tr>
<tr>
<td>Pt</td>
<td>0.5</td>
<td>0.007</td>
<td>0.1</td>
</tr>
<tr>
<td>Ni</td>
<td>0.1</td>
<td>0.007</td>
<td>0.1</td>
</tr>
<tr>
<td>Bi</td>
<td>18.1</td>
<td>18.61</td>
<td>36.6</td>
</tr>
<tr>
<td>Sb</td>
<td>19.8</td>
<td>20.99</td>
<td>5.3</td>
</tr>
<tr>
<td>Ag</td>
<td>0.2</td>
<td>0.008</td>
<td>0.2</td>
</tr>
<tr>
<td>Te</td>
<td>34.4</td>
<td>34.79</td>
<td>32.4</td>
</tr>
</tbody>
</table>

|                  | Wt.% At.% | Wt.% At.% | Wt.% At.% |
| Pt               | 32.6     | 32.46      | 32.4    |
| Ni               | 32.3     | 32.46      | 32.4    |
| Bi               | 11.17    | 16.61      | 16.6    |
| Ag               | 0.02     | 0.008      | 0.008   |
| Te               | 34.79    | 34.79      | 34.79   |

* Totals

& Davison (1976) but no systematic study has been carried out to determine their mode of occurrence, apart from microprobe studies associated with routine, generally unpublished documentation of the sulfide mineralogy of the first two nickel orebodies discovered, Lunnon and Durkin Shoots. This work established the presence of sperrylite, palladian melonite and Pd-Bi tellurides of uncertain composition.

Gold and telluride-bearing quartz and quartz-carbonate hydrothermal veins, commonly associated with porphyritic sodic rhyolite and dacite intrusive bodies, are a minor feature of the Kambalda area. Where these veins cut the nickel sulfide mineralization, unusual mineral suites containing lead, bismuth, silver and palladium tellurides have been recorded. In the occurrence described here from Lunnon Shoot an ‘opaque’ modal analysis determined by point count gave 84.5% altaite, 6.1% rucklidgeite, 4.7% galena, 3.5% volynskite, 1.0% hessite, 0.2% chalcopyrite, with trace amounts of gold, michenerite, hawleyite (greenockite) and melonite.

Michenerite occurs as small 50-200µm subhedral to euhedral inclusions in altaite. Because of their greater hardness, these inclusions can generally be recognized by very slight relief differences developed during polishing. Grains are of distorted diamond shape to “kite” shape (Figs. 1, 2) or equant. In reflected light the mineral is pale pinkish purple, virtually indistinguishable from the associated volynskite. The absence of the cream or white tints referred to by Cabri et al. (1973) and Huang et al. (1974) is puzzling, but may be due to the fact that all our observations have been made on inclusions of michenerite in altaite. Although many grains are zoned from a core of testibiopalladite to a margin of michenerite, no color differences can be detected between these compositional zones, either in air or in oil immersion (Fig. 1).

Hardness measurements were made by indenting compositionally-different zones with 10 and 20g loads using a Vickers indenting objective; the resulting indentations are shown in Figure 1. The brittle nature of the mineral and the small grain size rendered heavier loads impracticable due both to fracturing of the grain and interference from neighboring grains. Determinations were calibrated using chalcopyrite.
(VHN 195) and stainless steel (VHN 580). Both these standards gave VHN values that increased with increasing load. However, the results were nearly constant within the range 20–200g, with anomalously low but reproducible values for loads of 5 and 10g. Correction factors based on these standards were applied to the hardness determinations to give a value of VHN 371 for testibiopalladite (anal. 1, Table 2) and of 333 for michenerite (anal. 3, Table 2).

The value for michenerite is close to those found previously using 25g loads: 311–321 (Cabri et al. 1973), and 302 and 315 for platinian michenerites (Cabri & Laflamme 1976). They exceed, however, the value of 189 found for a platinian michenerite at a 10g load (Cabri & Laflamme 1976); this is consistent with our experience with the standards, as described above. Testibiopalladite determinations were performed at loads of 5 and 10g by P.M.M.R.G. (1974) and show the same tendency of low values, increasing with increasing load (Table 1). The greater hardness of testibiopalladite relative to michenerite, suggested by the comparable determinations, at a 10g load, of 267 (P.M.M. R.G. 1974) and 189 (Cabri & Laflamme 1976), is confirmed in our study.

Evidence of compositional zoning in michenerite (Fig. 2) was first found in our samples by examining uncoated polished surfaces in a JSM–2 scanning electron microscope equipped with a wide-angle back-scattered electron detector (Robinson & Robinson 1978). Zones are concentric and show a progressive but somewhat steplike decrease in antimony and increase in bismuth from core to margin. Some reversals in zoning, whereby narrow, antimony-rich layers develop in the outer zone of michenerite, can be seen as dark (i.e., low average atomic number) concentric bands in the back-scattered electron image (Fig. 2).

Grains that are completely enclosed in altaite are concentrically zoned. However, those that have a core of testibiopalladite at the contact of quartz and altaite have grown asymmetrically, giving a michenerite mantle on the three sides of the grain that are in contact with the altaite, and a continuous variation from michenerite...
through testibiopalladite to michenerite along the quartz interface. This suggests nucleation of the mineral after quartz crystallization. Whether growth was entirely from a hydrothermal fluid as seems likely from the zoning reversals or whether exsolution from altaite contributed to the outer bismuth-rich zones cannot be determined from existing data.

Scans across a zoned crystal (Fig. 3) were made using a Materials Analysis Company electron-probe microanalyzer operated at 19.3 kV. Spot analyses from each of the three main compositional zones are given in Table 2. The microprobe analyses were made using crystal spectrometers LiF (BiLα, PtLα, NiKα), RAP (PbMα) and PET (PdLα, SbLα, TeLα, AgLβ); the standards were synthetic Bi₂Te₃(Bi,Te), synthetic PbTe(Pb), elemental Pt, Ni, Pb, Sb, Te and Ag, and corrections were made by the MAGIC IV program of Colby (1971).

Michenerite and testibiopalladite compositions have been calculated to formule in a variety of ways. Cabri et al. (1973) and Cabri & Lafîmme (1976) calculate (Pd+Pt+Ni) = 1; Genkin et al. (1972) and P.M.M.R.G. (1974) calculate (Bi+Sb*Te) = 2. In this paper, a compromise calculation based on a total of 3 atoms is adopted.

The core (analysis 1) has the composition of a bismuthian testibiopalladite (Pd₀.₉₆Pt₀.₀₂Ni₀.₀₁)₂₀.ₐ₈(Sb₀.₇₄Bi₁.₈₉Ag₀.₀₁)₂₀.ₐ₈Te₁.₀₈ in which there is slight substitution of Pt and Ni for Pd and some substitution of Te for Bi (or Sb). The analysis is similar to those reported from southwestern China (P.M.M.R.G. 1974) of (Pd₀.₉₆Ni₀.₀₄)₂₀.ₐ₈(Sb₀.₄₄Bi₀.₃₅)₂₀.ₐ₈Te₁.₀₅ and Pd₀.₈₄(Sb₀.₆₇Bi₀.₃₁)₂₀.ₐ₈Te₁.₀₄. Silver determinations were made using AgLβ to avoid the interference PdLβ-AgLα pointed out by Cabri et al. (1973) as a possible explanation for the 1.8 wt.% Ag reported in michenerite by Genkin et al. (1972). Although count rates are low, values between 0 and 0.3 wt.% Ag were consistently determined, with an average value of 0.2 wt.% Ag. The silver has been arbitrarily assigned as substituting for (Sb, Bi). Lead was sought but fell below detection limits.

Analysis 2 is from the intermediate zone which has a composition (Pd₀.₉₇Pt₀.₀₂Ni₀.₀₁)₂₁.₀₆-(Bi₀.₆₆Sb₀.₃₄Ag₀.₀₁)₂₀.₀₆Te₁.₀₆. It is similar in composition to the michenerite reported by Feather (1976) from Witwatersrand, Pd₁₀.₀₁(Bi₀.₆₆Sb₀.₃₄)-Te₁.₀₁. Analysis 3 is from the marginal Bi-rich zone, with a composition similar to many reported michenerites.

Figure 4 shows the compositional fields of michenerites from Sudbury and testibiopalladites from China plotted in the triangular diagram Pd₃Te–Bi₂Te–Sb₂Te. The composition of zones

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**Fig. 4.** Compositional limits, in atomic percent, of zoned michenerite-testibiopalladite from Kambalda, relative to michenerite from Sudbury (Cabri et al. 1973, Cabri & Lafîmme 1976) and testibiopalladite from China (P.M.M.R.G. 1974). Pd=ₓ(Pd+Pt+Ni).
in the Kambalda michenerite-testibiopalladite have been deduced from the line scan and are controlled by spot analyses. Despite the apparent continuity of compositional variation in the X-ray scans, the sharp boundaries between the main compositional zones in the back-scattered electron image (Fig. 2) indicates that there is a step-like compositional variation between the core and margin and that not all possible compositions between michenerite and testibiopalladite were encountered in the study.

Conclusions

The first occurrence of testibiopalladite outside China is reported from Kambalda, Western Australia, where it occurs as cores to zoned inclusions of michenerite-testibiopalladite in altaite. A step-like, irregular increase in bismuth towards the margin of the zoned grains may reflect growth from hydrothermal solutions of changing composition or progressive exsolution from altaite. Experimental studies within the system Pd-Bi-Sb-Te are needed to clarify stability relationships between testibiopalladite and michenerite.

Acknowledgements

The manuscript has been improved by discussions and critical comment by Dr. E. H. Nickel. Synthetic telluride standards were prepared by A. B. Fletcher, and diagrams were drawn by C. R. Steel.

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Received January 1978; revised manuscript accepted February 1978.