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Andrieslombaardite, a new Rh mineral from the Onverwacht platinum pipe, Republic of South Africa

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Abstract

A hundred years after the discovery of the Merensky Reef in 1924, it is appropriate to present the new mineral andrieslombaardite in honour of Andries Frederik Lombaard who was instrumental in its discovery. Andrieslombaardite, RhSbS, was first described as an unknown mineral from placer deposits associated with the Tulameen Alaskan-Uralian type complex, British Colombia, Canada (Raicevic and Cabri, 1976) but has since been reported from several other deposits including the Driekop, Mooihoek, and Onverwacht Pt pipes in the Bushveld Complex, South Africa.

The mineral and the name were approved by the Commission on New Minerals Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) based on data in the holotype sample from Onverwacht and a co-type sample from the Yubdo stream, Birbir River, Ethiopia. Andrieslombaardite in the Onverwacht sample is a single 8 x 20 μm grain attached to laurite in a matrix of altered silicate and Fe-hydroxide minerals. In contrast, there are many grains of pale brownish gray andrieslombaardite in the Yubdo samples up to 25 x 55 μm in size, included in Pt-Fe alloys, some associated with erlichmanite, and others attached to bornite and chalcopyrite.

The reflectance values (*R%*) measured in air and in oil at the COM wavelengths are 48.3 and 33.0 (470 *nm*), 49.3 and 34.0 (546 *nm*), 51.0 and 35.9 (589 *nm*), and 51.8 and 36.7 (650 *nm*). The colour values *x, y, Y, λd,* and *Pe* in air are 0.317, 0.322, 50.3, 580, and 3.2, and in oil are 0.319, 0.324, 35.6, 579, and 4.5.

The composition of andrieslombaardite is ideally RhSbS, but it contains variable amounts of Fe, Pt, Pd, and Ir that may substitute for Rh. The mineral is cubic with unit-cell dimensions of

a = 6.0278(4) Å, V = 219.01(6) Å^3 and Z = 4. It is was synthesized at 400 and 550 °C using stoichiometric elemental amounts. It is a member of the cobaltite group.

The mineralization of the intrusive dunite pipes was probably introduced at high temperatures, under magmatic conditions. The primary assemblages were to a certain degree overprinted and redistributed by low-temperature hydrothermal fluids. The Alaskan-Uralian-type complexes crystallized from mantle-derived melts. The Pt-Fe alloys in these intrusions and in subsequent eluvial and alluvial deposits contain inclusions of many PGM, including minerals such as andrieslombaardite that were formed at some post-magmatic stage because of PGE remobilization during hydrothermal or metamorphic episodes.

Introduction

A mineral with the composition RhSbS was first reported as a potential new mineral occurring as inclusions in Pt-Fe alloys from placers and was later found in several other deposits. It was first reported as a very rare mineral included in a Pt-Fe nugget from the south bank of the Tulameen River, British Columbia, approximately 49°27.5'N; 120°35.5'W (Raicevic and Cabri, 1976). The mineral was later also described by Cabri et al. (1981) as inclusions in placer Pt-Fe alloy grains from the Yubdo stream, Birbir River, Ethiopia (8.8360°N; 35.6693°E), from the Mooihoek Pt pipe, South Africa (24°36'24.90"S, 30°07'47.54"E by Rudashevsky et al. (1992), and from the Driekop Pt pipe, South Africa (24°32'43.04"S, 30°6'6.94"E) by Melcher and Lodziak (2007). More recently, grains of RhSbS composition were described by Tolstykh et al. (2011) and Northern Urals by Kuzmin et al. (2020) from the dunite of the Svetloborsky intrusion in the Urals Platinum Belt and from the clinopyroxenite-dunite Zheltaya Sopka massif.

Most of the physical and chemical properties of the RhSbS mineral from Yubdo were reported by Cabri et al. (1981) including detailed measurements of the optical properties. Because the grains were too small to extract for X-ray diffraction analysis the data was not sufficient to officially propose as a new mineral species with a name. The grain characterized in this proposal is from the Onverwacht platinum pipe, Limpopo Province, Republic of South Africa (24°39'9.04"S; 30°9'59.57"E). The grain was first described by Oberthür *et al.* (2021) and is smaller than the grains from Yubdo but techniques now available were successfully applied to determine the crystallography. The sample had been collected on the surface at the Onverwacht mine during an excursion of the Mineralogical Institute of the RWTH Aachen to South Africa in

1969, sample RW15169. The aim of the study was to characterise a mineral known first reported in 1976 but that was not possible to characterise using analytical techniques until recently.

Approval of andrieslombaardite as a new mineral species

The mineral and its name andrieslombaardite were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (2022-076). The name andrieslombaardite was selected to avoid confusion with "lombaardite" (IMA: discredited and no longer listed) or lombardoite (IMA 2016-058). As a note, re-examination of the original "lombaardite" (Nel et al., 1949) by Neumann and Nilssen (1962) showed that it was a mixture of fibrous "epidote" and dark-colored tourmaline (schorl) (mindat.org). The name is for Andries Frederik Lombaard (1877-1954) who played a major role in the discovery of platinum in the Bushveld Complex and especially the Merensky Reef. His death certificate (film #007751152, National Archives of South Africa) shows that he was born and died in Burgersfort not far from the platinum pipes and where the eastern limb of the Merensky Reef was first discovered (Fig. 1).

The first account of Lombaard's contribution to the discovery of platinum on his farm Maandagshoek in the Lydenburg district (renamed Mashishing in 2006) of the eastern Bushveld complex is in an unpublished report by Merensky (1924). Wagner (1925) published the first account of Lombaard's contribution to the Pt discoveries. These discoveries led to mining three Pt pipes (Mooihoek, Driekop and Onverwacht) as well as the "Lombaard" reef, now known as the Merensky Reef. A detailed chronological account of published articles, a book, and unpublished records is given in the Supplementary Data File. Some inaccuracies in Lehmann

(1955) is an entertaining 1955 biography of Hans Merensky (1871-1952) in the chapters on platinum are corrected in the Supplementary Data File.

The holotype specimen from Onverwacht (South Africa: sample RW15169) that was analyzed by EDS and microdiffraction Laue is archived at the Canadian Museum of Nature, Catalogue number CMNMC 90353. The specimens from Yubdo (Ethiopia) on which EPMA and optical properties were measured that may be considered to be co-type samples are archived at the British Museum, Catalogue numbers BM1928,246 and BM1928,247.

Geological setting

The geological setting of the unique platiniferous dunite pipes of the Bushveld Complex was reviewed by Scoon and Mitchell (2004) and recently by Oberthür et al. (2021). The pipes are discordant orebodies which perpendicularly cut through the layered cumulate wall rocks and display complex internal chemical and mineralogical zonation first described by Wagner (1929). Four mineralized pipes occur in the central sector of the eastern limb of the Bushveld Complex (Fig. 1) and three were mined between 1925 and 1930. Wagner's (1929) diagrammatic geological section across the Onverwacht pipe, as modified by Oberthür et al. (2021), is reproduced in Figure 2. Specific characteristics of the mineralization are the virtual absence of sulphides and Pt being the predominant platinum-group element (PGE). According to the hypothesis of Oberthür et al. (2021), the PGE mineralization is not related to the well-established mechanism of sulphide collection. Instead, it was introduced in the form of nanoparticles and small droplets of PGM, which coagulated to form larger grains during evolution of the mineralizing system. Concomitant supercritical magmatic to hydrothermal fluids were continuously active and caused a certain redistribution of the initial PGE inventory and possibly added further quantities of PGE from lower parts of the mineralizing system.

The Yubdo zoned mafic/ultramafic Alaskan-Uralian-type intrusion occurs south of Kurmuk in the Yubdo Daleti Tulu-Dimtu area in Ethiopia (Belete, 2000). According to Molly (1959) the Yubdo dunite massifs in western Ethiopia were similar to those in the Urals except for not having nests or schlieren of chromite; rather, the chromite occurs as scattered grains and olivine is invariably serpentinized. Molly describes the capping of the dunites as “birbirites”, derived from a deep alteration of the dunite consisting almost exclusively of secondary silica and iron oxides. Platinum occurs in uneconomic quantities, generally <0.05 g/ton, in the dunite (Molly, 1959). The resistant minerals including Pt-Fe alloys were released in the course of intense physical and chemical weathering and then concentrated in eluvial and alluvial deposits (Cabri et al., 2022).

Occurrence and associated minerals

There was no comprehensive mineralogical account of the Onverwacht orebody and its mineralization until Oberthür et al. (2021) described the ore mineralogy and the platinum-group mineral (PGM) assemblages of the Onverwacht mineralization. The holotype crystal of andrieslombaardite is attached to laurite in a matrix of heavily altered fayalite which has been largely replaced by unidentified secondary Fe-hydroxides (Figure 3).

The mineralogy of the Pt-Fe alloy grains from Yubdo, Ethiopia, is described by Cabri et al. (1981). They analyzed and described a large number of PGM. Among the many PGM included in the Pt-Fe alloys are several inclusions of andrieslombaardite associated with erlichmanite and other andrieslombaardite grains are attached to bornite and chalcopyrite.

Two grains of RhSbS from the Mooihoek Pt pipe were reported to occur as inclusions in possibly tetraferroplatinum by Rudashevsky et al. (1992). Melcher and Lodziak (2007) in their study of a concentrate from the Driekop Pt pipe show a colour image of one RhSbS grain within a polymineralic PGM assemblage rimmed by ferroan platinum (Pt,Fe). Isoferroplatinum (Pt_3Fe) occurs in the center adjacent to zoned hollingworthite (RhAsS), surrounded by geversite ($PtSb_2$) and insizwaite ($PtBi_2$). Other PGM include unnamed (Pt, Pd)(Bi, Sb), possible tatyanaite ($Pt_9Cu_3Sn_4$), and an osmium lamella.

Appearance, Optical and Physical properties

The andrieslombaardite grain from Onverwacht is subhedral and about 8 x 20 μm in size. It appears grayish white compared to the bluish laurite in reflected light (Fig. 3). The grains of andrieslombaardite from the Yubdo stream were found included in two Pt-Fe alloy nuggets and were described as pale brownish gray varying in size from about one μm up to 25 x 55 μm. One of the largest grains was subhedral, with an angular, dentate outline on which the spectral reflectance values and color values were measured (Tables 1 and 2).

Raman Spectroscopy

A Raman spectrum was collected with a Jobin-Yvon Horiba system using a 100x objective, λ = 532 nm laser and an estimated beam size of 2 μm. Spectrum was collected over the range 100 - 1000 cm^{-1} and shows only two peaks: a sharp, a strong one at 208 cm^{-1} and a less intense, broader one that was modeled with two peaks: 322 and 361 cm^{-1}. The Raman spectrum is very similar to that of ullmannite.

Chemical composition and synthesis

Andrieslombaardite from Onverwacht (sample RW15169) was analyzed by EDS at 20 kV, 1 nA, and a ~ 1 µm beam spot. In an EDS layered image for Ru, Ir and Sb, andrieslombaardite shows an Ir-rich zone near the contact with laurite (Fig. 4). EDS analyses were done on Ir-poor and Ir-rich andrieslombaardite and are given in Tables 3 and 4.

The empirical formula calculated on the basis of three atoms for the Ir-poor area is $(Rh_{0.89}Fe_{0.11}Pt_{0.04}Pd_{0.01}Ir_{0.01})_{\Sigma 1.06}Sb_{0.99}S_{0.95}$ and the simplified formula is (Rh,Fe,Pt,)SbS. The ideal formula is RhSbS, which requires Rh 40.08, Sb 47.43, S 12.49, total 100 wt. %. The empirical formula for the Ir-rich andrieslombaardite calculated on the basis of three atoms is $(Rh_{0.69}Ir_{0.22}Fe_{0.11}Pt_{0.03})_{\Sigma 1.05}(Sb_{0.93}As_{0.05})_{\Sigma 0.98}S_{0.97}$.

The RhSbS phase was first synthesised by Hulliger (1963) who reported a unit-cell of *a* 6.072 Å. Our syntheses were done by heating pure elements in an evacuated quartz tube at 400° and 500° C and sample 2818 (Table 8) was later heated at 550° C. No articles on the Rh-Sb-S ternary system could be found in the materials science literature. One can conclude from our limited experiments that RhSbS is stable from 400° to 550° C where it is a homogeneous phase based on EPMA (Table 5) with a composition of $Rh_{1.00}Sb_{1.00}S_{1.00}$.

The analyses reported of RhSbS from Yubdo, Mooihoek and Driekop are given in Table 5, together with that of the synthetic equivalent.

X-ray diffraction and crystal structure analyses

As the single grain of andrieslombaardite was too small to be extracted from the Onverwacht sample, neither conventional single-crystal X-ray nor powder X-ray diffraction studies could be conducted.

Laue X-ray microdiffraction was performed instead at the 12.3.2 beamline of the Advanced Light Source, Lawrence Berkeley National Lab (Tamura, 2014), using a *pink* beam (energy range 6-22 keV) focused to about 1 µm. Laue microdiffraction analysis (Tamura, 2014) shows the structure is cubic with *a* = 6.0278(4) Å.

Refined unit-cell parameters from Laue data are cubic with space group $P2_13$ (#198) and unit-cell dimensions *a* = 6.0278(4) Å, *V* = 219.01(6) Å^3 and *Z* = 4. The calculated X-ray powder diffraction pattern for andrieslombaardite is given in Table 6. The unit-cell compares well with *a* = 6.0250(1) Å refined by Rietveld refinement of powder X-ray diffraction data collected from synthetic RhSbS (sample 2818) to R_{wp} = 5.39 % (Table 7). Differences in the unit-cell edges may be ascribed to differences in chemistry. The observed powder X-ray diffraction pattern for synthetic RhSbS (sample 2818) is shown in Table 8, in combination with Rietveld-derived pattern.

An *in-situ* Laue pattern, obtained using synchrotron X-ray microdiffraction, was used to investigate the crystal structure of the mineral. The crystal structure was refined to R_{wp} =

11.09%. Performing a partial refinement using the corrected integrated intensities of 93 Laue reflections with the ullmannite as the starting model (substituting Ni by Rh) gave the refined data given in Table 9. An isostructurality with pyrite with disorder on the Sb and S sites resulting into the Pa-3 (#205) space group, cannot be excluded from the indexation of the Laue pattern alone, but leads to a much worse refinement.

Classification and relationship to known minerals

According to the Dana Classification, andrieslombaardite belongs to 02.12.03 cobaltite group (cubic or pseudocubic crystals), 02.12.03.17 andrieslombaardite. According to the Strunz Classification the mineral belongs to 02 Sulfides, 02.EB M:S = 1:2 with Fe, Co, Ni, PGE, *etc*. 25 andrieslombaardite.

Discussion and Conclusions

Larger grains of RhSbS from Yubdo had been studied by Cabri et al. (1981) but at the time were too small for extraction and characterization by X-ray diffraction. It is now possible to obtain a crystal-structure analysis by using non-destructive synchrotron radiation. This will permit many more minerals to be characterized in the future especially those that commonly occur as small grains such as the PGM.

In contrast to driekopite (McDonald et al., 2023), which so far has only been found in a concentrate from the Driekop Pt pipe, andrieslombaardite has also been reported from several locations such as Mooihoek and Onverwacht, in Pt-Fe alloy placer grains derived from the Yubdo Alaskan-Uralian intrusion, as well as in the bedrock of other Alaskan-Uralian intrusions suggesting its paragenesis is not restricted to these unique Pt pipes. Though the synthetic equivalent has been synthesized at 400° and 500° C, there is no published account of phase relations in the Rh-Sb-S ternary system.

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Figure captions

Fig. 1. Geological overview of part of the eastern Bushveld Complex showing the localities of the Atok (now called Bokoni) Mine and the platiniferous pipes. T= Twyfelaar, D = Driekop, M = Mooihoek, O = Onverwacht. Reproduced from Oberthür et al. (2021).

Fig. 2. Diagrammatic geological section across the Onverwacht pipe reproduced from Wagner (1929) by Oberthür et al. (2021) with the scale corrected. Legend from Wagner 1. Bronzitite with finely disseminated chromite; 2. Lower Chromite; 3. Olivine dunite and wehrlite; 4. Main body of hortonolite-dunite; 4a. Veins of hortonolite-dunite; 5. Vein of diallage-hornblende-hortonolite rock, merging locally into hortonolite-dunite; 6. Upper Chromite; 7. Platinum-bearing rubble and eluvium.

Fig. 3. Andrieslombaardite from Onverwacht, RW15169 Reflected light photomicrograph (left) of andrieslombaardite (white) attached to laurite (bluish) in a matrix of fayalite (darkest gray). The entire area is transected by secondary Fe-hydroxides (light gray). On the right is a corresponding BSE image of the same area.

Fig. 4. EDS layered image for Ru, Ir and Sb andrieslombaardite and laurite in Onverwacht sample. Green area = laurite, red area = Ir-rich RhSbS, yellow area = Ir-poor RhSbS.