

Article

Zoned Laurite from the Merensky Reef, Bushveld Complex, South Africa: “Hydrothermal” in Origin?

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Abstract: Laurite, ideally $(\text{Ru},\text{Os})\text{S}_2$, is a common accessory mineral in podiform and stratiform chromitites and, to a lesser extent, it also occurs in placer deposits and is associated with Ni-Cu magmatic sulfides. In this paper, we report on the occurrence of zoned laurite found in the Merensky Reef of the Bushveld layered intrusion, South Africa. The zoned laurite forms relatively large crystals of up to more than 100 μm , and occurs in contact between serpentine and sulfides, such as pyrrhotite, chalcopyrite, and pentlandite, that contain small phases containing Pb and Cl. Some zoned crystals of laurite show a slight enrichment in Os in the rim, as typical of laurite that crystallized at magmatic stage, under decreasing temperature and increasing sulfur fugacity, in a thermal range of about 1300–1000 $^{\circ}\text{C}$. However, most of the laurite from the Merensky Reef are characterized by an unusual zoning that involves local enrichment of As, Pt, Ir, and Fe. Comparison in terms of Ru-Os-Ir of the Merensky Reef zoned laurite with those found in the layered chromitites of the Bushveld and podiform chromitites reveals that they are enriched in Ir. The Merensky Reef zoned laurite also contain high amount of As (up to 9.72 wt%), Pt (up to 9.72 wt%) and Fe (up to 14.19 wt%). On the basis of its textural position, composition, and zoning, we can suggest that the zoned laurite of the Merensky Reef is “hydrothermal” in origin, having crystallized in the presence of a Cl- and As-rich hydrous solution, at temperatures much lower than those typical of the precipitation of magmatic laurite. Although, it remains to be seen whether the “hydrothermal” laurite precipitated directly from the hydrothermal fluid, or it represents the alteration product of a pre-existing laurite reacting with the hydrothermal solution.

Keywords: laurite; sulfides; fluids; platinum group elements (PGE); platinum group minerals (PGM); Merensky Reef; Bushveld Complex; South Africa

1. Introduction

Minerals of ruthenium are very rare and only five of them, namely anduoite $(\text{Ru},\text{Os})\text{As}_2$, laurite $(\text{Ru},\text{Os})\text{S}_2$, ruarsite RuAsS , ruthenarsenite $(\text{Ru},\text{Ni})\text{As}$, and ruthenium $(\text{Ru},\text{Ir},\text{Os})$, have been approved by the International Mineralogical Association (IMA). They occur as accessory minerals associated with mafic–ultramafic rocks, especially with chromitite, and as nuggets in placer deposits. Among the minerals of ruthenium, laurite is the most common. It was discovered in 1866 in a placer from Laut, Banjar, South Kalimantan Province, Borneo, Indonesia [1]. Laurite is a common constituent of the suite of platinum group minerals (PGM) inclusions (usually less than 20 μm) in podiform and stratiform chromitites [2–4]. Less frequently, laurite has been reported from placers and Ni-Cu magmatic sulfide deposits [5–7]. Laurite forms a complete solid solution with erlichmanite (OsS_2) [5], and their typical mode of occurrence, i.e., included in chromite grains, indicate that they crystallized at high temperatures, in a thermal range of about 1300–1000 $^{\circ}\text{C}$ prior to, or coeval with, the precipitation of the host chromitite [2–4]. The reciprocal stability of laurite and erlichmanite is strongly controlled

by sulfur fugacity and temperature. In particular, laurite precipitates at a higher temperature and lower sulfur fugacity, compared to erlichmanite. This order of crystallization can be observed in the zoning of the small crystals of laurite and erlichmanite enclosed in fresh chromite grains that, typically, show an Os-poor core, grading into a high-Os rim [2–4]. This magmatic zoning can be obliterated by low temperature processes such as serpentinization and weathering, as documented in laurite associated with podiform chromitites [8–10]. During alteration processes at low temperature, laurite and erlichmanite lose their original S and release part of Os and Ir to form secondary Ru-Os-Ir alloys, in which the lost S may be replaced by Fe-oxide [8–10]. The occurrence of laurite in the Bushveld Complex of South Africa has been documented by several authors [2,7,11–17]. Most commonly, the mineral occurs as small polygonal grains enclosed in chromite grains of the Critical Zone chromitite layers and has only occasionally been found as part of the sulfide ore of the Merensky Reef. In this contribution, we have investigated in detail the mineral chemistry of the laurite associated with the sulfide-rich zone of the Merensky Reef. The grains are characterized by an unusual zoning and composition compared with laurite inclusions in the Bushveld chromitites, suggesting that the mineral was generated under different thermodynamic conditions in the two cases.

2. Sample Provenance and Petrographic Description

The Bushveld layered intrusion is located in the central part of the Transvaal province, north of Pretoria, South Africa (Figure 1A), and it is divided into Eastern, Western, and Northern limbs (Figure 1B). The Bushveld intrusion is well known among economic geologists because it contains the world's largest deposits of platinum group elements (PGE), namely: the UG-2 chromitite and the Merensky Reef [18]. The noun Merensky Reef refers to a sulfide-bearing pegmatoidal feldspathic pyroxenite enriched in PGE, marked at the bottom and top, by two centimetric layers of chromitite. The Reef can be traced for a total strike of about 280 km, marking the limit between the Critical and Main Zone [18,19]. The investigated samples were collected by one of the authors (G.G.) in the Rustenburg underground mine, during the third International Platinum Symposium held in Pretoria from 6 to 10 July 1981 [20,21]. The Rustenburg mine is located in the Western limb of the Bushveld Complex, about 100 km west of Pretoria (Figure 1B,C). Here, four different zones of Bushveld (undifferentiated in Figure 1C) are intruded by the Pilanesberg Alkaline Complex [22]. Four square polished blocks, about 2.5×2.5 cm (Figure 2), were prepared for petrographic and mineralogical investigation. The blocks consist of a thin layer of chromitite, about 0.2 cm thick, in contact with pegmatoidal feldspathic pyroxenite and large blebs of sulfide. In agreement with observations made by several authors [21,23,24], the sulfide-rich zone contains accessory actinolite, micas, talc, chlorite, and a serpentine subgroup mineral.

3. Methods

The polished blocks were previously studied by reflected-light microscope. Quantitative chemical analyses of laurite were performed with a JEOL JXA-8200 electron microprobe (JEOL, Tokyo, Japan), installed in the E. F. Stumpfl laboratory, Leoben University, Leoben, Austria, operated in WDS (wavelength dispersive spectrometry) mode. Major and minor elements were determined at 20 kV accelerating voltage and 10 nA beam current, with 20 s as counting time for the peak and 10 s for the backgrounds. The beam diameter was about 1 μ m in size. The $K\alpha$ lines were used for S, As, Fe and Ni; $L\alpha$ for Ir, Ru, Rh, Pd, and Pt, and $M\alpha$ for Os. The reference materials were pure metals for the six PGE (Ru, Rh, Pd, Os, Ir and Pt), synthetic NiS, natural pyrite and niccolite for Ni, Fe, S and As. The following diffracting crystals were selected: PETJ for S; PETH for Ru, Os, Pd and Rh; LIFH for Fe, Ni, Ir and Pt; and TAP for As. Automatic correction was performed for the Ru-Rh and Rh-Pd interferences. The detection limits were calculated by the software and are: Os (0.07 wt%), Ir (0.06 wt%), Ru, Pd, and Pt (0.04 wt%), Rh (0.03 wt%), Fe, Ni, As and S (0.02 wt%). The grains smaller than 10 μ m were analyzed by EDS. The same instrument was used to obtain back-scattered electron images (BSE) and X-ray elemental distribution maps.

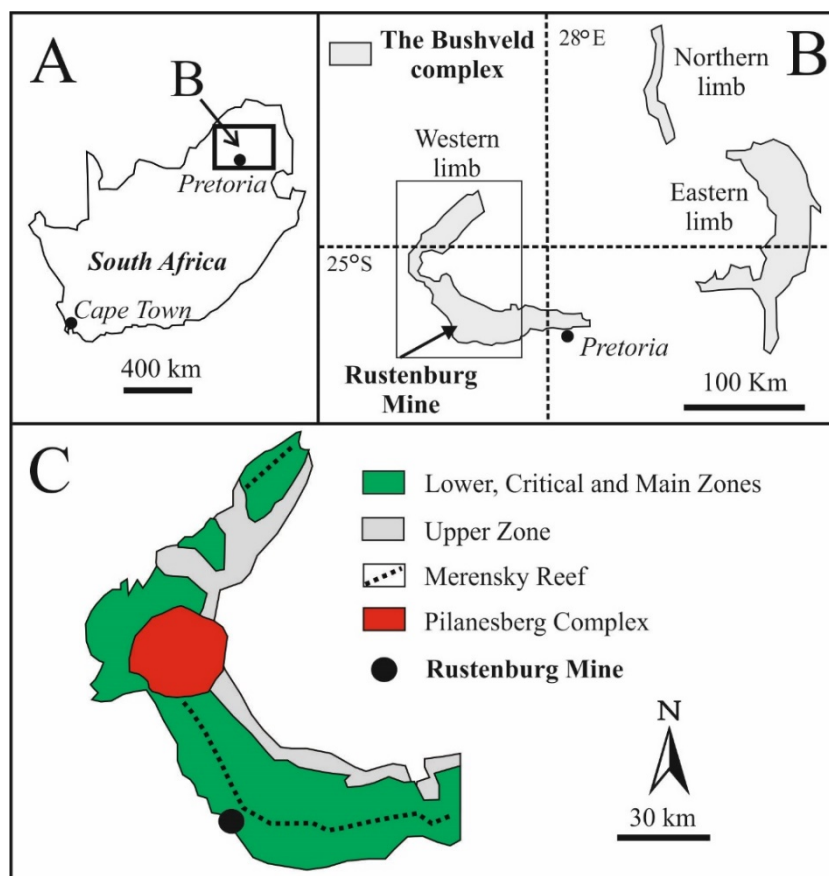


Figure 1. The Bushveld Complex, South Africa (A) and locations of the Rustenburg mine and the Merensky Reef (B,C) in the Western limb (modified after [15,18]).

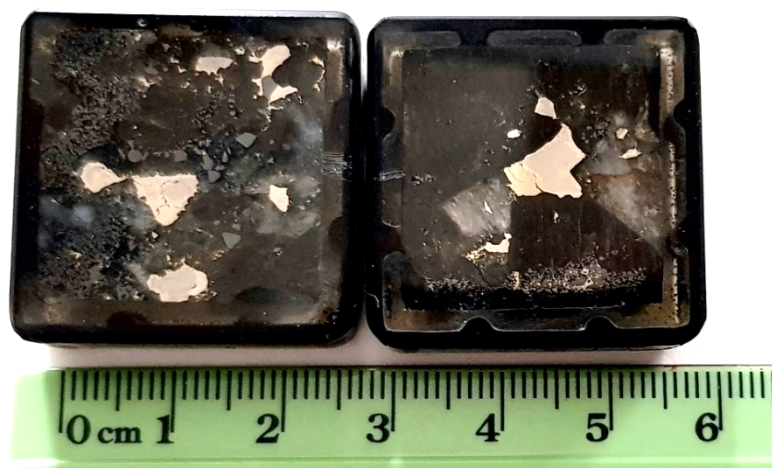


Figure 2. Example of the studied polished blocks from the Merensky Reef, showing the sulfide blebs (creamy-yellow) and the cumulitic chromitite (small polygonal dark grey grains) in the pegmatoidal feldspathic pyroxenite.

4. Laurite: Morphology, Texture, and Composition

The investigated samples contain laurite in two different textural positions, either included in fresh chromite of the thin chromitite layer (Figure 3A), or at the contact between sulfide patches (pyrrhotite, chalcopyrite, pentlandite) and serpentine (Figure 3B–D).

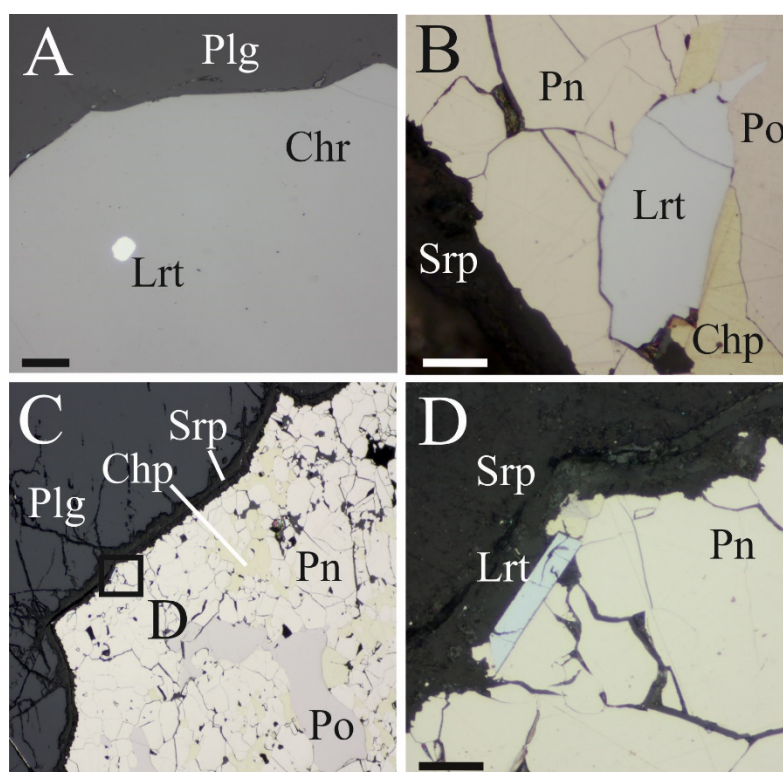


Figure 3. Digital image in reflected plane polarized light showing laurite from the Merensky Reef. (A) Laurite enclosed in fresh chromite. (B,C) Zoned laurite and (D) enlargement of (C). Abbreviations: Lrt = laurite, Plg = plagioclase, Chr = chromite, Srp = serpentine, Pn = pentlandite, Po = pyrrhotite, Chp = chalcopyrite. Scale bar = 20 μm .

Quantitative analyses of laurite enclosed in chromite and associated with sulfides are listed in Tables 1 and 2, respectively. Laurite included in chromite forms tiny crystals, usually not exceeding 10 μm in size, characterized by euhedral to subeuhedral morphology and homogenous composition. Laurite associated with sulfides and serpentine is bigger, up to more than 100 μm , and may occur as single crystals or clusters of grains (Figure 3B–D), characterized by subeuhedral to anhedral shape. The BSE images of large laurite display remarkable zoning emphasized by marked contrast in the electronic reflectivity (Figure 4A–D). Laurite in the sulfide assemblage is accompanied by a complex association of precious minerals comprising: cooperite (PtS), moncheite (PtTe_2), platarsite (PtAsS), rustenburgite (Pt_3Sn), Pt-Fe alloy, undetermined Pt-Te-Bi and Pd-Te-Bi compounds, Au-Ag alloy, and the recently discovered PGM bowlesite PtSnS [21].

Table 1. Selected wavelength dispersive spectrometry (WDS) electron microprobe analyses of Merensky Reef laurite enclosed in chromite.

Sample	As	S	Ru	Os	Ir	Rh	Pt	Pd	Ni	Fe	Total
wt%											
mr18a	1.69	36.81	50.36	5.42	2.85	1.24	0.00	1.79	0.03	1.00	101.18
mr8a	1.85	36.93	49.99	4.97	3.03	1.06	0.00	1.68	0.08	0.90	100.48
Sample	As	S	Ru	Os	Ir	Rh	Pt	Pd	Ni	Fe	
at%											
mr18a	1.28	65.25	28.32	1.62	0.84	0.69	0.00	0.96	0.03	1.02	
mr8a	1.40	65.58	28.16	1.49	0.90	0.59	0.00	0.90	0.08	0.91	

Table 2. WDS electron microprobe analyses of Merensky Reef zoned laurite.

Sample	As	S	Ru	Os	Ir	Rh	Pt	Pd	Ni	Fe	Total
wt%											
MR2a1	1.08	37.50	39.32	4.79	7.23	1.09	0.00	1.32	0.26	6.54	99.13
MR2a2	1.28	36.97	37.20	7.97	9.49	0.90	0.00	1.18	0.06	5.76	100.81
MR2a3	1.63	37.63	43.23	2.53	6.22	1.38	0.00	1.35	0.42	5.87	100.27
MR2a4	1.51	37.58	45.24	3.15	5.75	1.32	0.00	1.55	0.81	4.23	101.15
MR2a5	1.38	37.68	43.61	3.59	6.02	1.35	0.00	1.47	0.90	4.73	100.73
MR2a6	1.74	37.32	42.99	2.78	6.46	1.37	0.00	1.41	0.65	5.22	99.94
MR2a7	1.44	38.69	44.54	1.88	5.27	1.19	0.00	1.47	0.49	5.24	100.21
MR2a8	1.42	39.13	44.65	2.00	4.50	1.63	0.00	1.58	0.39	5.44	100.73
MR2a9	1.50	38.46	43.86	1.86	6.06	1.05	0.10	1.42	0.53	5.28	100.13
MR2a10	1.54	38.98	43.03	2.77	6.25	1.16	0.00	1.45	0.31	6.17	101.66
MR2a11	2.22	38.17	44.63	1.57	5.35	1.53	0.00	1.63	0.57	4.57	100.23
MR2a12	9.72	28.45	28.24	5.90	13.43	1.75	7.20	1.05	0.80	3.05	99.57
MR2a13	3.66	36.78	42.64	1.90	5.85	2.02	1.78	1.58	0.63	4.35	101.20
MR2a14	2.90	37.25	43.43	1.64	5.83	1.98	1.04	1.55	0.54	4.75	100.91
MR2a15	2.74	36.97	41.61	2.55	6.73	1.77	0.85	1.48	0.76	5.57	101.02
MR2a16	1.39	39.25	44.22	2.38	5.75	1.08	0.00	1.39	0.42	5.26	101.14
MR2a17	1.41	39.21	44.41	1.92	5.11	1.12	0.00	1.37	0.34	5.74	100.63
MR2a18	1.49	39.68	44.34	1.70	4.52	1.18	0.00	1.75	0.31	6.26	101.24
MR2a19	1.40	39.70	43.20	1.73	5.22	1.38	0.00	1.42	0.35	6.38	100.80
MR2a20	1.42	38.14	41.29	3.31	6.79	1.36	0.00	1.49	0.27	5.78	99.84
MR2a21	1.42	39.38	44.15	2.30	5.31	1.11	0.00	1.38	0.41	5.51	100.97
MR2a22	1.49	39.29	45.22	1.47	4.26	1.23	0.00	1.44	0.22	5.84	100.46
MR2a23	1.50	39.63	43.90	1.38	4.63	1.32	0.00	1.48	0.39	6.40	100.63
MR2a24	1.54	37.92	43.50	3.35	7.10	0.82	0.00	1.55	0.82	4.61	101.20
MR4a1	2.06	41.46	33.93	0.94	2.68	3.03	0.57	1.49	0.23	14.19	100.58
MR4a2	3.90	38.45	35.37	1.51	2.98	3.50	2.53	1.61	0.30	10.13	100.27
MR4a3	8.19	32.52	33.93	3.15	2.83	2.69	8.69	1.37	0.36	5.66	99.38
MR4a4	4.32	37.85	37.63	2.52	2.25	2.75	3.79	1.58	0.35	7.79	100.83
MR4a5	5.78	34.99	34.15	3.55	3.08	2.80	5.61	1.50	0.31	7.78	99.56
MR4a6	6.88	34.58	36.72	2.47	2.64	2.68	7.33	1.36	0.35	5.90	100.90
MR4a7	7.94	32.54	33.50	3.92	4.15	2.51	8.20	1.41	0.31	5.97	100.44
MR4a8	4.26	37.60	36.69	3.21	3.26	2.54	2.95	1.62	0.27	8.77	101.17
MR1a1	1.38	37.10	42.11	4.44	9.00	1.18	0.00	1.40	0.56	4.03	101.19
MR1a2	1.36	37.54	42.06	4.85	8.61	1.22	0.00	1.35	0.56	3.82	101.37
MR1a3	1.44	36.34	42.08	4.46	8.24	1.09	0.00	1.45	0.71	3.70	99.51
MR1a4	1.43	37.43	41.91	4.47	8.97	1.10	0.00	1.43	0.52	3.94	101.21
MR1a5	1.45	37.60	39.58	6.03	7.48	1.14	0.00	1.22	0.12	5.98	100.59
MR1a6	1.46	38.23	37.79	5.25	6.84	1.31	0.00	1.24	0.13	8.68	100.92
MR1a7	1.45	36.94	41.04	7.93	7.14	1.09	0.00	1.31	0.73	3.75	101.38
MR1a8	2.03	36.96	41.34	2.77	9.50	1.56	0.00	1.45	0.67	4.13	100.41
MR1a9	1.51	37.75	36.32	7.72	8.20	1.21	0.00	1.10	1.39	4.95	100.16
MR1a10	1.69	36.81	50.36	5.42	2.85	1.24	0.00	1.79	0.03	1.00	101.18
MR1a11	1.85	36.93	49.99	4.97	3.03	1.06	0.00	1.68	0.08	0.90	100.48

Table 2. Cont.

Sample	As	S	Ru	Os	Ir	Rh	Pt	Pd	Ni	Fe
at%										
MR2a1	0.81	65.69	21.85	1.41	2.11	0.59	0.00	0.70	0.25	6.58
MR2a2	0.97	65.76	20.99	2.39	2.82	0.50	0.00	0.63	0.05	5.88
MR2a3	1.20	64.94	23.67	0.74	1.79	0.74	0.00	0.70	0.39	5.82
MR2a4	1.12	64.99	24.82	0.92	1.66	0.71	0.00	0.81	0.77	4.20
MR2a5	1.02	65.21	23.94	1.05	1.74	0.73	0.00	0.76	0.85	4.70
MR2a6	1.29	64.96	23.74	0.82	1.88	0.74	0.00	0.74	0.62	5.21
MR2a7	1.05	65.89	24.06	0.54	1.50	0.63	0.00	0.75	0.45	5.13
MR2a8	1.02	65.97	23.89	0.57	1.26	0.86	0.00	0.80	0.36	5.26
MR2a9	1.10	65.81	23.81	0.54	1.73	0.56	0.03	0.73	0.50	5.19
MR2a10	1.11	65.72	23.02	0.79	1.76	0.61	0.00	0.73	0.28	5.98
MR2a11	1.63	65.43	24.27	0.45	1.53	0.82	0.00	0.84	0.53	4.50
MR2a12	8.48	58.03	18.27	2.03	4.57	1.11	2.41	0.64	0.89	3.57
MR2a13	2.73	64.07	23.56	0.56	1.70	1.10	0.51	0.83	0.60	4.35
MR2a14	2.15	64.45	23.84	0.48	1.68	1.07	0.30	0.81	0.51	4.72
MR2a15	2.03	64.14	22.90	0.75	1.95	0.96	0.24	0.77	0.72	5.55
MR2a16	1.01	66.26	23.68	0.68	1.62	0.57	0.00	0.71	0.39	5.10
MR2a17	1.02	66.10	23.75	0.55	1.44	0.59	0.00	0.69	0.31	5.56
MR2a18	1.06	66.04	23.41	0.48	1.25	0.61	0.00	0.88	0.28	5.98
MR2a19	1.00	66.30	22.89	0.49	1.45	0.72	0.00	0.72	0.32	6.11
MR2a20	1.05	65.91	22.63	0.96	1.96	0.73	0.00	0.78	0.25	5.73
MR2a21	1.03	66.27	23.58	0.65	1.49	0.58	0.00	0.70	0.38	5.32
MR2a22	1.07	66.01	24.10	0.42	1.19	0.64	0.00	0.73	0.20	5.63
MR2a23	1.07	66.11	23.23	0.39	1.29	0.68	0.00	0.74	0.35	6.13
MR2a24	1.14	65.45	23.82	0.97	2.04	0.44	0.00	0.80	0.78	4.56
MR4a1	1.39	65.32	16.96	0.25	0.71	1.49	0.15	0.71	0.20	12.84
MR4a2	2.78	64.02	18.68	0.42	0.83	1.82	0.69	0.81	0.28	9.68
MR4a3	6.50	60.32	19.97	0.98	0.88	1.55	2.65	0.77	0.37	6.02
MR4a4	3.13	64.09	20.21	0.72	0.63	1.45	1.06	0.81	0.32	7.58
MR4a5	4.40	62.15	19.24	1.06	0.91	1.55	1.64	0.80	0.30	7.94
MR4a6	5.25	61.69	20.78	0.74	0.78	1.49	2.15	0.73	0.34	6.04
MR4a7	6.29	60.18	19.66	1.22	1.28	1.45	2.49	0.79	0.31	6.34
MR4a8	3.09	63.62	19.69	0.91	0.92	1.34	0.82	0.82	0.25	8.52
MR1a1	1.04	65.42	23.56	1.32	2.65	0.65	0.00	0.74	0.54	4.08
MR1a2	1.02	65.85	23.41	1.43	2.52	0.66	0.00	0.72	0.54	3.85
MR1a3	1.11	65.22	23.96	1.35	2.47	0.61	0.00	0.78	0.70	3.81
MR1a4	1.08	65.77	23.36	1.32	2.63	0.60	0.00	0.76	0.50	3.98
MR1a5	1.08	65.67	21.93	1.77	2.18	0.62	0.00	0.64	0.11	6.00
MR1a6	1.07	65.12	20.43	1.51	1.94	0.70	0.00	0.63	0.12	8.49
MR1a7	1.10	65.50	23.09	2.37	2.11	0.60	0.00	0.70	0.71	3.81
MR1a8	1.53	65.24	23.15	0.82	2.80	0.86	0.00	0.77	0.65	4.19
MR1a9	1.14	66.34	20.25	2.29	2.41	0.66	0.00	0.58	1.33	5.00
MR1a10	1.28	65.25	28.32	1.62	0.84	0.69	0.00	0.96	0.03	1.02
MR1a11	1.40	65.58	28.16	1.49	0.90	0.59	0.00	0.90	0.08	0.91

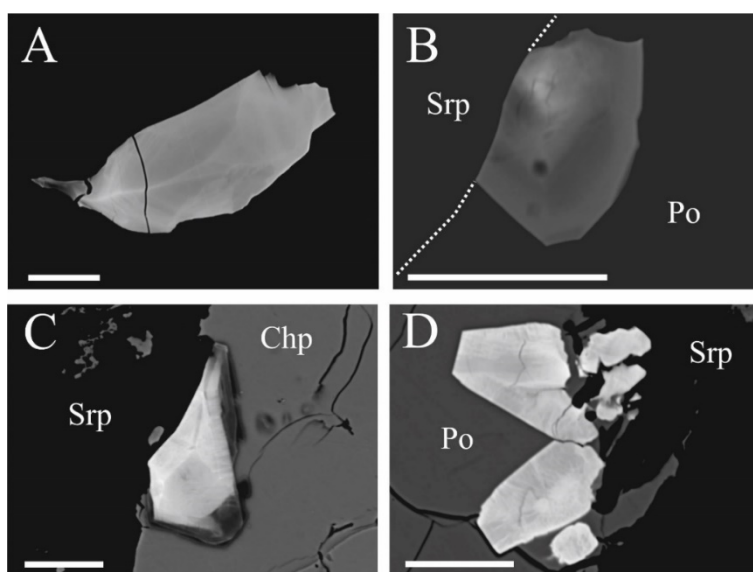


Figure 4. Back-scattered electron (BSE) images of zoned laurite. (A) See reflected-light image of Figure 3B for the mineralogical assemblage of the grain. (B) Laurite in contact with pyrrhotite and serpentine, (C) laurite in contact with chalcopyrite and serpentine and (D) laurite grains in contact with pyrrhotite and serpentine Abbreviations as in Figure 3. Scale bar = 20 µm.

As previously reported by [14], abundant Pb-Cl minerals, less than 10 µm in size, were also observed enclosed in the sulfides (Figure 5A), and qualitatively identified by EDS (Figure 5B). The EDS overlap between Pb and S was checked by a WDS semi-quantitative analysis that gave a composition (wt%) of 77.8 for Pb and 18.9 for Cl, very similar to the mineral analyzed by [14].

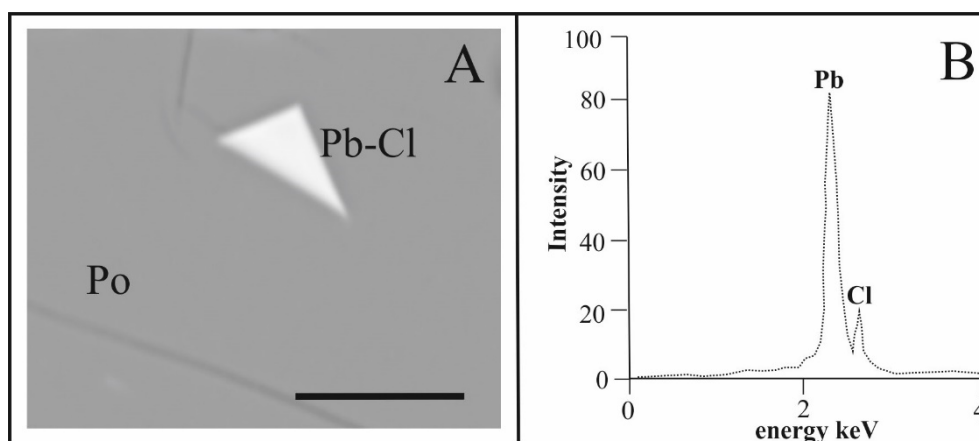


Figure 5. (A) BSE image of a Pb-Cl mineral (Pb-Cl) enclosed in pyrrhotite (Po), scale bar = 10 µm, and (B) its EDS spectrum (see the text for the Pb-S overlap).

Electron microprobe analyses of the zoned laurite (Table 2) and elemental distribution maps (Figures 6–8) showed unusual enrichments in As, Ir, Os, Pt, and Fe. Distribution of Rh, Pd, and Ni was not visible in the X-ray maps because of the low concentrations, while Cu (not analyzed, but visible in Figure 7) was due to a Cu-phase filling fissures in laurite. Substitution of As for S occurs systematically from a homogeneous background of about 1.00–1.50 wt% (Figure 6) up to patchy enrichment of 3.66–9.7 wt% (Figures 7 and 8). The enrichments of Os and Ir are closely related and may occur either at the rim of grains as described by [14] (Figure 6), or as irregular patches (Figures 7 and 8). The Pt appears to be particularly concentrated, up to 8.69 wt%, in the As-rich zones (Figures 7 and 8).

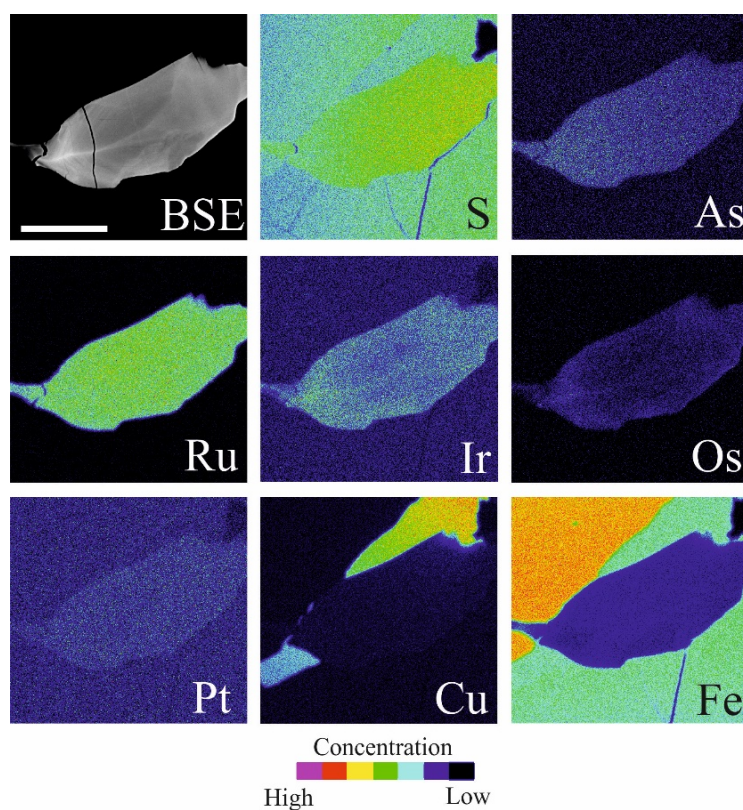


Figure 6. BSE image and X-ray element-distribution maps of S, As, Ru, Ir, Os, Pt, Cu, and Fe in zoned laurite from the Merensky Reef. See Figures 3B and 4A for the paragenetic assemblage. Scale bar = 20 μm .

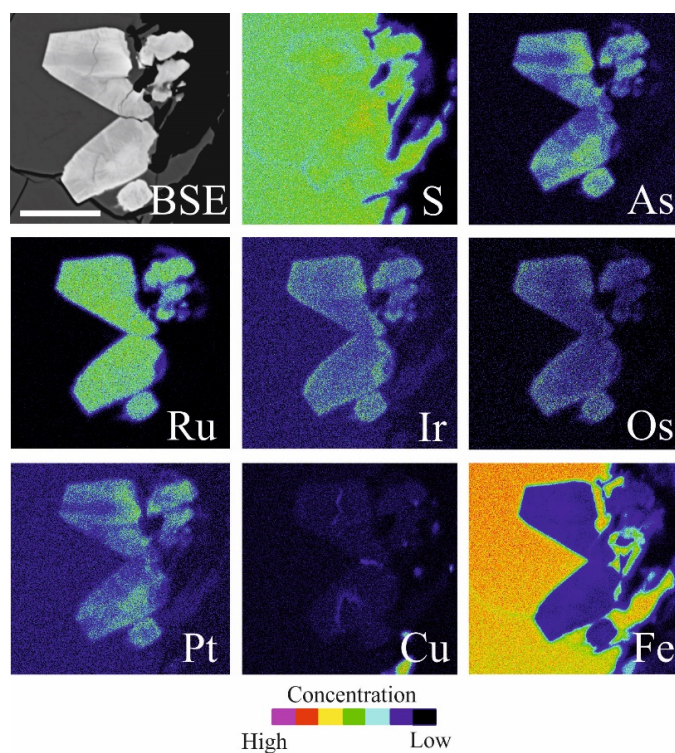


Figure 7. BSE image and X-ray element-distribution maps of S, As, Ru, Ir, Os, Pt, Cu, and Fe, showing the zoning of the laurite from the Merensky Reef, see reflected-light image of Figure 4D for the mineralogical assemblage. Scale bar is 20 μm .

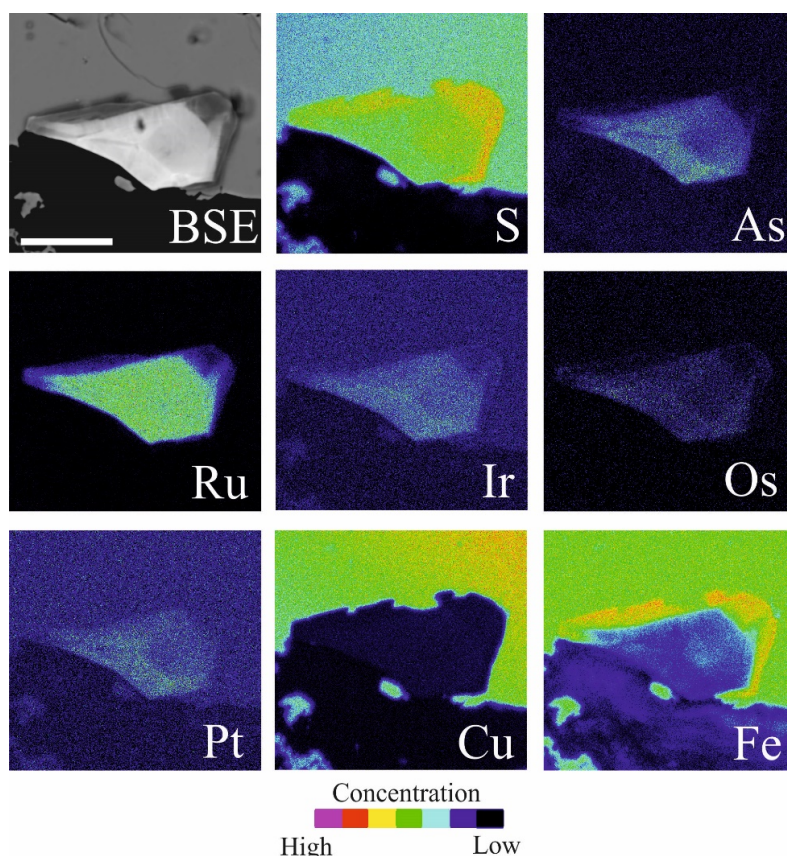


Figure 8. BSE image and X-ray element-distribution maps of S, As, Ru, Ir, Os, Pt, Cu, and Fe, showing the zoning of the laurite from the Merensky Reef, see reflected-light image of Figure 4C for the mineralogical assemblage. Scale bar is 20 μm .

The Ru-Os-Ir (wt%) ternary diagram (Figure 9) shows that the zoned laurite of the Merensky Reef are significantly enriched in Ir, compared with laurite enclosed in the chromitite of the same Reef, and other chromitite layers of the Bushveld. They also do not display the Ru-Os negative correlation inferred by the Ru-Os substitution trend due to the laurite-erlichmanite solid solution trend (Figure 8). Based on more than 1000 published analyses, and unpublished data of the authors, laurite associated with ophiolitic, stratiform, and Alaskan-type magmatic chromitites exhibit a pronounced negative correlation between Ru and Os ($R = -0.97$). In contrast, the correlation matrix calculated from our electron microprobe analyses (Table 3) indicates that zoned laurite of the Merensky Reef are characterized by the absence of Ru-Os correlation ($R = -0.07$).

Table 3. Element correlation in the zoned laurite for the Merensky Reef.

at%	As	S	Ru	Os	Ir	Rh	Pt	Pz	Ni	Fe
As	1.00									
S	−0.98	1.00								
Ru	−0.56	0.53	1.00							
Os	0.10	−0.14	−0.07	1.00						
Ir	0.04	−0.09	−0.04	0.56	1.00					
Rh	0.72	−0.70	−0.68	−0.25	−0.42	1.00				
Pt	0.97	−0.95	−0.58	0.06	−0.10	0.75	1.00			
Pd	0.03	−0.05	0.45	−0.37	−0.50	0.20	0.03	1.00		
Ni	0.07	−0.09	−0.02	0.20	0.50	−0.12	−0.01	−0.21	1.00	
Fe	0.11	−0.10	−0.78	−0.35	−0.37	0.56	0.18	−0.27	−0.29	1.00

Note: the relevant correlations are highlighted in bold.

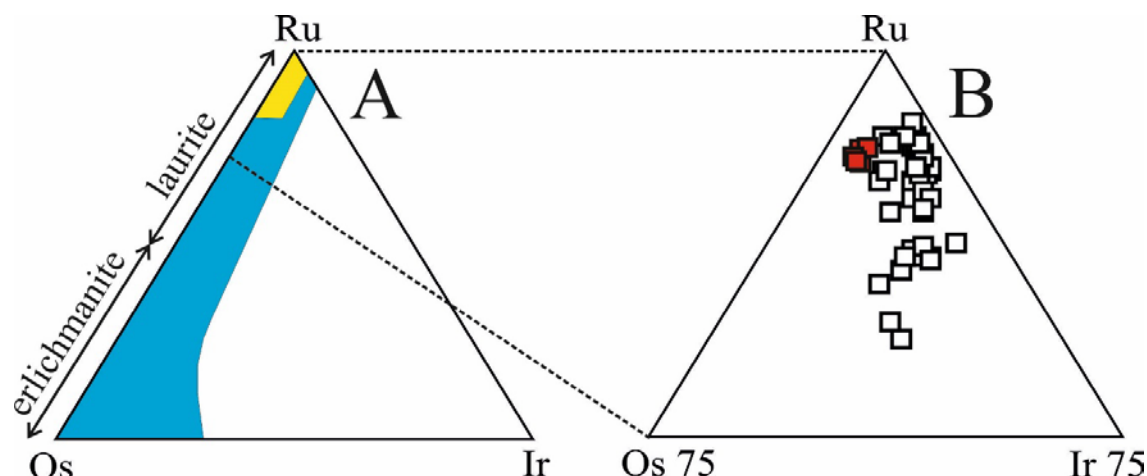


Figure 9. (A) Ru-Os-Ir ternary diagram (wt%) for magmatic laurite enclosed in the Lower-, Middle-, and Upper-group chromitite layers: from the Bushveld Complex (yellow field) and podiform chromitite (blue field). Compositional fields after [11,12] and unpublished data of the authors. (B) Merensky Reef zoned laurite (open square) and laurite enclosed in the Merensky Reef chromite (red square).

In addition, the high concentrations of As (up to 9.72 wt%), Pt (up to 9.72 wt%), and Fe (up to 14.19%) (Table 2), distinguish the zoned laurite of the Merensky Reef from the laurite inclusions in different types of chromitite (ophiolitic, stratiform, Alaskan-type).

The correlation matrix (Table 3) and distribution X-ray maps (Figure 7) clearly support a positive correlation between Pt-As ($R = +0.97$), and a negative correlation of both elements with S ($R = -0.95$ and -0.98 , respectively). The possible existence of submicroscopic inclusions of sperrylite (PtAs_2) or platarsite (PtAsS) in laurite was carefully checked, and discarded.

The fact that the sum of S+As atoms is consistently close to stoichiometry ($S + \text{As} = 2.00$) supports that Pt and As are parts of the laurite structure. Notably also the high concentrations of Fe are not due to exotic inclusions, but Fe appears to be the major substitute for Ru, showing a negative correlation of $R = -0.78$ (Table 3), that is a clear discrepancy with common magmatic laurite in general.

5. Origin of the Zoned Laurite in the Merensky Reef

Several theories for the origin of the Merensky Reef have been proposed, and they have been recently summarized by [25]. The proposed genetic models include: (i) gravitational settling of crystals that precipitated in the magma chamber during the orthomagmatic stage; (ii) hydrodynamic sorting of a mobilized cumulate slurry in a large magma chamber, under slow cooling; (iii) crystallization at the crystal mush-magma interface caused by a replenishment event; (iv) interaction of a hydrous melt with a partially molten cumulate assemblage; (v) intrusion of magmas as sills into undifferentiated norite; and (vi) intrusion of magma into a pre-existing cumulate pile ([25] and references therein).

To explain the formation of the coarse-grained feldspathic orthopyroxenite enriched in PGE, and associated chromitite in the Merensky Reef, several authors have invoked the reaction between a late-stage hydrous melt with an unconsolidated cumulate assemblage [23–27]. On the basis of natural observations supported by experimental results, formation of tiny Os-Ir-Ru PGM inclusions in chromitite can be modeled by a sequence of crystallization events controlled by sulfur fugacity and temperature (T) [2–4]. The sulfur fugacity is expected to increase with decreasing T in magmatic systems between about 1300–1000 °C, and a consistent order of crystallization can be observed. Alloys in the system Os-Ir-Ru are the first to precipitate, followed by laurite, usually characterized by a core-to-rim increment of Os content, and finally, erlichmanite. Incorporation of IrS_2 molecules in the laurite structure is generally low, controlled by Ir activity in the system. However, the systematic substitution of Os for Ru can be remarkable, and the composition can enter the field of erlichmanite if sulfur fugacity increases sufficiently during magmatic crystallization.

At a first instance, the Os enrichment observed at the rim of some zoned laurite of the Merensky Reef may correspond to such a magmatic crystallization trend. However, other characteristics of the Merensky Reef zoned laurite, such as the unusual zoning that involves local enrichment of As, Pt, Ir, and Fe (Figures 7 and 8), and the absence of Ru–Os substitution, are in apparent contrast with this conclusion. The observed zoning also does not reflect a fluctuation of the sulfur fugacity, suggested to explain the oscillatory zoning of Ru and Os, described in the laurite from the Penikat Layered Complex of Finland [28]. The presence of abundant minerals containing Pb and Cl and occurring enclosed in the sulfides associated with the zoned laurite indicates the presence of Cl in the system [14]. According to [14], the Cl-rich phase precipitated from a late-stage solution or formed as a result of replacement of a precursor galena by an aqueous hydrochloric solution in the final stage of hydrothermal alteration, at low-temperature. Theoretical and experimental work coupled with natural observations suggest that both Cl and As may be important for the transport and mobilization of the PGE during metasomatic and hydrothermal events [23,28–32].

The textural position and the coarse grain size of laurite crystals, as well as their paragenesis including hydrous silicates, suggest crystallization at a late stage from a volatile-rich melt enriched in As and Cl, after coalescence of an immiscible sulfide liquid. The close stabilization of serpentine points to relatively low temperatures for the precipitation of zoned laurite, certainly much lower than those required for the crystallization of tiny laurite included in the chromite seams of the Merensky Reef. Although it is not possible to provide a precise temperature for the genesis of the zoned laurite in the Merensky Reef, we suggest they were in the range of 400–200 °C, similar to temperatures calculated for PGM deposition in the hydrothermal Waterberg platinum deposit of Mookgophong, South Africa [31]. Therefore, we can suggest that the zoned laurite of the Merensky Reef is “hydrothermal” in origin, having crystallized in the presence of a Cl- and As-rich hydrous solution, at temperatures much lower than those typical of the precipitation of magmatic laurite. Although, it remains to be seen whether the “hydrothermal” laurite precipitated directly from the hydrothermal fluid, or it represents the alteration product of a pre-existing laurite reacting with the hydrothermal solution.

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