

## THE OCCURRENCE OF Pb-Cl-(OH) AND Pt-Sn-S COMPOUNDS IN THE MERENSKY REEF, BUSHVELD LAYERED COMPLEX, SOUTH AFRICA

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### ABSTRACT

An unusual phase rich in Cl (78.4 wt.% Pb, 19.2% Cl) and close in composition to penfieldite [Pb<sub>2</sub>Cl<sub>3</sub>(OH)] was found as a ~5 µm inclusion in chalcopyrite, in a spatial association with platinum-group minerals, in a sulfide-poor (≤5 vol.% of base-metal sulfides) enstatite orthocumulate of the Merensky Reef, Bushveld layered complex, South Africa. This seems to be the first reported occurrence of a Pb-Cl-(OH) compound in mafic-ultramafic rocks. The associated platinum-group minerals are members of the braggite series, cooperite (which forms large intergrowths with braggite: up to 0.5 mm in the longest dimension), members of the rustenburgite-atokite and merenskyite-moncheite series, zoned laurite, and an unknown stannosulfide of Pt, the likely chemical formula of which is PtSnS. The stannosulfide probably formed at a hydrothermal stage from microvolumes of a late-stage fluid or liquid. The Cl-rich phase precipitated from a late-stage solution rich in Cl, or formed as a result of replacement of a precursor mineral (probably galena) by an aqueous hydrochloric solution at a very low temperature, at the final stage of hydrothermal alteration.

*Keywords:* Cl-rich phase, platinum-group minerals, stannosulfide of Pt, Merensky Reef, Bushveld complex, mafic-ultramafic rocks, layered intrusion, South Africa.

### SOMMAIRE

Nous documentons la présence d'une phase inhabituelle riche en Cl (78.4% Pb, 19.2% Cl, en poids) se rapprochant de la composition de la penfieldite [Pb<sub>2</sub>Cl<sub>3</sub>(OH)] en inclusion d'environ 5 µm dans la chalcopyrite, étroitement associée à des minéraux du groupe du platine dans un orthocumulat à enstatite à faible teneur en sulfures de métaux de base (≤5% du volume) provenant du banc minéralisé de Merensky, complexe stratiforme de Bushveld, en Afrique du Sud. Cet indice semble offrir le premier exemple d'un composé à Pb-Cl-(OH) dans des roches mafiques-ultramafiques. Lui sont associés des minéraux du groupe du platine: membres de la série de la braggite, cooperite (en intercroissance avec la braggite, atteignant jusqu'à 0.5 mm en dimension maximale), membres des séries rustenburgite-atokite et merenskyite-monchéite, laurite zonée, et un stannosulfure de Pt méconnu, dont la composition serait PtSnS. Le stannosulfure se serait probablement formé à un stade hydrothermal à partir de microvolumes d'un fluide ou liquide tardif. Le minéral riche en Cl a précipité d'une solution tardive chlorée, ou bien s'est formée par remplacement d'un précurseur, probablement la galène, en présence d'une solution aqueuse hydrochlorique à température très faible, au stade ultime de l'altération hydrothermale.

*Mots-clés:* phase riche en Cl, minéraux du groupe du platine, stannosulfure de Pt, banc de Merensky, complexe de Bushveld, roches mafiques-ultramafiques, massif intrusif stratiforme, Afrique du Sud.

### INTRODUCTION

During an examination of a collection of polished sections of cumulate assemblages at the Institute of Geosciences, University of Oulu, an unusual Cl-rich phase (19.2 wt.% Cl), close in composition to penfieldite [Pb<sub>2</sub>Cl<sub>3</sub>(OH)] was found in a sample (Bu-38A) of

enstatite orthocumulate from the Merensky Reef, Bushveld igneous complex, South Africa. We describe this phase and the associated platinum-group minerals (PGM), one of which is an unknown stannosulfide of Pt. This occurrence is of interest because phases with high concentrations of Cl are very rare in mafic-ultramafic rocks. In addition, the Merensky Reef is well

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known as one of the major deposits of platinum-group elements (*PGE*) in the world, and Cl is considered to have been an important agent in the hydrothermal mobilization and deposition of Pd and Pt in those deposits (*e.g.*, Boudreau *et al.* 1986).

#### SAMPLE DESCRIPTION

The sample characterized in this study is a coarse-grained enstatite orthocumulate taken from the teaching collection at the University of Oulu, enriched in the *PGE*, from the Merensky Reef (specific location not known). It consists mainly of cumulus enstatite (65–70 vol.%), intercumulus plagioclase (*ca.* 20 vol.%) and disseminated base-metal sulfides ( $\leq 5$  vol.%), which are in an intercumulus position. In general, this rock is only slightly altered, although a secondary amphibole after the pyroxene is quite abundant in places. Pyrrhotite is

the main sulfide in this rock, followed by pentlandite, chalcopyrite and pyrite. The accessory minerals include a Cr-rich oxide (probably chromite) and intercumulus phlogopite and quartz.

Results of the wavelength-dispersion electron-microprobe analyses show that the enstatite is relatively enriched in Mg ( $\text{En}_{75-77}\text{Fs}_{21-23}\text{Wo}_{1.4-3.4}$ ; seven analyses). It contains an elevated amount of Cr (0.14 to 0.51 wt.%  $\text{Cr}_2\text{O}_3$ , mean 0.3%), as is typical at the Critical Zone (*e.g.*, Naldrett *et al.* 1986, Naldrett & Von Gruenewaldt 1988, Ballhaus *et al.* 1988, Eales *et al.* 1993). Our analyses of the intercumulus plagioclase ( $n = 4$ ) gave a wide range of the composition:  $\text{An}_{69-44}\text{Ab}_{30-55}\text{Or}_{0.6-1.2}$ . Intercumulus phlogopite (19.6 wt.% MgO) is enriched in Ti (3.5 wt.%  $\text{TiO}_2$ ), Cr (1.3 wt.%  $\text{Cr}_2\text{O}_3$ ) and contains 0.4 wt.% Cl. A similar composition (19.1 wt.% MgO, 4.2 wt.%  $\text{TiO}_2$ , 1.5 wt.%  $\text{Cr}_2\text{O}_3$ , and 0.5 wt.% Cl) was previously reported from the Merensky Reef by Ballhaus & Stumpf (1986). The enrichment in Cl is an important characteristic of intercumulus mica in the Upper Critical Zone, Bushveld complex (Johan & Watkinson 1985).

TABLE 1. CHEMICAL COMPOSITION<sup>§</sup> OF PLATINUM-GROUP MINERALS FROM THE MERENSKY REEF, BUSHVELD COMPLEX

	Brg	Cpr	Rsb	Mon	Mrk-Mon	Lrt core	Lrt rim
Pt wt. %	61.15	85.35	76.33	42.86	23.19	n.a.	n.a.
Pd	17.88	0.58	6.16	n.d.	13.24	n.a.	n.a.
Ni	3.72	0.68	n.a.	n.d.	n.d.	n.a.	n.a.
Ru	n.a.	n.a.	n.a.	n.a.	n.a.	52.18	48.18
Os	n.a.	n.a.	n.a.	n.a.	n.a.	1.25	7.69
Ir	n.a.	n.a.	n.a.	n.a.	n.a.	5.54	6.91
Sn	n.a.	n.a.	18.23	n.a.	n.a.	n.a.	n.a.
Te	n.a.	n.a.	n.a.	53.05	58.46	n.a.	n.a.
Bi	n.a.	n.a.	n.a.	2.05	6.41	n.a.	n.a.
S	17.24	13.40	n.a.	n.a.	n.a.	41.04	37.22
Total	99.99	100.01	100.72	97.96	101.30	100.01	100.00
Pt <i>apfu</i>	0.58	1.00	2.60	1.02	0.49	-	-
Pd	0.31	0.01	0.38	-	0.51	-	-
Ni	0.12	0.03	-	-	-	-	-
Ru	-	-	-	-	-	0.85	0.83
Os	-	-	-	-	-	0.01	0.07
Ir	-	-	-	-	-	0.05	0.06
$\Sigma M$	1.01	1.04	2.98	1.02	1.00	0.91	0.96
Sn	-	-	1.02	-	-	-	-
Te	-	-	-	1.93	1.88	-	-
Bi	-	-	-	0.05	0.13	-	-
S	0.99	0.96	-	-	-	2.10	2.03

Abbreviations: Brg: braggite, Cpr: cooperite, Rsb: rustenburgite, Mon: moncheite, Mrk-Mon: merenskyite-moncheite series, Lrt: laurite. The atoms per formula units (*apfu*) were calculated on the basis of  $\Sigma \text{atoms} = 2$  (braggite and cooperite),  $\Sigma \text{atoms} = 3$  (moncheite, merenskyite and laurite), and  $\Sigma \text{atoms} = 4$  (rustenburgite). n.a.: not analyzed, and n.d.: not detected.

<sup>§</sup> Results of energy-dispersion (EDS) electron-microprobe analyses. The analyses of the Cl-rich phase and associated *PGM* were carried out at 15 kV and 1.7 nA, using a JEOL JSM-6400 scanning-electron microscope equipped with a LINK eXL energy-dispersion spectrometer. Synthetic PbTe, PtTe<sub>2</sub>, KCl and pure elements were used as standards. Counting periods were 100 s, and a finely focused beam (*ca.* 1  $\mu\text{m}$ ) was applied. The spectra were processed by ZAF-4 on-line program. The estimated errors in the EDS analyses of the Cl-rich phase are 0.4 wt.% for Pb and 0.1 wt.% for Cl. Wavelength-dispersion (WDS) electron-microprobe analyses of silicate minerals were carried out using a JEOL-733 electron microprobe. The operating conditions were 15 kV and 15 nA, and the following X-ray lines and standards were used: SiK $\alpha$ , CaK $\alpha$  (wollastonite), MgK $\alpha$  (periclase), KK $\alpha$  (orthoclase), NaK $\alpha$  (jadeite), AlK $\alpha$  (synthetic Al<sub>2</sub>O<sub>3</sub>), TiK $\alpha$  (rutile), FeK $\alpha$ , CrK $\alpha$ , VK $\alpha$ , NiK $\alpha$ , MnK $\alpha$  (pure elements), FK $\alpha$  (BaF<sub>2</sub>), and ClK $\alpha$  (KCl). The raw data were ZAF-corrected on line.

#### PLATINUM-GROUP MINERALS AND THE Cl-RICH PHASE

##### Sulfides of Pt and Pd

The sulfides of Pt and Pd (members of the braggite series and cooperite) strongly predominate over other *PGM* in the mineralized rock from Merensky. These two sulfides occur in a relatively coarse intergrowth (up to 0.5 mm) located at the contact of base-metal sulfides and a silicate mineral (Fig. 1a). A large grain of cooperite (0.2 mm) in Figure 1b occurs between two crystals of cumulus enstatite; this observation implies that the cooperite (and the braggite intergrown with it: Fig. 1a) crystallized after the enstatite. The compositions of the braggite and cooperite are close to being stoichiometric (Pt,Pd,Ni)S and PtS, respectively (Table 1).

##### Rustenburgite and merenskyite-moncheite

Members of the rustenburgite (Pt<sub>3</sub>Sn) – atokite (Pd<sub>3</sub>Sn) and merenskyite (PdTe<sub>2</sub>) – moncheite (PtTe<sub>2</sub>) series form inclusions in the base-metal sulfides and in silicate minerals and occur as tiny grains ( $\leq 10 \mu\text{m}$ ). The rustenburgite, (Pt<sub>2.60</sub>Pd<sub>0.38</sub>) $\Sigma_{2.98}$ Sn<sub>1.02</sub>, is relatively poor in Pd. There are grain-to-grain variations in the amount of Pd and Bi in the merenskyite-moncheite solid solution (Table 1).

##### Zoned laurite

A zoned crystal of laurite, (Ru,Os,Ir)S<sub>2</sub>, *ca.* 10  $\mu\text{m}$  across, was encountered as an inclusion in a silicate mineral. The margin of the grain is enriched in Os (7.7 wt.% Os), whereas the core is poor: 1.3% Os (Table 1).

Kingston (1966) also reported this pattern of zoning in laurite from the Merensky Reef; he found the erlichmanite component ( $\text{OsS}_2$ ) to be enriched in the rim (10 wt.% Os) relative to the core (3% Os). The level of Os enrichment observed in the rim of these two crystals is quite uniform. In contrast, laurite-erlichmanite from placer deposits may show a relative enrichment in Os in the core and Ru in the rim (Cabri *et al.* 1996).

#### Unknown stannosulfide of Pt

A stannosulfide of Pt (Table 2) occurs as submicrometric grains ( $\leq 4 \mu\text{m}$ ), associated with hydrous silicates (Figs. 1c, d) and as minute inclusions in pentlandite. The presence of Pt, Sn and S in this compound is clearly shown by element-distribution maps (Fig. 2). Because

of its small grain-size, this phase, likely a new species of PGM, could not be characterized further.

#### Cl-rich phase

A phase rich in Pb and Cl was found as a small (*ca.*  $5 \mu\text{m}$ ) roundish inclusion in chalcopyrite (Fig. 3). Contents of Pb and Cl in this material (Table 3) are nearly identical to those of well-characterized penfieldite, first described as a product of alteration of lead-rich slag at Lávrión, Attiki, Greece (Genth 1892), and more recently from Baratti, Italy (Merlino *et al.* 1995). Owing to the small grain-size, no X-ray-diffraction data could be obtained. Thus it cannot be excluded that the inclusion is in fact another Pb-Cl-bearing secondary phase, like fiedlerite,  $\text{Pb}_3\text{Cl}_4(\text{OH})\cdot\text{H}_2\text{O}$ , also first discovered at

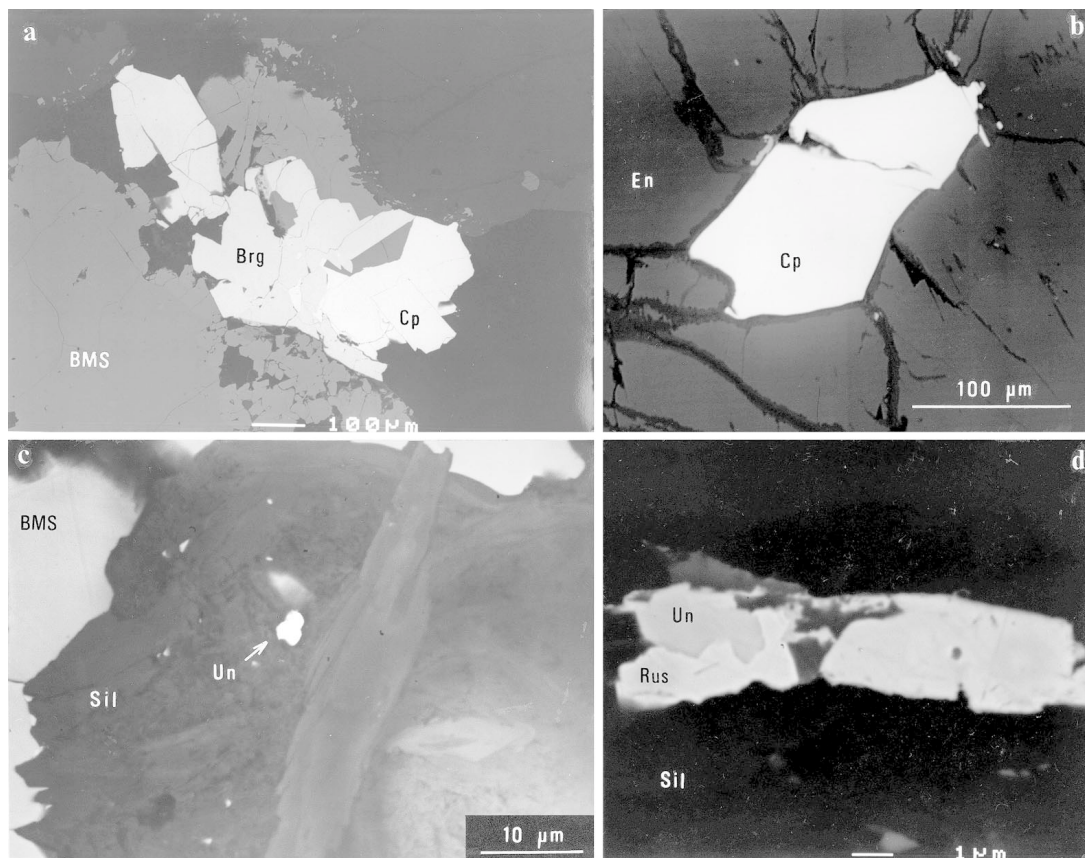


FIG. 1. (a) A relatively coarse intergrowth of braggite (Brg) and cooperite (Cp) located at the contact of base-metal sulfides (BMS) and silicate minerals (black). (b) A grain of cooperite (Cp) located at the border between two crystals of cumulus enstatite (En). (c) A tiny grain of unnamed stannosulfide of platinum (Un) associated with hydrous silicates (Sil). BMS: base-metal sulfides. (d) An intergrowth of the unnamed stannosulfide (Un) with rustenburgite (Rus) located among hydrous silicate minerals (Sil). Back-scattered electron images.

Lávrion. However, we contend that the compositional data reported in Table 3 conform more closely to penfieldite.

## DISCUSSION

### *The platinum-group minerals*

The presence of relatively coarse intergrowths of the Pt–Pd–(Ni) sulfides is indicative of high-grade PGE mineralization. The rock-forming silicate minerals, base-metal sulfides and the PGM (Table 1) display general compositional and textural similarities with those reported from various parts of the Merensky Reef (*cf.* Brynard *et al.* 1976, Schweltnus *et al.* 1976, Vermaak & Hendriks 1976, Kingston & El-Dosuky 1982, Kinloch & Peyerl 1990).

The stannosulfide that we have described here seems to be a new phase in the system Pt–Sn–S. The Pt:Sn:S atomic proportions of the phase are close to 1:1:1 (Table 2), and the likely chemical formula thus is PtSnS. This stannosulfide may correspond to the Pt–Sn–S phase of Hendriks and coworkers (1968–1976) (unpublished

report cited in Cousins & Kinloch 1976), also from the Merensky Reef; the composition of the latter phase was never published, and thus is not available. The stannosulfide from the Bushveld complex clearly differs in composition from a phase related to platinumian berndtite (SnS<sub>2</sub>) grown by a chemical vapor transport, the reported formula of which is (Pt,Sn)S<sub>2</sub>, with the

TABLE 2. CHEMICAL COMPOSITION\* OF UNNAMED STANNOSULFIDE OF PLATINUM FROM THE MERENSKY REEF, BUSHVELD COMPLEX

	Weight %				Atomic proportions ( $\Sigma$ atoms = 3)			
	1	2	3	4	1	2	3	4
Pt	58.20	58.66	57.91	57.90	1.03	1.06	1.06	1.07
Sn	32.61	31.57	32.41	33.41	0.95	0.94	0.98	1.02
S	9.55	9.03	8.64	8.10	1.03	1.00	0.96	0.91
Total	100.36	99.26	98.96	99.41				

\* Results of quantitative SEM / EDS electron-microprobe analyses. See Table 1 for analytical conditions.

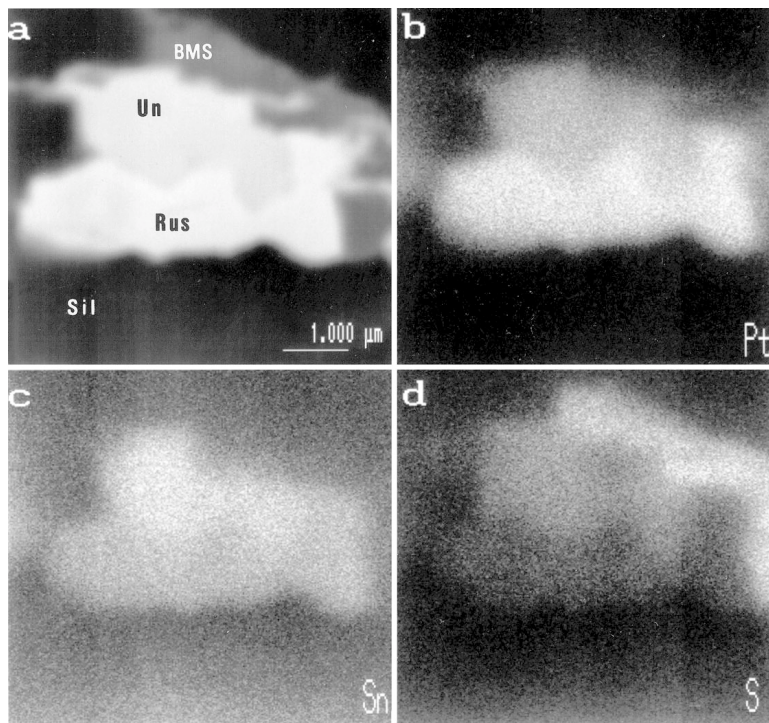


FIG. 2. Back-scattered electron image (a) and X-ray maps for Pt (b), Sn (c), and S (d) of the unnamed stannosulfide of platinum (Un), which is associated with rustenburgite (Rus). Magnification of the intergrowth shown in Figure 1d. BMS: a base-metal sulfide. Sil: a hydrous silicate.

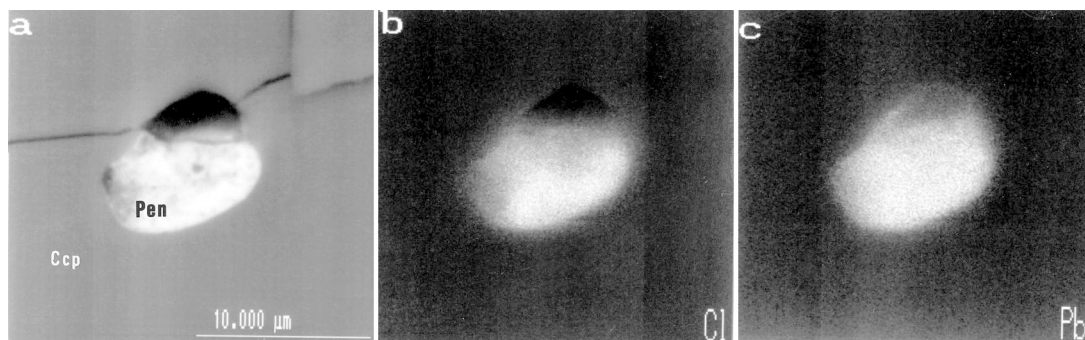


FIG. 3. Back-scattered electron image (a) and X-ray maps for Cl (b) and Pb (c) of the Cl-rich phase close to penfieldite in composition (Pen) from the Merensky Reef. Ccp: host chalcopyrite.

TABLE 3. CHEMICAL COMPOSITION\* OF Cl-RICH PHASE FROM THE MERENSKY REEF, BUSHVELD COMPLEX

	Bushveld, Merensky Reef (this study)	Penfieldite <sup>§</sup> Baratti, Italy	Atom proportions Pb = 2 apfu	
	1	2	1	2
Pb wt.%	78.40	78.41	Pb	2.00
Cl	19.20	19.31	Cl	2.86
F	n.a.	0.09	F	0.03
O	n.a.	3.30**	OH	0.75
H	n.a.	0.21**		1.09
OH*	2.40	—		
Total	100.00	101.32		

\* Results of quantitative SEM/EDS electron-microprobe analysis. n.a.: not analyzed.  
\* Estimated by the difference of the analysis total to 100 wt.%. \*\* Calculated values.  
See Table 1 for analytical conditions. § Merlino *et al.* (1995).

Pt:Sn ratio equal to 1 (Tomm *et al.* 1998). The formula (Pt,Sn)<sub>2</sub>S<sub>2</sub> requires confirmation, however, because Pt and Sn are distinct in terms of their crystal chemistry, and the existence of substitution relationships between these elements is considered highly unlikely. A likely formula for the phase synthesized by Tomm *et al.* (1998) is PtSn<sub>4</sub>S<sub>4</sub>, involving Pt<sup>4+</sup> and Sn<sup>4+</sup> to maintain the charge balance.

#### The Cl-rich phase

The close similarity of composition of the Pb-Cl-rich phases from Bushveld and Baratti (Table 3) suggests that the phase spatially associated with the PGM in the Merensky Reef is penfieldite [Pb<sub>2</sub>Cl<sub>3</sub>(OH)]. Penfieldite is a rare mineral first discovered on the slags of Lávrion, Greece (Genth 1892). There, penfieldite and the associated hydroxy- and oxychloride minerals, like fiedlerite, are the products of corrosion of old slags and ancient Pb-containing objects in the marine environment

(e.g., Merlino *et al.* 1995, and references therein); seawater is believed to have contributed the Cl (Rewitzer & Hochleitner 1989).

Penfieldite is destroyed above 200°C, and laurionite PbCl(OH) is stable with respect to both penfieldite and fiedlerite (Edwards *et al.* 1992, Merlino *et al.* 1995). In addition, various Pb oxychloride phases form under low-temperature conditions. For example, damaraite Pb<sub>4</sub>Cl<sub>2</sub>O<sub>3</sub> is associated with a late-stage vein paragenesis in Mn-rich ore lenses in the Kombat mine, Namibia (Criddle *et al.* 1990), and mendipite, Pb<sub>3</sub>O<sub>2</sub>Cl<sub>2</sub>, and blixite, Pb<sub>2</sub>Cl(O,OH)<sub>2-3x</sub>, are found in a zone of weathering in a Zn-Pb-Ag deposit at Elura, Australia (Scott 1994).

The Cl-rich phase from the Merensky Reef contains 19.2 wt.% Cl (Table 3). This phase is richest in Cl among various Cl-bearing minerals reported from the Bushveld complex: intercumulus chlorapatite (≤7 wt.% Cl: Boudreau *et al.* 1986), mica (up to 1% Cl: Johan & Watkinson 1985), and amphibole (<0.5% Cl: Ballhaus & Stumpfl 1986). Together, these minerals suggest equilibrium with a brine present among the cumulus minerals at a low temperature.

There are a few other occurrences of hydroxychloride phases reported from mafic-ultramafic complexes. These phases are (Fe,Mn)(OH)Cl and Fe<sub>2</sub>(OH)<sub>3</sub>Cl from the Strathcona Deep Copper zone, Sudbury (Springer 1989), a hibbingite-like phase (Dahlberg & Saini-Eidukat 1991) and hibbingite, Fe<sub>2</sub>(OH)<sub>3</sub>Cl (Saini-Eidukat *et al.* 1994), discovered in partially serpentinized troctolite in the Duluth complex, Minnesota. More recently, members of the hibbingite – kempite [Mn<sub>2</sub>(OH)<sub>3</sub>Cl] series have been reported from the Noril'sk complex, Siberia (Saini-Eidukat *et al.* 1998). Interestingly, unnamed Pd-Bi chlorides also were documented at Noril'sk (Karpenkov *et al.* 1981) and Sudbury (Li & Naldrett 1993).

The Cl-rich compound from the Merensky Reef may be a primary hydrothermal phase precipitated from a

late-stage solution rich in Cl. It may also be secondary, formed at the expense of a pre-existing mineral (presumably Pb-rich, like galena), which may have reacted with a low-temperature aqueous hydrochloric solution at a very late stage of hydrothermal alteration. It is unclear whether or not the fractures observed in chalcopyrite (Fig. 3a) existed at a late stage of crystallization of the Merensky Reef. If they did, they may have been open, so that the late-stage Cl-rich solution percolated along these fractures, reacted with the galena (?), and produced the Pb–Cl-rich phase by local dissolution. On the other hand, lead chloride complexes are important in the transport and deposition of Pb by hydrothermal solutions of moderate to high salinity (Seward 1984). Thus, the precursor mineral for the Cl-rich phase was not necessarily Pb-rich, and both the Cl and Pb may have been mobile in the form of Pb chloride complexes, and could have been contributed by the infiltrating solution.

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