Magma Mixing as a Trigger for Sulphide Saturation in the UG2 Chromitite (Bushveld): Evidence from the Silicate and Sulphide Melt Inclusions in Chromite

YAO Meijuan^{1,*}, CAO Ye^{2,*}, LIU Jiajun³ and REN Zongbao⁴

1 School of Atmospheric Sciences, Sun Yat-sen University, Zhuhai 519082, China

2 School of Environment and Energy, Peking University, Shenzhen 518055, China

3 State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing 100083, China

4 Department of Geology & Mining, China National Nuclear Corporation, Beijing 100013, China

Abstract: It is of great importance to understand the origin of UG2 chromitite reefs and reasons why some chromitite reefs contain relatively high contents of platinum group elements (PGEs: Os, Ir, Ru, Rh, Pt, Pd) or highly siderophile elements (HSEs: Au, Re, PGE). This paper documents sulphide-silicate assemblages enclosed in chromite grains from the UG2 chromitite. These are formed as a result of crystallisation of sulphide and silicate melts that are trapped during chromite crystallisation. The inclusions display negative crystal shapes ranging from several micrometres to 100 µm in size. Interstitial sulphide assemblages lack pyrrhotite and consist of chalcopyrite, pentlandite and some pyrite. The electron microprobe data of these sulphides show that the pentlandite grains present in some of the sulphide inclusions have a significantly higher iron (Fe) and lower nickel (Ni) content than the pentlandite in the rock matrix. Pyrite and chalcopyrite show no difference. The contrast in composition between inter-cumulus plagioclase (An₆₈) and plagioclase enclosed in chromite (An₁₃), as well as the presence of quartz, is consistent with the existence of a felsic melt at the time of chromite saturation. Detailed studies of HSE distribution in the sulphides and chromite were conducted by LA-ICP-MS (laser ablation-inductively coupled plasma-mass spectrometry), which showed the following. (I) Chromite contained no detectable HSE in solid solution. (II) HSE distribution in sulphide assemblages interstitial to chromite was variable. In general, Pd, Rh, Ru and Ir occurred dominantly in pentlandite, whereas Os, Pt and Au were detected only in matrix sulphide grains and were clearly associated with Bi and Te. (III) In the sulphide inclusions, (a) pyrrhotite did not contain any significant amount of HSE, (b) chalcopyrite contained only some Rh compared to the other sulphides, (c) pentlandite was the main host for Pd, (d) pyrite contained most of the Ru, Os, Ir and Re, (e) Pt and Rh were closely associated with Bi forming a continuous rim between pyrite and pentlandite and (f) no Au was detected. These results show that the use of ArF excimer laser to produce high-resolution trace element maps provides information that cannot be obtained by conventional (spot) LA-ICP-MS analysis or trace element maps that use relatively large beam diameters.

Key words: HSE, melt inclusion, UG2 chromitite, LA-ICP-MS, Bushveld

1 Introduction

The Bushveld Igneous Complex (BIC) is well known because it is the largest layered mafic-ultra mafic intrusion on Earth and contains the largest reserves of PGEs in the world. It hosts several substantial PGE-bearing chromitite layers, including the UG2, within the Critical Zone. The spatial association between chromitites and PGE enrichment in the BIC has been noted by numerous authors (e.g. Hall et al., 1908; Von Gruenewaldt et al., 1986; Teigler et al., 1993; Barnes et al., 2016). The UG2 chromitite layer, with low volumes of sulphides, contains the world's largest PGE resources. There are several ideas prevalent in the literature that concern the origin of chromitites. These models are divided into two groups: the 'onstage' model and the 'offstage' model. In the 'offstage'

^{*} Corresponding author. E-mail: yaomeijuan1016@126.com; caoye@pkusz.edu.cn

model, the chromite formed outside the portion of the preserved intrusion and was then transported into its present position as a chromite-rich slurry (Eales, 2000; Mondal et al., 2007; Voordouw et al., 2009). In the 'on stage' model, the chromite crystallised in situ (Maier et al., 2008; Naldrett et al., 2012). However, the highly chalcophile nature of PGEs suggests that they partitioned into a sulphide liquid, and therefore, are present in the base metal sulphides (BMSs: pyrrhotite, pentlandite, chalcopyrite and pyrite) formed from this liquid. The relationships among PGEs, chromite and sulphides in the UG2 chromitite layer remains enigmatic. Naldrett et al. (2009) suggested that PGEs are concentrated either as inclusions in the chromite itself or by the collection of immiscible sulphides with the chromite. According to some authors, PGEs may be present in solid solution within the chromite (Capobianco et al., 1994).

In this study, we investigated the sulphide and silicate inclusions in chromite grains from the UG2 chromitite, which record the composition of early-stage melts in the system, because the chromite host prevents further interaction with the rest of the system, allowing the sulphide melt to cool and crystallise within an essentially closed system (Capobianco et al., 1994). We took advantage of recent developments in LA-ICP-MS analysis by 'rastering' areas of interest to produce sequences of parallel closed-spaced, line scans, which were combined using the Iolite software (Ulrich et al., 2009) to produce element distribution maps. Highly siderophile elements were detected in the chromitite, including sulphides interstitial to chromite and sulphide inclusions enclosed within chromite. Sulphide inclusions within chromite were compared with interstitial sulphides to establish whether, and to what extent, interstitial sulphides were later affected by secondary processes (e.g. hydrothermal processes).

2 Mineralisation Background of BIC

The BIC covers an area of about 65 000 km², and these ultra basic and basic rocks intrude into the sedimentary and volcanic rocks of the Transvaal Super group. The BIC comprises four distinctive igneous suites: Rooiberg Group, Rustenburg Layered Suite (RLS), Granophyres and a suite of late Bushveld granites. The Rustenburg suite is preserved in five lobes: the far-western, western, eastern and northern lobes (Fig.1), which may have been connected to each other and linked to a feeder chamber at depth. In addition, there is a little-known fifth southeastern lobe that is obscured by younger sediments (Kinnaird et al., 2002; Naldrett et al., 2012).

The RLS is up to 9 km thick and is subdivided into five zones. The Marginal Zone (0–800 m thick), which consists of norite with minor pyroxenite; the Lower Zone



Fig. 1. Simplified geological map of the Bushveld Complex (after Cawthorn et al., 2006).

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(800–1300 m thick), composed mainly of orthopyroxenite, harzburgites and dunites (Cameron, 1979) and the Critical Zone (1300–1800m thick), which overlies the Lower Zone and is the principal focus of this paper. The base of the Critical Zone is marked by the incoming of cumulus chromite. The zone is divided into two parts (Cameron, 1980, 1982): the Lower Critical Zone, which consists primarily of orthopyroxenites, chromities and some harzburgites, and the Upper Critical Zone, which is marked by the incoming of cumulus plagioclase. The Critical Zone is overlain, by norites, gabbros and anorthosites of the Main Zone (3,000–3,400 m thick), which are themselves capped by ferro-gabbros and ferro-diorites of the Upper Zone (2,000–2,800 m thick) (Molyneaux, 1974).

The chromitite layers occur in the Critical Zone and can be traced along the strike for ~200 km, barring abundant disruptions by potholes, replacement pegmatoids, pipes, dykes and faults (McLaren et al., 1982). The chromitite layers are divided into the Lower, Middle and Upper Groups. Chromitite seams of the Lower Group occur entirely within the Lower Critical Sub-zone, those of the Middle Group straddle the contact between the Lower and Upper Critical Sub-zones and those of the Upper Group are contained within the Upper Critical Sub-zone. The Dwaars River chromitites comprise a UG2 seam that lies~125 m above the UG. The UG3 chromitite seam is only sporadically developed throughout Bushveld and is absent from the Dwaars River area. The UG2 Reef is a platiniferous chromititc layer, and depending on the geographic location within the BIC, it is evident $\sim 20-400$ m below the Merensky Reef. The chromitite is usually 1m thick, but the thickness can vary from 0.4 to 2.5 m.

3 Samples and Methods

The samples analysed were a sub-set of the samples documented in Naldrett et al. (2012). A 60cm core of the UG2 chromitite reef was sampled at the Waterval shaft and sliced at 3cm intervals. The resulting samples were labelled UG2-1-1 to UG2-1-21 from top down. Microprobe analyses of the chromite showed that the Pt content ranged from 500 to 10000 ppb (Naldrett et al., 2012). Representative samples were mounted in a standard 2.5 cm epoxy holder and polished. The areas of interest were then analysed with a JEOL JSM-6400 scanning microprobe equipped with an Oxford Instruments INCA EDS system (Central Analytical Facility, Laurentian University). Images of several potential targets were taken to help identify the phases in the produced LA-ICP-MS maps.

LA-ICP-MS analyses were conducted at the Chemical

Fingerprinting Laboratory, Laurentian University. Highresolution maps were created using a beam diameter of 5-10µm and ablated speeds of half the beam diameter (e.g. 2.5µm/s for a 5µm beam diameter). We used an ArF excimer laser with a wavelength of 193nm, coupled to a quadrupole ICP-MS. The laser was fired at a fluency of \sim 10J/cm², with a repetition rate of 5 Hz. The masses of the isotopes³³S, ⁵²Cr, ⁵⁷Fe, ⁵⁹Co, ⁶⁰Ni, ⁶⁵Cu, ¹⁰¹Ru, ¹⁰³Rh, ¹⁰⁵Pd, ¹²⁵Te, ¹⁸⁷Re, ¹⁸⁹Os, ¹⁹⁰Os, ¹⁹³Ir, ¹⁹⁵Pt, ¹⁹⁷Au and ²⁰⁹Bi were analysed using Po725 and NIST 610 as the standard. The Iolite software processed the data by combining parallel adjacent line scans into trace element distribution maps and trace element concentrations in time-resolved spectra (Ulrich et al., 2009). The major chemical elements present in the sulphides and silicates were detected using an electron microprobe at Geosciences Laboratories under the analytical conditions of 20 kV and 30 nA. The internal standard used for the calculation of PGE content was ⁵⁷Fe.

4 Results

The UG2 chromitite layer is composed of chromite, silicates, BMS and numerous platinum group mineral (PGM) species. Chromite grains have an average diameter of ~0.1mm with smooth grain margins. The silicates mainly consist of orthopyroxene, plagioclase and phlogopite. The sulphides interstitial to chromite grains are mostly pentlandite, chalcopyrite, minor pyrite and millerite, but pyrrhotite is absent.

4.1 Inclusions within chromite

Melt inclusions are observed within chromite grains, some of which are the sulphides of a typical magmatic assemblage: pyrrhotite, pentlandite and chalcopyrite. Some pentlandite/pyrrhotite inclusions may have contained other phases that were not exposed on the polished surface. Some sulphide inclusions are attached to the following silicates: orthopyroxene, mica, amphibole, plagioclase, rutile and rarely quartz, apatite and zircon (Fig. 2). Hornblende is the amphibole present in these inclusions. The inclusions display negative crystal shapes ranging in size from several micrometres to 100 µm. One of the sulphide inclusions (Fig. 3) in chromite, up to 80µm in diameter, contains pyrrhotite, chalcopyrite, pentlandite and pyrite. When chalcopyrite and pentlandite inclusions were detected they always have smaller diameters. Millerite is a nickel-rich sulphide, which is also associated with chalcopyrite inclusions.

4.2 Electron microprobe analysis data

The major elements of the silicates and sulphides are analysed. The data show that inclusions of hornblende are





Fig. 2. Backscattered images of silicate and sulphide melt inclusions in chromite.

Sulfide assemblages found within chromite consisted of chalcopyrite and pentlandite, usually together (Fig. 2a, c-top right, 2d). In some cases millerite was observed (Fig. 2b). Complex sulfide-oxide-sulfide assemblages (Fig. 2e and 2f) are also observed.

(ccp: chalcopyrite, chr: chromite, cpx: clinopyroxene, phl: phlogopite, pl: plagioclase, pn: pentlandite, rt: rutile)



Fig. 3. Complex sulfide assemblage found in a chromite grain. This assemblage consisted of pyrrhotite (po), pentlandite (pn), pyrite (py), and chalcopyrite (ccp) in chromite.

(a and b) are backscattered electron (BSE) and reflected light images of the chromite host and the inclusion. No cracks were detected on the polished surface. (c) is a laser ablation ICP-MS map of major and trace element distribution in the sulfide assemblage. The transition elements on the top row (Fe, Co, Ni,Cu) can be used bo map the extent of the four sulfide phases present (po, py, pn, ccp, respectively). The two most significant aspects are: (1) The partitioning of Ru, Os, and Ir into pyrite, Rh into ccp, and Pd, into pn; (2) The presence of Pt as a bismuthide phase along the pn-py grain boundary, which cannot be detected on the BSE or reflected light images. Gold was below detection limit as well as Te (an important ligand for HSE along with Bi).

characterised by a high Mg content. The most abundant amphibole inclusions are magnesio-hornblende and edenitic-hornblende with less tremolitic-hornblende, edenite and magnesio-hastingsitic-hornblende. Phlogopite is the main mica present and is characterised by low F and Cl concentrations. There is no compositional variation between the phlogopite inclusions and the phlogopite in the matrix. The plagioclase inclusions are distinctly more salic than those in the rock matrix. The plagioclase inclusions range in composition from $An_{6.2}$ to $An_{20.8}$, whereas in the rock matrix, the composition is $An_{59.0}$ to $An_{75.7}$ (Table 1). The orthopyroxene inclusions range from $En_{87.6}$ to $En_{90.3}$, whereas the orthopyroxenes in the rock matrix range from $En_{85.1}$ to $En_{87.7}$ (Fig. 4 and Table 2). The electron microprobe data of the sulphide inclusions (Tables 3 and 4) show that pentlandite has a significantly higher Fe and lower Ni content than pentlandite present in the rock matrix (Table 4). The electron microprobe data of pyrite and chalcopyrite show no difference between the inclusions and rock matrix.

4.3 LA-ICP-MS analysis

We investigate the distribution of HSEs in the sulphide assemblages and chromite grains. The major element maps (Ni, Cu, S, Cr) allow for the identification of the major phases (pentlandite, chalcopyrite, pyrite and chromite) of the interstitial assemblages. No PGMs are observed or detected in the chromite grains analysed. The most common sulphide assemblage is chalcopyrite and pentlandite (Fig. 5) in this chromitite layer. Cobalt, Pd and Ir occur in solid solution in the pentlandite inclusions. Rhodium (Rh) and Pd distribution in pentlandite is roughly similar with notable exceptions. The larger pentlandite grain (right) does not contain as much Rh as the small grain (left of the image). The Rh distribution in the larger grain is not uniform, and higher concentrations of Rh occur along the grain boundary. Ruthenium (Ru) content in pentlandite is also irregular. Some discrete Pt-Bi phases (likely alloys) are present along the pentlandite grain boundary. Au, Os and Re are not detected in this assemblage.

The element images of the four-phase sulphide inclusion (Fig. 3) show that pyrrhotite does not contribute significantly to the bulk HSE. Rhodium is the only element present in chalcopyrite. Pentlandite is the dominant host for Pd. The elements Ru, Os, Ir and Re are concentrated in pyrite. Platinum, along with Rh, appears as a rim between pyrite and pentlandite, and is associated



Fig. 4. Comparison of the compositions of orthopyroxene in inclusions and outside.

with Bi. Gold is not detected in the sulphide inclusion. Cobalt occurs dominantly in pyrite but is also present in pentlandite.

The interstitial sulphide assemblage (Fig. 6a and b) of the minerals pyrite, pentlandite and chalcopyrite is contrasted with the four-phase sulphide inclusion (Fig. 3). Palladium, Rh and Ru mainly concentrate in pentlandite, and the only HSE present is Pd, which occurs dominantly in pentlandite. Chalcopyrite also contains some Pd. Rhodium concentration in pentlandite is still irregular. The top part of the inclusion has higher content of Rh than the bottom part. Ruthenium is present in both pentlandite and pyrite. Iridium is mainly present in pyrite. Platinum, Bi and Te match well with neither pyrite nor pentlandite, and are more commonly present between the pyrite and pentlandite grain boundaries. Some discrete Au is present on the sulphide grain boundary. No Os and Re are detected in this area.

The secondary pyrite (Fig. 6c and d) present in the chromitite does not contain PGEs. There are some small pentlandite grains (top right) and chalcopyrite grains (bottom right). Rhodium and Pd mainly concentrate in

 Table 1 Comparison of plagioclase composition inside (wt%) inclusions and in matrix

		_								
		SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	Total	Ab	An	Or
enclosed	UG2-1-1(1)	66.02	20.47	1.36	11.05	0.39	99.28	91.6	6.2	2.1
	UG2-1-4 (2)	68.64 (3.58)	19.43 (2.34)	1.94 (0.65)	9.86 (1.06)	0.10 (0.03)	99.98	89.8 (2.1)	9.6 (2.0)	0.6 (0.1)
	UG2-1-18 (2)	65.84 (0.14)	21.62 (0.02)	2.64 (0.06)	10.47 (0.19)		100.57	87.7 (0.3)	12.2 (0.4)	
	UG2-1-21 (3)	63.70 (0.63)	22.48 (0.83)	3.82 (0.65)	9.65 (0.22)		99.65	82.0 (0.3)	17.7 (3.1)	
interstitial	UG2-1-1 (9)	50.04 (0.54)	31.43 (0.29)	14.88 (0.43)	3.18 (0.22)		99.53	29.4 (3.6)	70.3 (3.8)	
	UG2-1-4 (3)	50.85 (0.32)	30.80 (0.20)	14.12 (0.23)	3.60 (0.15)	0.11 (0.01)	99.48	31.4 (1.3)	68.0(1.3)	0.62 (0.04)
	UG2-1-21 (5)	52.91 (0.27)	29.28 (0.23)	12.46 (0.19)	4.34 (0.09)	0.29 (0.02)	99.28	38.0 (0.8)	60.3 (0.8)	1.7 (0.1)
enclosed	average	65.76 (2.48)	21.25 (1.64)	2.75 (1.07)	10.08 (0.67)		99.84	86.6 (4.4)	12.9 (4.8)	
interstitial	average	51.03 (1.36)	30.69 (1.00)	14.03 (1.13)	3.59 (0.55)	0.13 (0.12)	99.48	31.5 (4.8)	67.9 (5.5)	0.7 (0.7)
enclosed	range	62.97-71.18	17.78-23.39	1.36-4.51	9.11-11.05			78.8-91.6	6.2-20.8	0-2.1
interstitial	range	49.24-53.21	29.04-32.07	12.18-15.62	2.77-4.49	0.02-0.31		24.3-39.4	59.0-75.7	0-1.8

The data of average and range is for all the analyzed data.

every HSE analysed in our experiment.
The detection limits and sensitivity of LA-ICP-MS
analyses are calculated using counts per second on a
Po725 standard. The standard NIST 610 is used to detect
Rhenium (Re) (Table 5). The absolute concentration data
show that the chromite analysed does not contain
detectable HSE in solid solution (Table 6). Ruthenium
(Ru) content is highest in pyrite (20.28 ppm). Rhodium
(Rh) occurs in chromite but not in pentlandite, and Rh
content is very high in the surrounding area (up to 2509.79
ppm). A pyrite grain that is intergrown with pentlandite,
has a high Rh content, and an inclusion between the
boundary of pentlandite and pyrite also had a high Rh

2.3-14.9

85.1-87.

9.7-12.4

1.2(0.9)

85.8(0.9) 89.3(0.8) 86.4(1.0) 87.6-90.3

9.31(0.56)

100.85 100.46

87.4(0.2)

(1.1(0.3))0.0(0.2) .7(0.4)2.6(0.2) 0.7(0.8)3.6(1.0)

> 90.0(0.2) 88.3(0.4)

88.9(0.3) 89.2(0.2

100.92 100.23 101.01 100.76 100.73 100.33

6.83(0.18)

0.10(0.18)

0.33(0.10)

34.33(0.23)

0.95(0.10)

33.40(1.16)

.28(0.13) .46(0.03) 90(0.23) 8.35(0.18) 7.26(0.50) 99(0)66 6.55-8.27 8.15-9.81

0.11(0.19)

0.171(0.004) 0.16(0.01) 0.17(0.01)

0.17(0.02)0.26(0.05)

33.71(0.29)

.27(0.21)

.21(0.33) 0.54(0.22)

0.54(0.02)

0.51(0.04)

0.084 (0.005) 0.09 (0.02)

57.68 (0.30)

57.8 (0.65)

0.14(0.01)

56.86 (0.55)

UG2-1-1 (3) UG2-1-4 (2)

enclosed

SiO₂

0.00 0.00

픱

Total

FeO

Fe₂O₃

MnO

CaO

NgO

Cr₂O₃

 Al_2O_3

10.8(0.2)

grain that is intergrown with pentlandite, content, and an inclusion between the ntlandite and pyrite also had a high Rh content. Palladium is ubiquitous mostly in solid solution in pentlandite. The Pd distributions inside and outside chalcopyrite are very similar, with a maximum of 48.62 ppm (Table 7).

pentlandite. Chalcopyrite has less Rh than pentlandite. A PGM grain occurring close to pentlandite contains almost

5 Discussion

The sulphide assemblages that are interstitial to chromite grains are mainly pentlandite, chalcopyrite, minor pyrite and millerite in the UG2 chromitite. The dominance of pentlandite and chalcopyrite, the presence of pyrite and the lack of pyrrhotite, all indicate that the sulphide mineralogy in this chromitite layer cannot represent a primary magmatic assemblage (Merkle, 1992). Naldrett et al. (2009) suggested that the present assemblage would not have existed at the time of the formation of the chromitite, and the pyrite must have formed because of loss of Fe to the chromitite, accompanied by a significant rise in f_{s_2} .

5.1 HSE distribution in the sulphide

The HSE distribution in the sulphide assemblage assists in understanding the processes of PGE redistribution in mono-sulphide solid solution (MSS). The UG2 chromitite samples analysed in this study show that Pd is enriched in pentlandite instead of chalcopyrite. This result concurs with the present sample set from the BIC (Osbahr et al., 2013, 2014) as well as the results from other layered intrusions (e.g. Dare et al., 2010). The enrichment of Pd in pentlandite of MSS origin cannot be explained by sulphide fractionation alone, because it is an incompatible element. Dare et al. (2010) studied samples from the Sudbury Complex and suggested that the Pd enrichment in pentlandite is caused by diffusion of Pd into the pentlandite from the nearby Cu-rich portion (intermediate solid solution and/or Pd-bearing PGM). They also believed that a small quantity of Pd originated from the Pd

Table 2 Comparison of orthopyroxene composition (wt%) inside inclusions and in matrix

0.00-0.58 0.19(0.17) 0.06(0.14)0.67(0.18)0.35(0.29) 0.00-0.86 0.19(0.01)0.20(0.01) 0.23(0.02) 0.17(0.02)0.22(0.02)0.19 - 0.250.14-0.2 0.83(0.14) 0.27(0.05)0.70(0.04)(89(0.13))0.28(0.09)0.15-0.48 0.67-1.07 32.55(0.10) 33.54(0.45) .70(0.39) 33.93(0.56) 32.58-34.63 31.27-32.65 31.99(0.53) 0.86(0.26) 0.62(0.04)0.40(0.02) 0.38(0.03) 0.39(0.03) 0.53-1.43 0.35-0.44 .36(0.06) 35(0.05) (0.33)35(0.05) 0.71(0.27)0.35-1.53 28-1.430.10 (0.03) 0.09 (0.02) 0.16 (0.02) 0.13 (0.02) 0.14 (0.03) 0.10-0.19 0.04-0.16 57.5 (0.47) 55.97-56.63 56.33 (0.33) 56.14(0.16) 56.20 (0.23) 57.42 (0.40) 56.42-58.27 UG2-1-18 (10) UG2-1-21 (6) JG2-1-21 (6) <u>UG</u>2-1-4 (3) average average range interstitial interstitial nterstitial enclosed enclosed

he data of average and range is for all the analyzed data

9	1		()			
	S	Fe	Ni	Cu	Co	Total
interstitial						
ccp (n=19)	35.04 (0.21)	30.38 (0.32)		34.50 (0.97)		99.92
pn (n=26)	33.20 (0.30)	24.65 (0.81)	40.49 (1.52)		0.82 (0.57)	99.17
py (n=13)	53.26 (0.20)	46.29 (0.60)				99.55
enclosed						
ccp (n=13)	34.53 (0.71)	29.77 (0.70)		33.95 (0.62)		98.24
pn (n=10)	33.25 (0.23)	27.83 (3.52)	37.84 (3.27)		0.34 (0.16)	99.25
py (n=3)	53.56 (0.45)	44.93 (0.23)			1.59 (0.16)	100.08
po (n=3)	39.67 (0.11)	59.83 (0.06)	0.36 (0.05)	0.03 (0.01)		99.89
mil (n=2)	34.57 (0.66)	2.78 (0.05)	59.42 (1.36)			96.77

 Table 3 Average composition of sulfides in the UG2 chromitite (in wt%)

ccp: chalcopyrite; pn: pentlandite; po: pyrrhotite, py: pyrite; mil: millerite; (n): number of analysis

Table 4 Comparison of the composition of pentlandite in inclusions and the matrix

	UG2	-1-4	UG2-1-1	8	UG2	-1-20
(wt%)	int (6)	enc (4)	int (2)	enc (1)	int (4)	enc (4)
S	33.35 (0.30)	33.31 (0.23)	33.02 (0.15)	33.13	33.08 (0.18)	33.13 (0.17)
Fe	25.16 (0.37)	23.84 (0.05)	23.46 (0.24)	29.62	23.95 (0.08)	31.15 (0.23)
Ni	40.45 (1.18)	41.57 (0.52)	42.01 (0.12)	36.16	42.06 (0.26)	34.90 (0.08)
Co	0.61 (0.31)	0.51 (0.06)	0.81 (0.02)	0.25	0.72 (0.02)	0.26 (0.002)
Apfu (ave)						
S	8.00	8.00	8.00	8.00	8.00	8.00
Fe	3.46	3.28	3.26	4.10	3.32	4.31
Ni	5.27	5.42	5.53	4.74	5.52	4.58
Co	0.08	0.07	0.11	0.03	0.10	0.04
Ni [#]	0.60	0.62	0.63	0.54	0.62	0.52

Int: interstitial; Enc: enclosed in chromite; $Ni^{\#} = Ni/(Ni+Fe)$; (n): number of analysis

Table 5 Detection limits and sensitivity of LA-ICP-MS analyses

	Ru	Rh	Pd	Re *	Os	Ir	Pt	Au
5 μm beam diameter								
Sensitivity (CPS/ppm)	137.26	142.79	160.58	242.84	197.12	192.31	123.81	74.11
Detection limit (ppm)	2.13	1.04	6.14	0.30				
10 µm beam diameter								
Sensitivity (CPS/ppm)	486.17	486.17	524.62	992.13	827.23	778.27	415.96	267.86
Detection limit (ppb)	560	230	1570	58.28		6.57	21.89	14.93

*Sensitivity calculated using CPS on Po725 standard, except for Re, for which CPS on NIST 610 was used.

Table 6 PGE concentration in chromite (ppm)

			UI /						
chromite	n		Ru	Rh	Pd	Os	Ir	Pt	Au
UG2-1-4 (10 μm)	55	ave		22.37	2.73		0.30	0.38	0.01
		stdev		26.95	2.50		0.54	0.59	0.01
		Range	bdl	bdl-94.31	bdl-10.69	bdl-0.01	bdl-2.82	bdl-2.28	bdl-0.04
UG2-1-6 (10 μm)	142	ave		0.28		0.02	0.05	0.29	0.02
		stdev		0.78		0.11	0.32	1.25	0.05
		Range	bd1-3.65	bdl-8.26	bdl-32.57	bdl-1.12	bdl-3.6	bdl-8.75	bd1-0.39
UG2-1-20 (5 µm)	87	ave		0.78	1.80	0.02	0.06	0.02	0.02
		stdev		2.48	2.64	0.08	0.21	0.09	0.05
		Range	bdl	bdl-20.9	bdl-16.4	bdl-0.44	bdl-1.31	bdl-0.49	bdl-0.34

that had originally partitioned into the MSS. Dare et al. (2010) further noted that the source of Pd is depleted during the diffusion process and that the later-forming veinlets and flames of pentlandite contained less Pd than the earlier formed coarse-granular pentlandite. This study reveals high Pd concentrations (215–1387 ppm) in different pentlandite grains, including sulphide inclusions, which suggests that the partitioning of large amounts of Pd into MSS occurred during an earlier magmatic stage (Osbahr et al., 2013). In the chalcopyrite-pentlandite assemblage, iridium is present in solid solution in the pentlandite, but when pentlandite is associated with primary pyrite, iridium goes into the pyrite. This shows that pyrite, which is a common sulphide in the UG2 chromitite layer, plays an important role in the HSE

mineralisation process, but the crystal process is still unsolved (Barkov et al., 1997; Tang et al., 2009; Lorand, 2010; Dare et al., 2010; Chai et al., 2013).

The high-resolution LA-ICP-MS element maps reveal geochemical information that cannot be obtained with conventional laser-ablation spot analysis, and these maps have definite advantages in resolving geochemical details and phase boundaries in hetero-geneous samples when compared to single-spot analyses. More importantly, the maps clearly show that single-spot analyses can lead to erroneous conclusions about the distribution of elements in such samples (Ulrich et al., 2009). However, the relative content, shown on a colour scale, can lead to some misunderstanding because sometimes different concentrations have the same element distribution colour.

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Fig. 5. Sulfide assemblage found in UG2 chromitite (1). This assemblage consists of chalcopyrite (ccp) and pentlandite (pn). (a) is the backscattered electron (BSE) image of this area; (b) is a laser ablation ICP-MS map of major and trace element distribution in the sulfide assemblage. Cobalt, Pd, Ir mainly distributed in solid solution in pentlandite. The bigger pn grain (right) does not contain as much Rh as the small grain (left of the image). And the Rh distribution in the larger grain is not uniform, the boundary has higher concentration. Ruthenium in pn is not uniform. Some discrete Pt-Bi phases (likely alloys) are present in the boundary of pentlandite. No Au, Os and Re are detected in this assemblage. The transition elements on the top row (Ni, Cu) can be used to map the extent of the sulfide phases present (pn, ccp). the presence of Pt as a bismuthide phase along the pn-py grain boundary, which cannot be detected on the BSE or reflected light images. (c and d) are the time-resolved intensity of the scan line (showed in Figure 5.a). (c) showing the partitioning of Rh, Pd, Ir and Ru into the pentlandite. (d) showing the intensity change of Ni and Cu as the laser ablated pentlandite and chalcopyrite.

The most typical example is that Pd always has the same colour as Ni, but in fact their contents are quite different. The absolute concentration calculation is necessary to help understand the HSE distribution; it shows that pyrite is an important host of Ru and that the Pd content in the chalcopyrite is stable. Rhodium is concentrated in variable amounts even in the same sulphide. In the sulphides, Pd concentration occurs in the following amounts: Pentlandite >> Chalcopyrite > Pyrite > Pyrrhotite.

5.2 Relationship between Chromite and PGEs

Two principal models have been proposed to explain the association of high PGE content within chromitite layers (Cawthorn, 1999). The first model considers that PGEs are present in solid solution in the chromite and that there is a chemical affiliation between these minerals (Capobincao et al., 1994). The second model proposes that PGMs are present as inclusions in chromite grains (Gijbels et al., 1974; Merkle, 1992; Guo et al., 2016; Sun et al., 2015). This study investigates how PGEs are distributed in the UG2 chromitite reef. The results do not detect PGEs in solid solution within chromite. Some sulphide inclusions, such as the four-phase inclusion (Figs. 2 and 3), which are observed within chromite grains, show that they are PGEconcentrated, but PGMs are not detected within these sulphides. This may be due to the size of the PGM inclusions, as researchers such as Wirth et al. (2013) found nanometre-sized PGMs in BMS. There have been numerous studies on PGMs that are not included within the chromite (Voordouw et al., 2010), and they always occur together with sulphides or beside them. This shows that sulphides also play an important role in the



Fig. 6. Sulfide assemblage found in UG2 chromitite (2). This assemblage consists of chalcopyrite (ccp), pyrite (py) and pentlandite (pn).

(a), the backscattered electron (BSE) image of (b); (b), a laser ablation ICP-MS map of major and trace element distribution of figure 6.a. The transition elements on the top row (Ni, Fe, Cu) can be used to map the extent of the sulfide phases present (pn, py, ccp). Palladium, Rh and Ru mainly concentrated in pn. Chalcopyrite also has some Pd. Rhodium in pn is still not uniform. The top part has higher content than the bottom part. Ruthenium not only present in pn but also in pyrite. Iridium mainly present in py. Platinum, Bi and Te neither match well with py nor pn, they more likely present between their boundaries. Some discrete Au is present in the sulfide grain boundary. No Os and Re be detected in this area. (c and d), the secondary py present in the chromitite shows that no PGE present in it. (c), the backscattered electron (BSE) image of (d). There are some small pn grains in the right top part and ccp grain in the right bottom. Rhodium and Pd mainly concentrated in pn. Chalcopyrite has Less Rh. A PGM grain beside pn almost has every HSE that analyzed in our experiment.

concentration of PGEs in the UG2 chromitite. Chromite is not a suitable mineral for solid substitution of PGEs, although PGEs may have a role in the mechanical settling out of refractory metals (Barnes et al., 1985). LA-ICP-MS analyses of some of the sulphide assemblages reveal that the sulphides included in chromite contain significant amounts of PGEs (e.g. the four-phase sulphide inclusion contains 250-860 ppm Pd in pentlandite). This is comparable with Pd content in whole sulphide inclusions (homogenised and unhomogenised) in the Platreef (Holwell et al., 2011), which range between 40 and 700 ppm in size. Therefore, our observations also support the notion of early, PGE-rich sulphides for PGE mineralisation in the BIC.

5.3 Melt inclusions in chromite

The sulphide inclusions trapped within the earliest phase of chromite crystallisation indicate a very earlystage sulphide liquid in the system, as they cooled and fractionated within a system that was essentially closed. Inclusions in chromite were documented by Li et al. (2005), Spandler et al. (2005) and Holwell et al. (2011) using samples from the Merensky Reef (BIC), the Stillwater Complex (USA) and the Platreef (BIC), respectively. However, the mineral assemblages documented by Li et al. (2005) and Spandler et al. (2005) consist only of silicates (no sulphides), whereas the samples documented by Holwell et al. (2011) consist only of sulphides (no silicates).We investigate the sulphideOct. 2017

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silicate assemblages in chromite in the UG2 chromitite, and the results provide unique evidence of the coexistence of sulphide and silicate melts at the time of chromite crystallisation. The morphology of the included sulphide droplets implies that when the inclusions are trapped by the crystallising chromite, they remain liquid as the chromite crystallises. Small chalcopyrite and millerite inclusions may occur because of the trapping of two separate sulphide liquids, one of which is Cu-rich and the other is Ni-rich. The results of the ablation of the inclusions reveal that they are very PGE rich. This shows that the initial magmatic sulphide present within the UG2 magma was already highly enriched in PGEs.

There is more Rh in chalcopyrite inclusions than with in pentlandite inclusions, but in the rock matrix, pentlandite contains more Rh than chalcopyrite. This implies that the sulphides in the rock matrix have been modified by hydrothermal fluids and/or fluid-rich melts that infiltrated during the crystallisation of the UG2 (Voordouw et al., 2010) and these processes may some sulphides remove that are responsible for the PGMs (Naldrett et al., 2009). The PGE distribution in pyrite is not uniform. The primary pyrite that is (Fig.2) associated with pentlandite contains some PGEs, including Os, Ir, Ru and Re, but the pyrite that is not associated with pentlandite has no PGEs (Fig. 5). This also provides good evidence for the modification.

5.4 Formation of the chromitite

Several models have been proposed for chromitite formation. One model proposes that chromite and orthopyroxene have crystallised in a staging chamber in cotectic proportions, and then have been winnowed out from the orthopyroxene– chromite–magma mixture during their subsequent introduction to the Bushveld chamber, with chromite spreading out across the cumulate–magma interface as a slurry. Eales (2000) proposed this model and calculated that the volume of magma

		d	u			foo				py		od
		Interstitial		enclosed		Interstitial		enclosed	Interstit	tial	enclosed	enclosed
ample	UG2-1-4	UG2-1-6	UG2-1-20	UG2-1-20	UG2-1-4	UG2-1-6	UG2-1-20	UG2-1-20	UG2-1-4	UG2-1-6	UG2-1-20	UG2-1-20
u	26	14	53	27	17	41	29	14	12	136	Π	6
Ru												
ave	9.47	10.00		3.92		19.09			20.28	0.72	6.99	
stdev	2.74	9.25		2.45		118.37			11.13	2.09	2.76	
Range	2.53-14.83	1.35-35.13	lþd	bdl-10.95	bdl-0.71	bdl-758	lbd	lbd	12.10-52.04	bdl-18.42	3.92-12.87	lbd
Rh												
ave	2509.79	142.87	308.72	1.94	26.27	14.88	20.74	15.72	1952.35	1.08	1.42	
stdev	1162.75	108.35	159.92	1.97	5.27	4.01	2.38	1.53	1596.99	4.93	0.8	
Range	398.34-4635	34.27-454.10	140-785.35	bdl-9.15	21.41-45.19	6.83-23.06	16.98-27.41	bdl-18.31	531.69-5927.75	bdl-28.67	bdl-3.17	bdl-1.35
Ъd												
ave	215.61	961.53	1387.56	856.72	48.62	33.26	48.33	45.45	152.25	2.98	15.68	20.22
stdev	48.77	347.35	238.12	249.24	3.76	26.03	15.27	40.02	151.38	9.41	11.9	35.83
Range	71.07-312.71	299.88-1551.42	533.56-1906.41	234.6-1345.04	44.58-59.85	13.96-189.63	33.81-99	bdl-183.06	14.37-502.28	bdl-53.54	bdl-34.70	bdl-113.79
Os												
ave		2.66	0.01	0.58		0.1	0.01	0.05	0.01	0.04	1.62	0.07
stdev		2.87	0.06	0.86		0.33	0.04	0.13	0.01	0.13	1.01	0.13
Range	bdl-0.08	0.13-8.57	bdl-0.38	bdl-3.28	bdl-0.02	bdl-1.90	bdl-0.19	bdl-0.46	bdl-0.04	bdl-0.81	0.28-3.36	bdl-0.39
lr												
ave	22.3	5.07	24.07	0.28		0.08	0.13	0.11	71.97	0.11	0.64	0.02
stdev	34.93	7.81	8.19	0.46		0.26	0.14	0.28	74.32	0.28	0.41	0.05
Range	0.18 - 124.84	0.69-28.76	4.38–55.15	bdl-1.64	bdl-0.05	bdl-1.44	bdl-0.56	bdl-0.76	17.31–288.47	bdl-1.96	0.24 - 1.69	bdl-0.15
Pt												
ave	26.1	429	13.98	2.98	0.13	6.37	0.51	0.04	171.34	1.04	2.92	0.25
stdev	28.78	1525.93	26.14	3.9	0.28	40.26	0.7	0.11	132.12	3.02	3.29	0.53
Range	0.33-103.82	1.04-5508	0.72-131.89	0.23 - 15.64	bdl-1.04	bdl-257	bdl-3.05	bdl-0.39	61.65-544.13	bdl-25.91	0.04 - 10.86	bdl-1.50
Αu												
ave	0.09	0.05	0.06	0.09	0.25	0.17	0.06	0.01	0.25	0.07	0.07	
stdev	0.15	0.12	0.17	0.19	0.25	0.34	0.06	0.03	0.14	0.16	0.2	
Range	hdl_0 56	Pd1 0 13	P41 0 00	FALO 7	10 05	1 1 2 1 1 2 2	1. 41 0 10	1-11 0 11	31000	1-11-1-04	5 U IF 1	

responsible for the chromite in the Critical Zone must have been 12 times the volume of the Zone itself. Mondal and Mathez (2007) showed that the Cr contents of orthopyroxene, above and below the UG2 chromitite, were very similar. Voordouw et al. (2009) described intrusive relationships between the chromitites (particularly the UG1) and enclosing rocks, which favoured the proposal that the chromite was introduced as a slurry. The forming of the chromitite layer requires chromite to be the sole liquid phase, and there have been many suggestions on how to achieve this, such as increasing f_{s_2} (Ulmer, 1969; Cameron et al., 1964) or increasing the pressure (Sen et al., 1984; Lipin, 1993). Irvine (1975) suggested that magma in the intrusion mixed with a felsic melt that existed at the top of the intrusion and that the hybrid initially had chromite as the sole liquidus phase. Kinnaird et al. (2002), Nex (2004) and Kottke-Levin et al. (2009) agreed with this mechanism.

The melt inclusions represent samples of the melt responsible for chromite crystallisation. The presence of the sodium-rich plagioclase provides additional evidence for the involvement of the mafic melt during the formation of chromite. The Mg-rich orthopyroxene and Mg-rich amphibole suggest that the existence of a high-Mg basaltic magma. The sulphide-silicate-oxide assemblages shown here are interpreted to result from the entrapment of coexisting silicate and sulphide melts during chromite crystallisation. These inclusions support the notion that magma mixing was the trigger for chromite saturation. The common link to the silicate inclusions from Merensky documented by Li et al. (2005) and the silicate inclusions from Stillwater documented by Spandler et al. (2005) are the involvement of a felsic component (e.g. the presence of quartz and An_{13} plagioclase in the samples studied; An₁₇ plagioclase documented by Li et al. (2005); mixing of trondhjemite and basalts for the Stillwater samples). Therefore, these inclusions are consistent with the existence of a felsic melt and support the hypothesis of magma mixing with felsic magma for chromite saturation. However, the nature of that felsic component is not well understood.

6 Conclusions

Pyrite is a common sulphide in the UG2 chromitite. The Ir goes into pyrite if pentlandite is associated with primary pyrite, which shows that pyrite plays an important role in the HSE mineralisation process. PGE behavior study of the UG2 chromitite shows that the sulphide inclusions and matrix sulphides have different PGE concentrations, which shows evidence that sulphides occurring in the rock matrix experienced additional processes.

There are no PGEs detected in solid solution in chromite. The sulphide inclusions observed within chromite grains contain significant amounts of PGEs, which support the notion that PGE-rich sulphides were responsible for PGE mineralisation in BIC.

The presence of the sodium-rich plagioclase provides additional evidence for the involvement of the mafic melt during the formation of chromite. The Mg-rich orthopyroxene and the Mg-rich amphibole suggest the existence of a high-Mg basaltic magma. These inclusions support the notion that magma mixing was the trigger for chromite saturation.

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About the first author

YAO Meijuan, female; born in 1981 in Shanxi Province; PdD; Now work in the School of Atmospheric Sciences, Sun Yatsen University. Research interests are terrestrial planetary geochemistry. Email: yaomeijuan1016@126.com; phone: 18801153825.