PGE Tenor and Metal Ratios within and below the Merensky Reef, Bushveld Complex: Implications for its Genesis

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The Merensky Reef is the consequence of several major influxes of magma into the Bushveld magma chamber that gave rise to at least two cyclic units, including the Pre-Merensky and Merensky cyclic units. Analysis of the S, Ni, Cu, platinum group element (PGE) and Au contents of 1140 samples from 24 profiles through the rocks forming these units and two profiles extending downward from the Reef to close to the UG-2 horizon of the Western Bushveld Complex provide important petrogenetic constraints on the origin of the Reef. Particular attention is paid to variations in the calculated PGE tenors and Cu/Pd ratios of sulfides, both vertically and laterally. All of the profiles show a decrease in Pt tenor and concomitant increase in Cu/Pd ratio upward across the pyroxenite of the Merensky unit and laterally away from certain centres that are interpreted as feeder zones. The data also document that more mafic horizons within the Merensky to UG-2 interval of the southwestern Bushveld are characterized by much lower Cu/Pd (<100–400) than the ambient ratio (~4000). This is interpreted as demonstrating that these horizons are the consequence of incursions of magma whose composition has been modified in a staging chamber by reaction with sulfide resident there. The favoured interpretation for the Merensky Reef is that the Bushveld chamber(s) was occupied by a resident magma crystallizing orthopyroxene and plagioclase. Pre-Merensky and, subsequently, Merensky magmas entered the chamber(s) intermittently from localized feeder structures, mixing or mingling with the resident magma and giving rise to the more mafic cumulates. At specific horizons, including the Merensky Reef, the mixing or mingling caused sulfide immiscibility. In these cases, as the new magma pulses flowed laterally away from the entry zones they deposited sulfide, becoming depleted in PGE. On coming to rest, the magma continued to segregate sulfide and crystallize pyroxene, so that the sulfides became progressively depleted in PGE and acquired a higher Cu/Pd upward through the pyroxenite. This model requires that the Merensky magmas could dissolve up to two orders of magnitude more PGE than current measurements on dry diopside–anorthite melts have indicated. It is suggested that very PGE-rich magmas can develop as a result of sulfide-unsaturated magma reacting with early formed sulfide in a staging chamber, dissolving FeS and enriching the remaining sulfide in PGE. Later magmas equilibrating with this enriched sulfide will themselves become highly enriched in PGE.

INTRODUCTION

The Bushveld intrusion contains 75% of the world's resources of Pt, 52% of Pd, 82% of Rh and 16% of Ni (Naldrett, 2004). Economic concentrations of these metals occur principally in three stratigraphic units, the UG-2 chromitite, the Merensky Reef (MR) and the Platreef. The 2004 annual reports of the three principal mining companies operating in the Bushveld (AngloPlatinum,

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Impala and Lonmin) indicate that UG-2 contains 58% of the known Pt resources, the Merensky Reef 32% and the Platreef 10%. Apart from these economically viable concentrations, the data of Maier & Barnes (1999) show that all of the cumulus rocks in the lower part of the complex are unusually enriched in platinum group elements (PGE). Median values for Pt and Pd respectively are 78 and 21 ppb in the Upper Critical Zone, 27 and 14 ppb in the Lower Critical Zone, and 10 and 11·5 ppb in the Lower Zone (these are values for cumulate rocks not including unusually PGE-rich horizons, such as chromitites, and the P1 and P2 reefs of the northwestern Bushveld). These values contrast with median values for the Main Zone of 5 ppb Pt and 3·5 ppb Pd, and for cumulate rocks from most other layered intrusions.

There have been many suggestions as to the origin of the Reef, which can be broadly classified into two schools, 'Uppers' and 'Downers'. The 'Uppers' school maintains that the metals have been concentrated from the underlying cumulates by ascending, chloride-rich fluids, and have been released at the cumulate–magma interface where accumulating sulfides 'fixed' the metals *in situ*. The 'Downers' consider that the metals were concentrated from above by descending sulfides that concentrated in cumulus rocks close to the cumulate–magma interface.

In this study we present new data on the distribution of Cu, S, the PGE and Au in 24 profiles across the Merensky Reef in the western part of the Bushveld Complex and discuss the implications of the data with respect to the origin of the Reef.

GEOLOGY OF THE BUSHVELD COMPLEX

The Bushveld Complex (Fig. 1) is the largest known mafic–ultramafic intrusion on Earth, extending 450 km east–west and 350 km north–south. It was intruded at 2·054 Ga (Scoates & Friedman, 2008). The country rocks consist mainly of Paleoproterozoic quartzite, argillite, dolomite and banded iron formation of the Transvaal Supergroup, although parts of the complex lie directly on Archean granitoids and greenstones.

Although the Bushveld intrusion is known primarily for its layered mafic igneous rocks, the Bushveld igneous event comprises four distinctive igneous suites: early mafic sills; the Rooiberg felsites, which now form the roof to much of the layered igneous series; the 8 km thick Rustenburg Layered Series comprising layered mafic–ultramafic rocks, along with accompanying dykes and sills; and lastly the Lebowa Granite Suite.

The stratigraphy of the Rustenburg Layered Series is divided into five zones (Fig. 2). The Marginal Zone (0–800 m thick) is formed of norite along with minor pyroxenite. The Lower Zone (800–1300 m thick) is composed
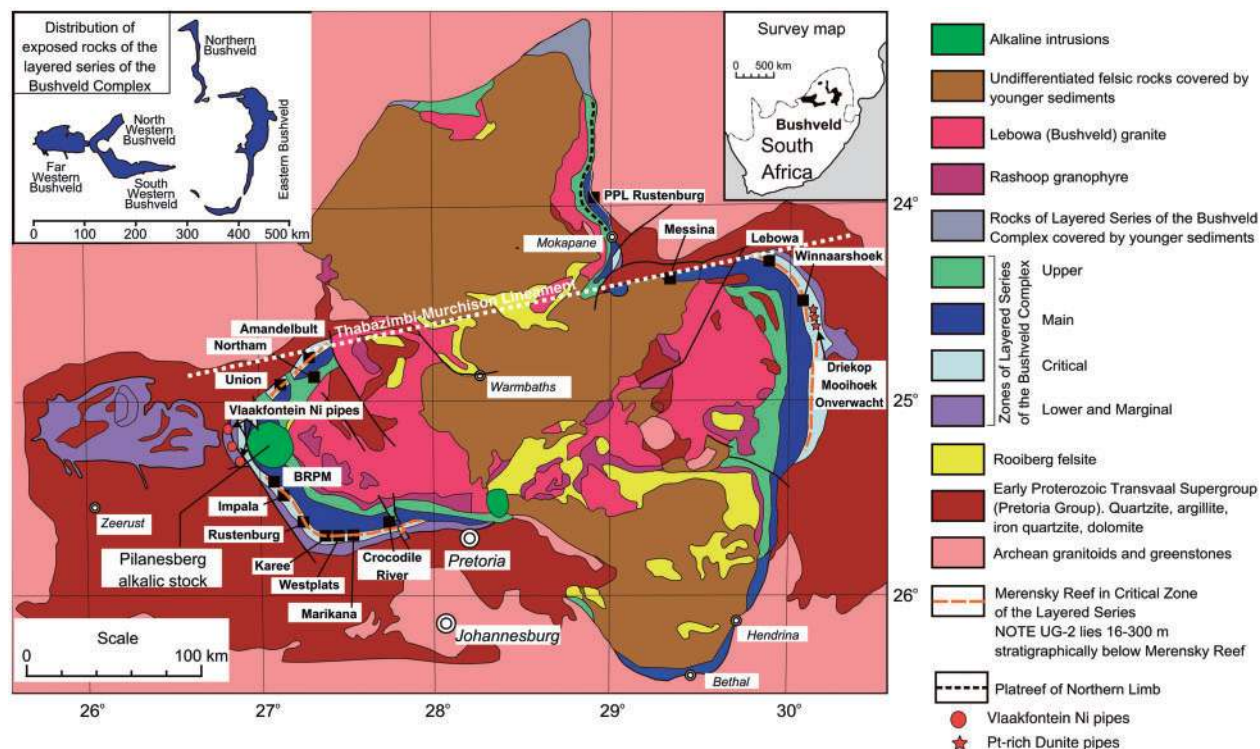

Fig. 1. Map of the Bushveld Complex. Modified after many sources given by Eales & Cawthorn (1996).

mainly of bronzitites, harzburgites and dunites (Cameron, 1978; van der Merwe, 2008), and is overlain by the Critical Zone (1300–1800 m thick). 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 consists primarily of bronzitites, chromitites and some harzburgites. The Upper Critical Zone is marked by the incoming of cumulus plagioclase, as represented by a 2–5 m horizon of mottled anorthosite, and can itself be subdivided into two parts; (1) a lower part consisting of anorthosites, norites and minor bronzitites, which occur in no systematic order and do not define classical cyclic units; (2) an upper part (starting at the base of the UG-1 chromitite unit and extending up through the UG-2 chromitite and Merensky Reef to the Bastard unit) that, in contrast to the lower part, comprises units made up of a regular succession of rock types (cyclic units), consisting of some or all of chromitite, harzburgite, bronzitite, norite and anorthosite, in most cases in that order. The Critical Zone is overlain, in turn, by gabbronorites of the Main Zone (3000–3400 m thick), which are capped by 2000–2800 m of ferrogabbros and ferrodiorites in the Upper Zone (von Gruenewaldt, 1973; Molyneux, 1974).

The layered series is at present preserved in five major compartments. Three of these, the Eastern Bushveld, the Southeastern Bushveld and the Western Bushveld, form semi-circular basin-like lobes (Fig. 1). Gravity and seismic data discussed by Cawthorn & Webb (2001) and Webb *et al.* (2004) are consistent with the Western and Eastern lobes originally having been contiguous. These two lobes show a full development of rock types from the Marginal Zone to the Upper Zone (see below). At the current level
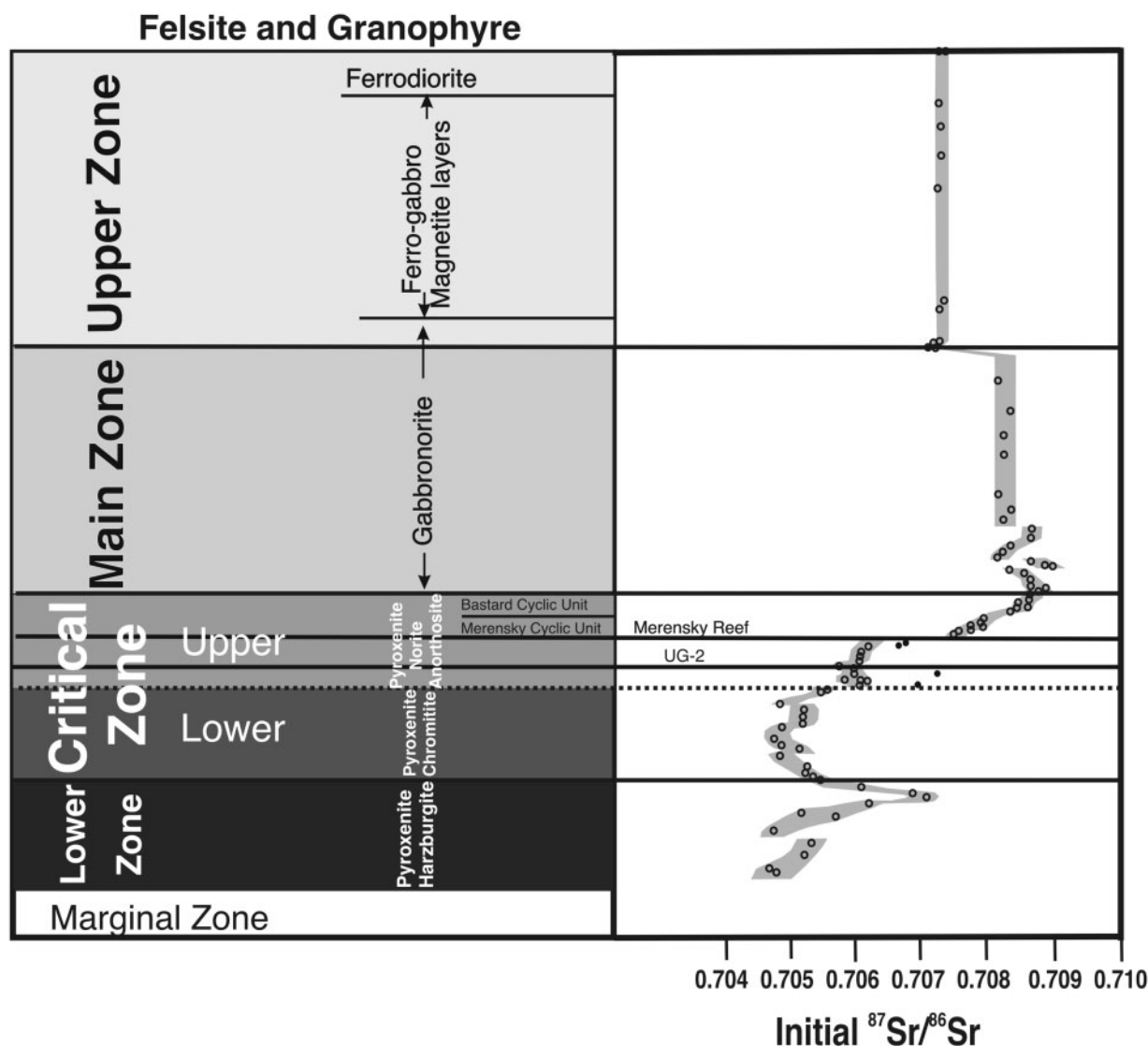

Fig. 2. Stratigraphic succession of the Rustenburg Layered Series showing variation in Sr isotope ratios [modified after Kruger (2005)].

of exposure, the Southeastern lobe appears to lack the lower two zones. The Western Bushveld lobe is effectively separated into two parts (Southwestern and Northwestern) by the later intrusion of the Pilanesberg alkalic intrusion. A fourth compartment (Far Western Bushveld) lies west of the Pilanesberg. Here, except for one or two minor localities, only marginal rocks of the layered series are preserved; another fully developed lobe probably existed in this area, but has been mostly removed by erosion. The fifth compartment, the Northern Limb, may well be part of another lobe although the rocks exposed along it exhibit some differences from those of the other bodies. Rocks that can be equated with the Lower and Critical Zones elsewhere are observed only in the extreme south of the limb (south of the Ysterberg–Planknek fault, van der Merwe, 2008). The Main and Upper Zones are present along much of the limb, although somewhat attenuated in comparison with the Eastern and Western lobes (Ashwal et al., 2005); a unit unique to this area, the Platreef, is present in the south, although only present north of the Ysterberg–Planknek fault.

The various zones and units vary greatly in thickness throughout the complex, and are absent in some areas. The lower zones vary in thickness partly because of their transgressive nature and appear to have had the most restricted development. In many places, the Critical Zone transgresses over a wider area of the Bushveld floor than the Lower Zone, and the Main Zone a still wider area. Von Gruenewaldt (1979) and Kruger (2005) have attributed the transgression to the progressive addition of new magma as the Complex crystallized, equating the emplacement to the progressive filling of saucer-like structures. Drawing on the data of Eales et al. (1990), Kruger & Marsh (1982) and Kruger (1994, 2005), Naldrett et al. (2008) have emphasized that much more magma must have passed through the Bushveld magma chamber than is represented by the rocks present today. They proposed that the missing magma escaped up the sides of the structure, interacting with the country rocks on the way, and that this has given rise to Platreef and other zones of marginal mineralization.

Seabrook et al. (2004) studied the Sr isotopic and Cr/MgO ratios of rocks from the Critical Zone below the Merensky Cyclic Unit (MCU) to the Main Zone just above the Bastard Unit. They concluded that two different magmas were present during the crystallization of these cyclic units, one of Main Zone type (referred to as T-type subsequently) contributing plagioclase and one of Critical Zone type (U-type) contributing orthopyroxene. They stressed that the compositions of the rocks of the Merensky and Bastard cyclic units are the result of the mixing of minerals, not magmas. On the contrary, Wilson & Chunnett (2006) concluded from their trace element study of the Merensky Reef and adjacent rocks in four boreholes in the southwestern Bushveld that these strata were the result of different degrees of mixing or mingling of U-type and T-type magmas on a very local scale (5 cm to 2 m).

The Merensky Reef in the Western Bushveld

Before describing the Merensky Reef it is necessary to define what is meant by the term. In this study we adopt the definition of Cawthorn et al. (2002), who proposed that it is 'a mineralized zone within or closely associated with ultramafic cumulates at the base of the Merensky (cyclic) unit'. We are mainly concerned with the Reef as it occurs in the northwestern and southwestern segments of the complex.

Comprehensive descriptions of the Merensky Reef and its stratigraphic setting in the Western Bushveld have been given by Leeb-du Toit (1986), Viljoen & Hieber (1986), Viljoen et al. (1986a, 1986b), Viljoen (1999), Wilson et al. (1999), Barnes & Maier (2002), Cawthorn et al. (2002), Smith et al. (2004), Godel et al. (2006) and Naldrett et al. (2008). Aspects of the geology within 100–200 m of the Reef that are important to the interpretations presented in this study are summarized below.

Stratigraphic setting of the Merensky Reef

A major change in the stratigraphic sequence of rocks within the interval between the top of the UG-2 and the Merensky Reef occurs at about the position of the much younger Pilanesberg intrusion (see Fig. 1). This is illustrated in Fig. 3, where it is seen that in the southwestern segment, the true vertical separation between the UG-2 and the Reef is of the order of 120 m whereas in the northwestern segment it is about 40 m (note the difference in scale in Fig. 3) (Maier & Eales, 1994, 1997). In general, large thicknesses of norite, leuconorite and anorthosite are present in the south, interrupted by more mafic horizons, whereas in the north the more felsic intervals are significantly thinner and less abundant, and the mafic units are both thicker and richer in pyroxene and olivine. In the NW, two PGE-enriched cyclic units, P1 and P2, both with associated chromite and olivine-rich rocks, are present 12–20 m above the top of UG-2. Possible equivalents in the SW might be the Boulder Bed (Maier & Eales, 1997; Figs 3 and 4d) and the 'platey olivine marker'. The former comprises ellipsoidal (elliptical in vertical section, circular in plan) 'boulders' of pyroxenite that contain PGE-rich sulfides (Maier & Barnes, 2003) enclosed in an anorthosite matrix that is also enriched in PGE (see below). The latter is an olivine–orthopyroxene–plagioclase cumulate with a distinctive platey fabric.

The Merensky cyclic unit is overlain by the Bastard cyclic unit, which is similar in many respects, except that the sulfides at its base are both less abundant and have much lower PGE tenors (see below). The Bastard unit is overlain by rocks belonging to the Main Zone.
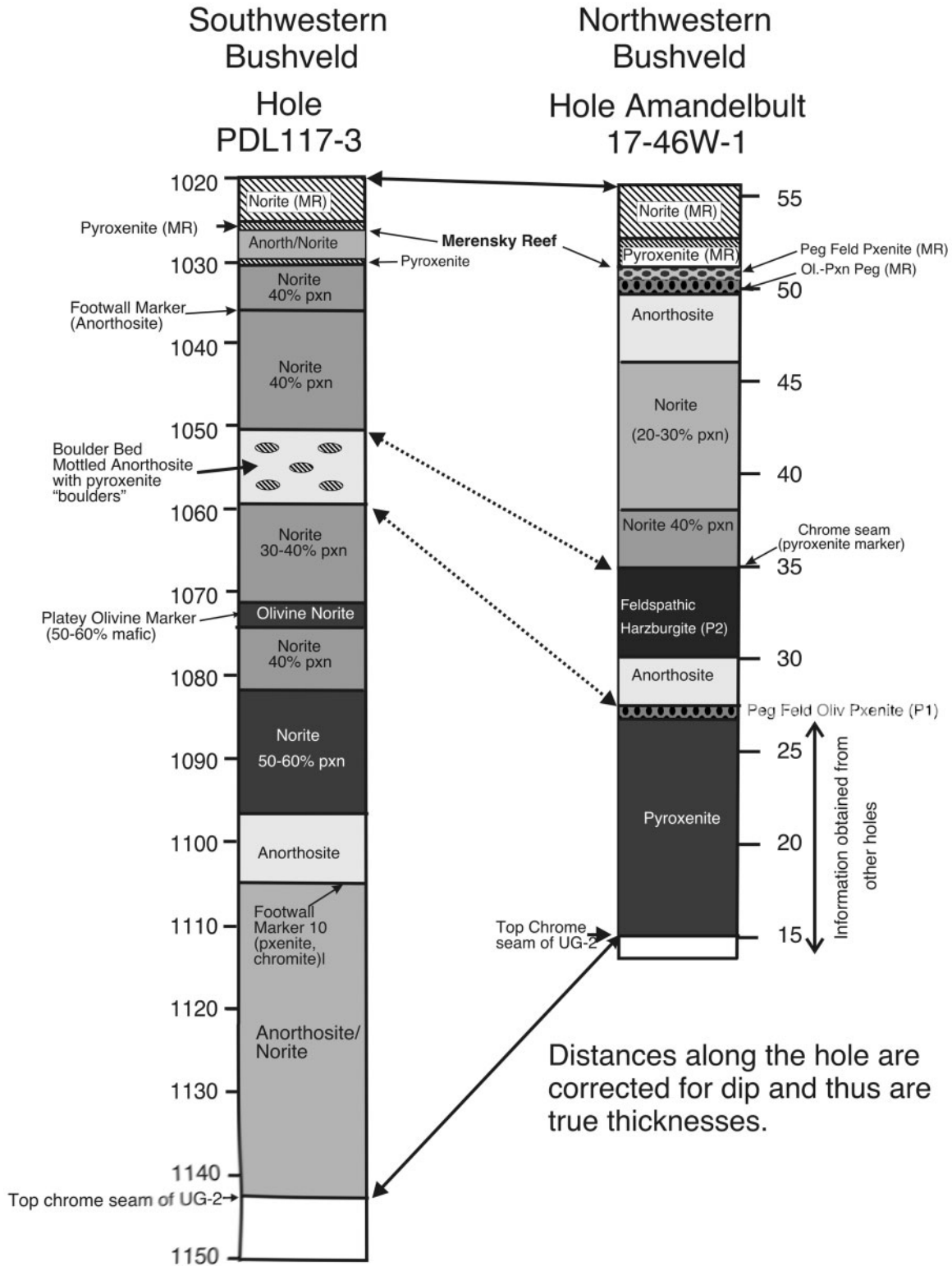
Fig. 3. A comparison of the stratigraphic succession between the Merensky Reef and the top chromite layer of the UG-2 in the Rustenburg (drill hole PDL 117-3) and Amandelbult (drill hole 17-46W-1) areas (see Fig. 1 for locations). (Note the greater overall thickness of anorthosite and norite in the former.)
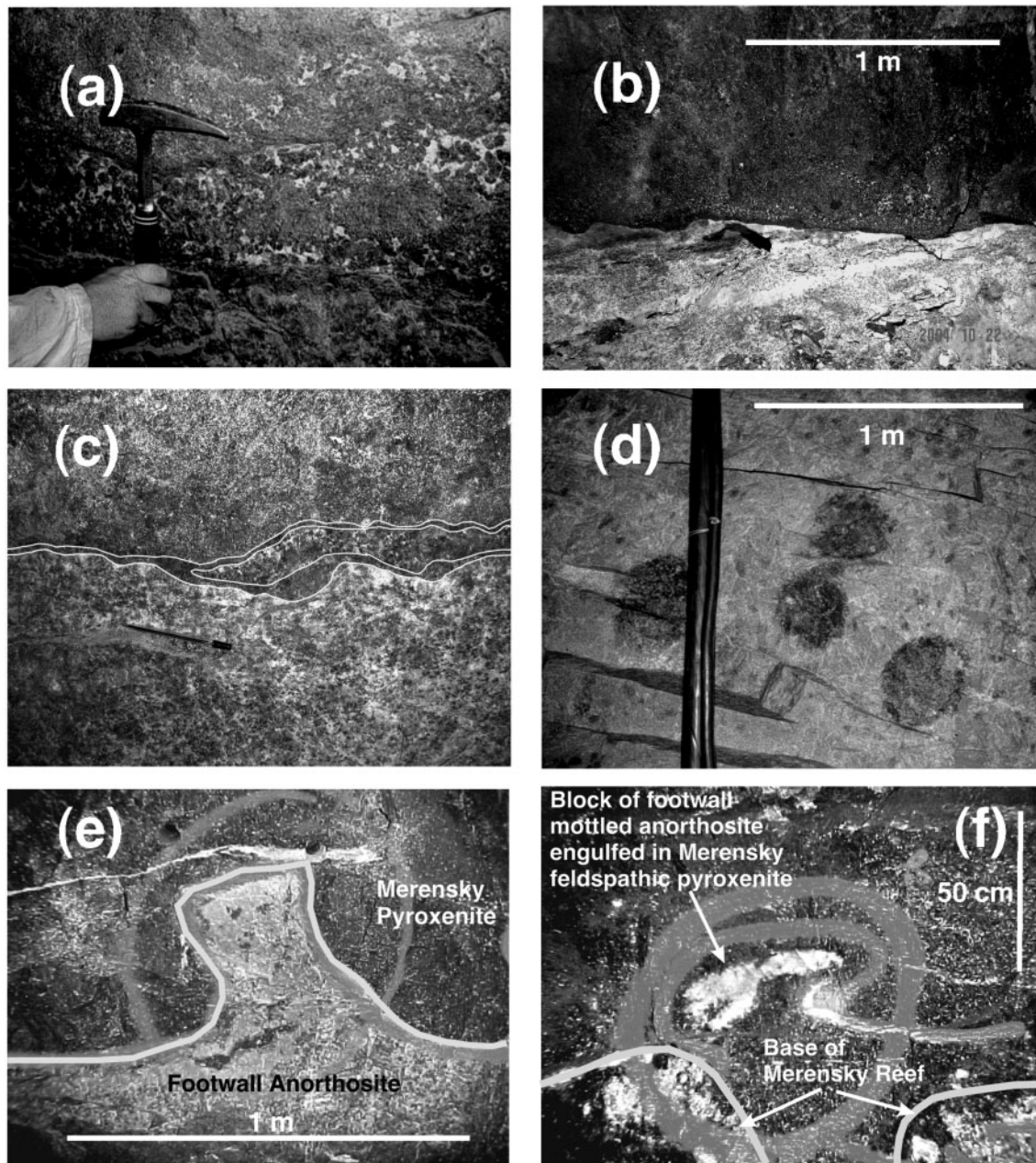
Fig. 4. (a) Typical 'normal' Merensky Reef at Townlands shaft (note the elliptical area with a normal fabric enclosed within that with a pegmatoidal fabric); (b) view of the base of the Merensky Reef at Eastern Platinum Mine showing the unconformity between the Reef and the layering in the underlying norites and anorthosites (note the variable thickness of the basal chromite) (photograph kindly supplied by Martin Slabbert, former shaft geologist); (c) photograph showing a transition from 'thin reef' to 'contact reef' [note how the thickness of the chromite is controlled by undulations in the contact (Townlands shaft)]; (d) a plan view of 'boulders' in the Boulder Bed (Townlands shaft): (e) the base of the Pre-Merensky cyclic unit, showing a block of footwall anorthosite thrust up into the overlying pyroxenite (photograph kindly supplied by Jaco Vermuelen); (f) a sliver of footwall anorthosite engulfed in pyroxenite of the Pre-Merensky cyclic unit (photograph kindly supplied by Jaco Vermuelen).

Rock units comprising the Merensky Reef

In its simplest form Merensky Reef comprises, from the bottom upwards: (1) a footwall anorthosite, norite or pyroxenite; (2) a lower chromite layer that ranges from 2 to >40 mm thick; (3) a varying thickness (0–10 m) of feldspathic pyroxenite (of which the upper 60 cm tends to be pegmatoidal) together with, in some areas, feldspathic harzburgite and dunite; (4) an upper chromite layer,

2–10 mm thick; (5) 30–225 cm of orthopyroxenite. Olivine is much more prevalent in the Reef in the northwestern Bushveld, although it also occurs intermittently throughout the southwestern portion. PGE-bearing sulfides may occur in footwall rocks as much as 1 m below the lower chromite layer (du Toit, 1986; Barnes & Maier, 2002), throughout the interval between the two chromite layers and up to several tens of centimetres above the upper chromite. In some areas a third chromite layer may occur within the pegmatoid or in the pyroxenite above the pegmatoid. The distance between the uppermost and lowermost chromite layers is very variable, ranging from zero in 'contact reef', which has only a single layer, to several metres. Figure 4a shows an example of pegmatoidal Reef, surrounding an elliptical zone with a normal cumulus texture. Cawthorn & Boerst (2006) have shown, on the basis of textural and trace element data, that zones with a pegmatoidal habit are the consequence of the recrystallization of non-pegmatoidal cumulates.

Lateral variations in the Reef

These are illustrated schematically in Figs 5 and 6. Figure 5 is a NW–SE cross-section illustrating aspects of the Reef in the southwestern Bushveld. In the SE (Eastern Platinum Mines), up to 10 m of Pre-Merensky cyclic unit pyroxenite is present, overlying interbanded norite and anorthosite. A chromite layer and uneconomic amounts of PGE-rich sulfides may be present at this contact. The Pre-Merensky pyroxenite is overlain by a thin chromite layer, which is taken to mark the contact with the overlying Merensky pyroxenite. This layer is completely missing in some areas and intermittent in others. Significant amounts of disseminated PGE-rich sulfide are present at the contact between the Pre-Merensky and Merensky pyroxenites, extending up to 1 m both above and below the contact (see data on TN72 discussed below). Reef thicknesses decrease progressively from 10 m to less than 1 m over a distance of about 4 km west from Eastern Platinum mine. Farther to the west in the Rustenburg area, there is no progressive change in thickness, and the Reef is referred to as 'Contact' (a single chromite seam with no Pre-Merensky pyroxenite present), 'thin' (3–10 cm separation of the chromite seams), 'normal' (15–30 cm separation) and 'thick' (30–60 cm separation). Variations from one type to another occur over lateral distances of 500 m or less, and tend to show a relationship to structures, such as faults and horst and graben structures, that pre-date or are contemporaneous with emplacement of the Bushveld Complex.

A major distinction between the Merensky Reef (MR) horizon in the NW and SW is that potholing is much more prevalent in the NW, where it is referred to as 'regional pothole'. Much of the currently mined Reef in this area lies at a level up to 16 m below that of the 'normal' Reef, as illustrated schematically in Fig. 6. Normal Reef is as described above. It thins towards the area of regional pothole, where the upper chromite layer and overlying Merensky pyroxenite cut down through the stratigraphy to level out at different horizons within the underlying footwall. Horizons that appear to have been particularly favoured are a feldspathic harzburgite (the Tarentaal) and an intermediate-level mottled anorthosite. Smith *et al.* (2004) have documented the distribution of different types of MR in part of the Northam Platinum mine (Fig. 7). Their data show that, even within the regional pothole, the down-cutting is irregular, and that down-dip to the SE the Reef reverts to its normal position in the stratigraphy.

Interaction of Pre-Merensky and Merensky proxenites with underlying rocks

Although the Regional Pothole Reef is the most dramatic illustration of irregularities between the Merensky Reef and the underlying cumulates, potholing on a smaller scale, forming structures typically 50–500 m in diameter and 3–12 m deep (Viljoen *et al.*, 1986a, 1986b; Viljoen, 1999), occur in both the northwestern and southwestern areas of the Bushveld. Furthermore, the base of the Reef is very commonly unconformable with respect to igneous layering in the footwall rocks. Figure 4b shows the marked unconformity between the Reef and the underlying banded norites and anorthosites at Western Platinum mines. A high degree of discordance is also present in the central to northwestern part of the southwestern Bushveld, where the Reef occupies a series of rolls with a wavelength of 2–12 m that undulate between defined marker horizons within the footwall that have a 6 m vertical separation ('Rolling Reef'). In places discrete masses of footwall rock project up into the Merensky pyroxenite (Fig. 4e) or occur entirely surrounded within it (Fig. 4f). The basal chromite of the Reef can be observed to thicken on some of the steps into the rolls, giving the impression that the chromite was carried as a bottom load, and became concentrated in hydraulic traps (Fig. 4c).

An interesting aspect of the northwestern Bushveld is the interaction between the magma responsible for the formation of the Merensky pyroxenite and the footwall rocks. Roberts *et al.* (2007) demonstrated that where, and only where, rocks of the Merensky cyclic unit have almost completely cut down through the Pre-Merensky pyroxenite and lie just a few tens of centimetres above the underlying anorthosite, the anorthosites contain olivine. The same process has affected the anorthosite forming the footwall to the NP2 Reef and the FWP2 Reef (Fig. 6). In comparison with unaltered anorthosite, these 'troctolitized' zones show an increase in MgO, CaO/(CaO + Na$_2$O), S and PGE and a decrease in SiO$_2$. Roberts *et al.* (2007) discussed how the troctolitization might have occurred, considering both the effect of an increase in the activity of water
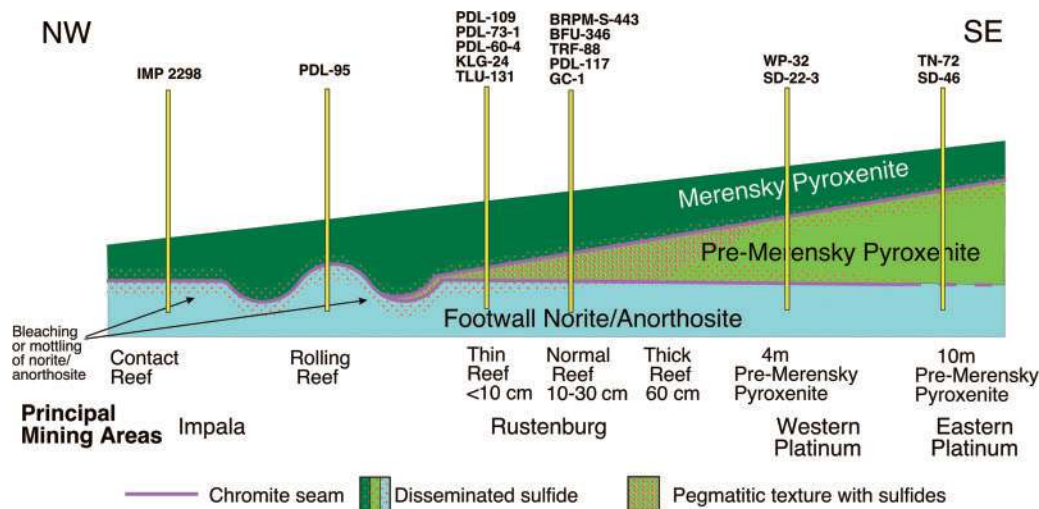
Fig. 5. SE–NW schematic section, showing variations in the Pre-Merensky and Merensky pyroxenites in the southwestern Bushveld. Whereas thick reef is predominant to the east and adjacent to the Pilanesburg in the extreme NW, reef types vary locally elsewhere, and tend to be related to structurally induced irregularities in the Merensky footwall. The vertical bars indicate the types of Reef investigated in this study.
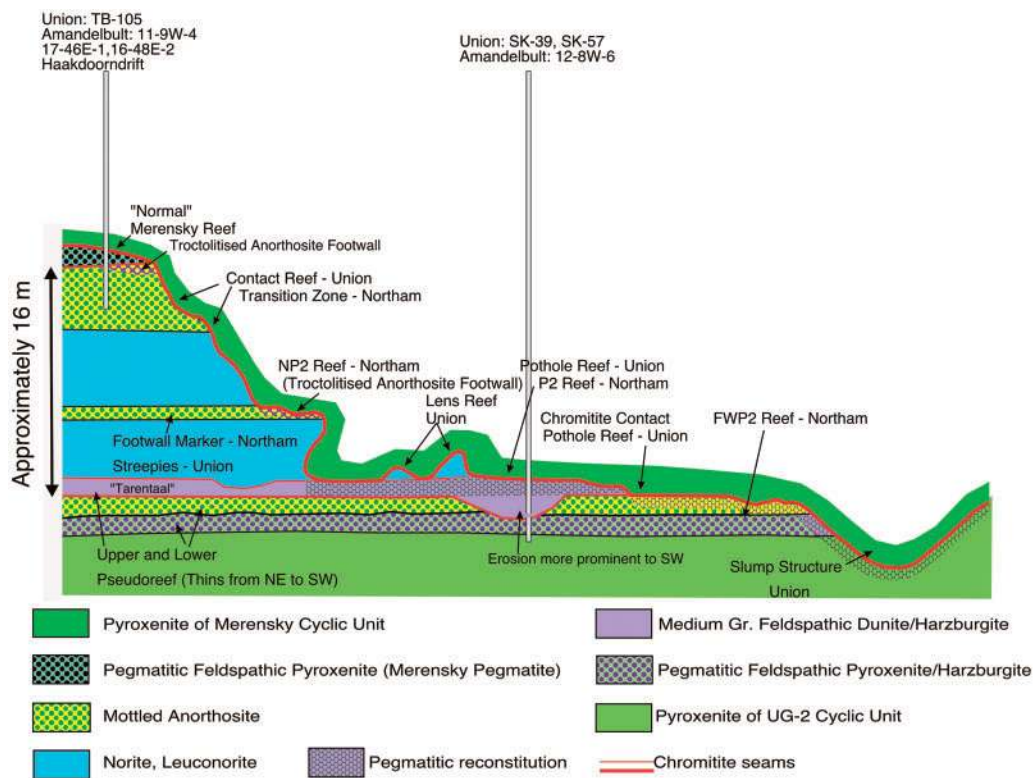

Fig. 6. Schematic section through the stratigraphic succession including the Merensky Reef in the NW Bushveld. This area is characterized by the extensive development of 'Regional Pothole Reef' within which the Merensky cyclic unit cuts down through the Pre-Merensky unit and underlying anorthosites and norites, and tends to bottom out above a distinctive feldspathic pyroxenite, the 'Tarentaal', that belongs to the P2 cyclic unit. In some areas it cuts through the Tarentaal and lies on the underlying anorthosite and in others, particularly at Union Section, it cuts through the anorthosite and underlying pyroxenite and harzburgite into a pyroxenite that is part of the UG-2 cyclic unit. The downcutting of the Merensky cyclic unit is also arrested by an intermediate anorthosite horizon, the Footwall Marker, and where it does this the Reef is referred to as NP2 Reef. Where the Merensky pyroxenite is in contact with, or close to, footwall anorthosite units these show the development of olivine that has been described by Smith *et al.* (2004) and Roberts *et al.* (2007) as 'troctolitization'. The vertical bars indicate the types of Reef investigated in this study. This section should be viewed in conjunction with Fig. 8, which shows variation in reef types at Northam Platinum mine. Figure modified after Viljoen (1999).
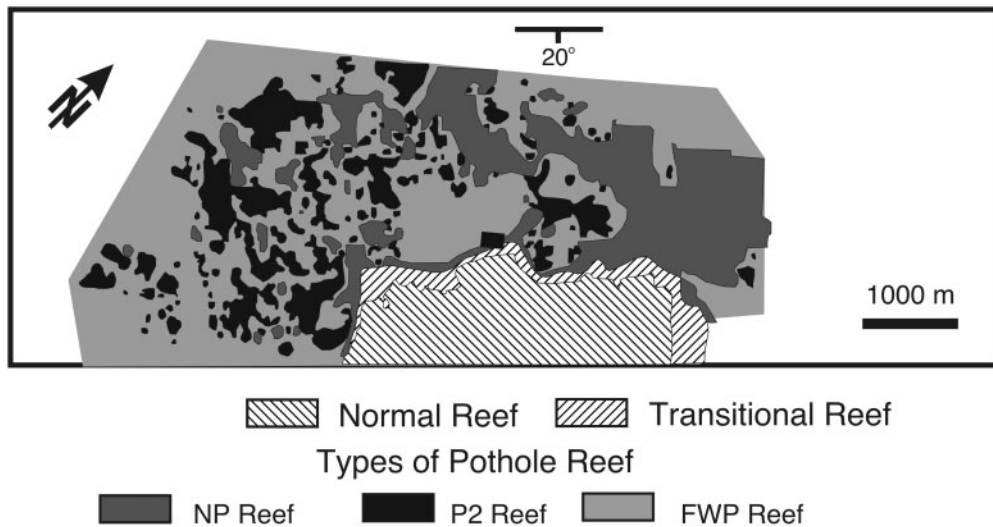
Fig. 7. Distribution of Reef types at Northam (after Smith *et al.*, 2004).

increasing the stability field of olivine [a mechanism that Boudreau (1999) has argued has affected the J-M Reef of the Stillwater Complex] and also the downward infiltration of primitive, spinel-saturated MCU liquid into partially consolidated anorthosite. They concluded that the fine grain size, textural relations between minerals and the distribution of sulfide and olivine are better explained by the reaction of the footwall rocks with a downward infiltrating magmatic liquid than by the upward streaming of aqueous volatiles.

Sulfides in the footwall to the Reef

Locally, sulfides occur in the footwall norites and anorthosites, apparently having settled from the overlying pyroxenite. The extent to which this has happened is variable. For example, in hole Impala 2298, greater than 1 wt % of high-tenor sulfides extend between 40 cm and 100 cm below the base of the chromite layer in the two deflections of this hole that were studied. The precise positioning of the two deflections with respect to each other in the plane of the Reef is not known, but would not be greater than a few metres.

Interpretation of relationship between the pyroxenites of the Pre-Merensky and Merensky cyclic units and the rocks forming their footwall

At least two influxes of magma, the Pre-Merensky and Merensky magmas, have contributed to the formation of the Merensky Reef. These appear to have been hot, energetic pulses that physically and thermally eroded the footwall rocks in many places to cause single potholes or, in the northwestern Bushveld, regional pothole reef. The influxes were probably hotter than the magma previously in the chamber because they appear to have deformed and partly engulfed the cumulates over which they flowed, giving rise to 'Rolling Reef' and structures such as those illustrated in Fig. 4b, e and f. The presence of olivine in the cumulates ascribed to the Pre-Merensky cyclic unit in the northwestern Bushveld indicates that here this magma was more primitive and probably hotter than its equivalent in the southwestern Bushveld. This is also borne out by the 'troctolitization' of the anorthosites (see above). Each pulse of magma deposited a layer of chromite at its base; field relations suggest that this was carried as a bottom load, that became concentrated in step-like structures and 'Rolling Reef' (Fig. 4c). This interpretation is contrary to that of Seagrove *et al.* (2005), who argued, primarily on the basis of density considerations, that the pyroxene grains forming the Pre-Merensky and Merensky pyroxenites did not settle directly from their source magmas onto the cumulates forming their present footwall. Rather, they proposed that a layer of T-type magma was injected beneath the Merensky magmas, and that the pyroxene grains settled through this to come to rest on the footwall (see discussion on density considerations below).

SAMPLING AND ANALYTICAL PROCEDURES

The locations of the 25 drill-hole profiles that have studied from the Western Bushveld are shown in Fig. 8. In many cases two deflections were sampled from each hole (see Electronic Appendix 1, available for downloading at http://www.petrology.oxfordjournals.org). Sampling was constrained by the amount of material available. In general, continuous sampling was undertaken on BQ core (37·5 mm diameter). Where this had not been sampled in
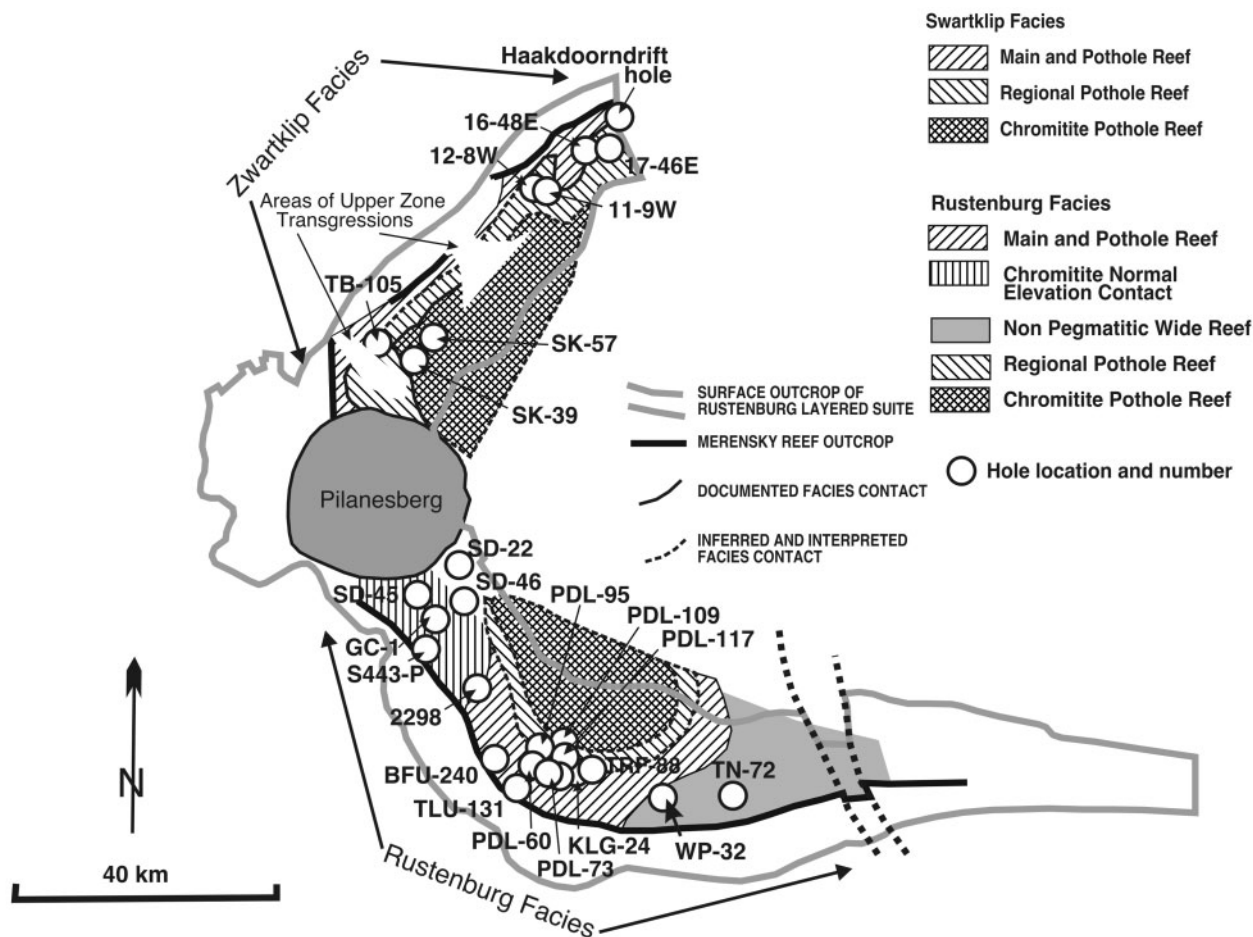
Fig. 8. Location of drill holes sampled for this study. Figure modified after Viljoen (1999).

the course of routine mine sampling, we were able to take half-core samples; in this case samples were selected at 10 cm intervals. Where half-core had been taken previously for mine sampling, we restricted ourselves to quarter-core samples, 20 cm in length. This scale of sampling is unsuitable for studying the fine structure across profiles through thinner sections of the Merensky Reef, but gives a reasonable picture of broad variations through the Merensky and Pre-Merensky cyclic units. In a number of cases we also obtained samples from underground that were sliced at 2 cm intervals (see below) to show the finer structure within the Reef. In two holes (PDL117 and 17-46E), in which variations across rocks lying in the footwall to the Reef were investigated, sampling was not necessarily continuous, but ranged up to one 30 cm sample every 1–1·5 m, depending on the anticipated detail in the profile.

Samples were crushed and milled at the analytical facility operated by Anglo American at their Research Laboratory in Johannesburg, where samples were also analysed for sulfide Ni, using the ammonium citrate leach technique (see discussion below). Whole-rock PGE, Ni, Cu

and S analyses were undertaken at the School of Geosciences, University of KwaZulu Natal, while it was under the supervision of one of the authors (A.W.). PGE and Au pre-concentration was by means of the standard Ni–S fire assay method and the analysis was completed by inductively coupled plasma mass spectrometry (ICP-MS) using an Elan Sciex 6100 system. International reference materials SARM6 and SARM7 were analysed to ensure the accuracy of the PGE data. Detection limits for PGE were better than 2 ppb for all elements. Cu, Ni and S were determined by X-ray fluorescence (XRF) using pressed pellets, matrix-matched standards and a Cr-target X-ray tube.

RESULTS

As discussed above, our sampling of the southwestern Bushveld was aimed to investigate four main aspects of PGE distribution: (1) variation across the Merensky Reef, the overlying pyroxenite of the Merensky cyclic unit and

the immediately underlying footwall rocks; (2) detailed variation within or very close to the Merensky Reef; (3) variation between the Merensky Reef and the top of the UG-2 cyclic unit (intermittent 30 cm samples); variation within the Merensky cyclic unit and thick Pre-Merensky cyclic unit at Eastern Platinum and Western Platinum mines. The full dataset for all holes except GC-1 and SD-22, -45 and -46 is given in Electronic Appendix 1. The data for the four exceptions can be found in the Electronic Appendix to the paper by Wilson & Chunnett (2006).

The primary objective of this study was to examine the variation in tenor of sulfides that make up the Merensky Reef. It is contended that the present amount of sulfide in the Reef is very close to the original sulfide content (see section on S/Se ratios below). The primary mineralogy of the major sulfides is pyrrhotite (po), pentlandite (pn) and chalcopyrite (cp), and the total amount of sulfide present in each sample has been calculated on the basis of analyses for S, Ni and Cu using the method outlined by Naldrett (2004, p. 15). The assumption that all but a negligible amount of the Ni is in the sulfide phases is not justified in the case of samples with a low sulfide content and high olivine or pyroxene content; thus many of the samples have been analysed for sulfide Ni as well as total Ni, and the former figure has been used in the calculation. It was found that the technique used for determining sulfide Ni (ammonium citrate leach) gave unreliable results when the samples were altered (particularly when serpentinized); some Ni appears to have been leached from minerals other than sulfide, with the consequence that too much sulfur is used up in calculating the Ni as pentlandite, and the remnant sulfur is a negative value, leading to a negative quantity of pyrrhotite. In these cases the calculation has been modified so that the total sulfur content of the sulfide phases alone was adjusted to be 36·1 wt %. This value is typical for sulfide-rich assemblages in which any Ni leached from non-sulfide environments is very small in comparison with that in sulfide. The error introduced by an uncertainty in the amount of Ni actually present in sulfide is relatively small; for example, if, in a sample containing 0·2 wt % Cu and 0·7 wt % S, all of the S remaining after that in chalcopyrite has been deducted is calculated as pentlandite, the total sulfide (chalcopyrite + pentlandite) content will be 2·09 wt %. If, on the other hand, the remaining S is calculated as pyrrhotite, and it is assumed that no pentlandite is present, the total sulfide (chalcopyrite + pyrrhotite) will be 1·86 wt % (i.e. an error of 11–12%). The variations in tenor documented in this study are orders of magnitude so that errors of up to 12% do not invalidate our conclusions.

A potentially more serious problem lies in the assumption that the present S content is the same as the original S content. Li *et al.* (2004) have drawn attention to the
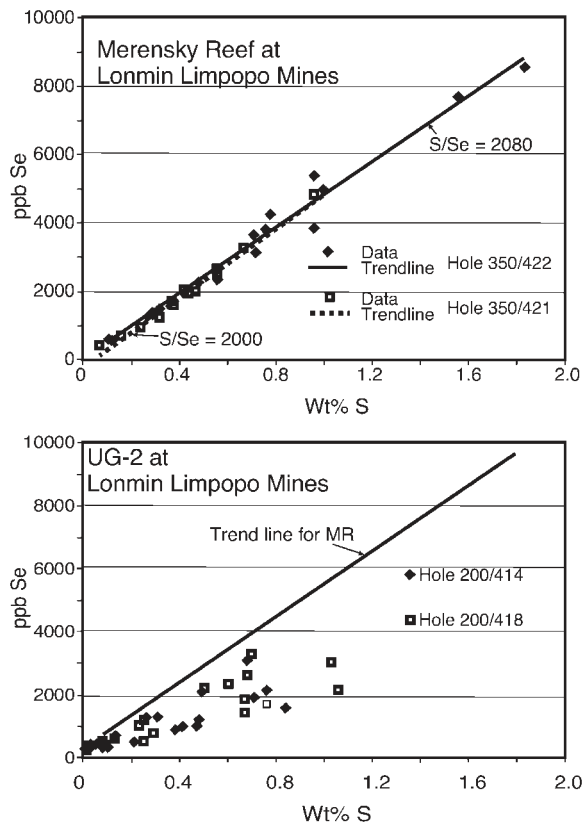

Fig. 9. Se vs S for both the Merensky Reef and UG-2 at Lonmin Limpopo Mine; the good correlation between S and Se in the Merensky samples, indicating a magmatic S/Se ratio of 2080, and the poor correlation in the UG-2 samples that have higher than magmatic ratios, should be noted.

replacement of base metal sulfides by secondary actinolite, epidote, calcite and magnetite in both the Merensky Reef and UG-2. They cautioned 'that the effects of secondary hydrothermal alteration on chalcophile element concentrations and distribution in the UG2 and Merensky Reef may be more significant than previously thought and should not be ignored in petrogenetic modeling'. As already mentioned, our samples were collected away from the more hydrothermally affected areas surrounding potholes. We sampled only those drill-hole intersections that appeared in hand-specimen to be entirely fresh, in which the sulfides showed sharp contacts with silicates and occupied interstitial locations characteristic of magmatic sulfide. As a further check on this aspect, we have determined the Se contents of those of our samples that have sufficient Se to be analysed with reasonable precision. Results are shown in Fig. 9 for the Lonmin Limpopo (Messina) mines (von Gruenewaldt *et al.*, 1990), which also includes data from a particularly sulfide-rich section of the UG-2 from the same locality. The sulfides of the UG-2 samples are highly altered, with all of the pyrrhotite replaced by

pyrite. The MR samples define linear trends with magmatic S/Se ratios of 2080; they contrast with the significantly greater scatter and higher S/Se ratios shown by the UG-2 samples. This is taken as evidence that the MR samples are relatively unaltered and that the present S content is close to the original content.

An important aspect of the interpretation of the tenor of PGE in the sulfides of the Merensky Reef is whether any given sample contains excess sulfides, or merely sulfide that has been forced out of solution during the crystallization of trapped intercumulus liquid. A reasonable S content for a magma that has evolved to the stage of that responsible for the Merensky Reef of the Bushveld Complex is 1000 ppm (Cawthorn, 2005b). Given that the amount of Ni–Cu–Fe sulfide is about 2·77 times that of the contained sulfur, 1000 ppm sulfur is equivalent to 0·28 wt % sulfide. All of the profile diagrams on which our data are presented contain a shaded area outlining the zone corresponding to the amount of sulfide that would be contributed by 10–40% of trapped, sulfide-saturated intercumulus liquid (0·028–0·112 wt % sulfide). Where the calculated sulfide content of our samples lies well above the shaded area, it is likely that this is due to the presence of excess sulfide; where the points fall within or below this area, excess sulfides are unlikely to have been present.

Variation in the footwall rocks to the Merensky Reef

Before discussing the variations across the Merensky Reef, it is important to understand variations in the footwall rocks to the Reef. This is particularly so in the case of the northwestern Bushveld, where much of the Reef is 'regional pothole' Reef. Here, as discussed above, rocks of the Merensky cyclic unit are present at much lower levels in the stratigraphy than their normal position. As discussed above (Fig. 6), the erosion has been halted by a number of horizons in the footwall, two of which, the P1 and P2 units, are ultramafic with associated chromite layers and accumulations of PGE-enriched sulfide. Where the Merensky Reef rests on these units, at first sight it appears to comprise two chromite layers and associated sulfide, although the lower chromite, some of the sulfide, and the enclosing rocks are not from the Pre-Merensky cyclic unit, but belong to the footwall units.

Two holes, one from each of the southwestern (PDL117-3) and northwestern (17-46W-1) areas of the Bushveld, were studied in detail from the viewpoint of Ni, Cu, PGE and S. Variations in Pt/Pd, Pt/Ru, Pt/Rh, Cu/Pd and Pt content in 100% sulfide (throughout this paper this value will be referred to as the Pt tenor), and wt % sulfide and ppb Pt in the samples are compared for the interval between the Reef and some tens of metres above the top chromite layer of the UG-2 (40 m in the case of PDL117-3 and 12 m in the case of 17-46W-1) in Fig. 10a and b.

Southwestern Bushveld

In the case of PDL117 in the southwestern Bushveld, the succession below the Reef and above UG-2 comprises a series of anorthosites, leuconorites and norites interrupted by three more mafic zones plus the 'Boulder Bed'.

The Boulder Bed (Jones, 1976; Maier & Barnes, 2003) is a distinctive horizon in the southwestern portion of the Bushveld within which rounded masses of pyroxenite (circular in plan view, ellipsoidal in cross-section and about 30–60 cm across; Fig. 4d) occur within mottled anorthosite. Their shape suggests that they settled as masses with a gelatinous consistency that sagged as they came to rest within a partially consolidated layer of cumulus plagioclase. Approaching the Pilanesburg intrusion, the horizon occupied by the Boulder Bed consists of a single, continuous pyroxenite, and Jones (1976) concluded that the 'boulders' at the same horizon SE of this were the consequence of the disruption of this layer. Maier & Barnes (2003) showed that the PGE concentrations in both 'boulders' and enclosing leuconorite or anorthosite at five locations around the Western Bushveld vary between 50 ppb and 70 ppm, and remarked on the similarity between the PGE concentrations in the pyroxenite of single 'boulders' and the enclosing anorthosite. Only one pyroxenite boulder was intersected in PDL117, and this is characterized by a fairly high Pt content (150 ppb), and a higher than ambient sulfide content. However, the mottled anorthosite in which the 'boulders' occur is unusual in containing higher than average concentrations of PGE (average for anorthosite), and yet relatively low sulfide concentrations, so that the calculated tenors are high.

In general, the sulfide contents are low between the Footwall Marker 10 (Fig. 10) and just below the Reef, making it unlikely that the magma was sulfide saturated (except for the one sample of a 'boulder' within the Boulder Bed, which indicates that the influx responsible for this was sulfide saturated). One of the most striking aspects of Fig. 10 is the decrease in Cu/Pd that is associated with the more mafic zones within the succession. The two dark vertical lines in Fig. 10 indicate the Cu/Pd ratio of (1) average Critical Zone rocks and (2) average mantle-derived magmas. The 'normal' Cu/Pd ratio of the rocks in the interval shown in Fig. 10 is close to that of the average Critical Zone (4000), but Cu/Pd decreases to values of 100 or less in the more mafic sections. Other metal ratios vary sympathetically with Cu/Pd over the interval shown in Fig. 10.

The behaviour of PGE in the Boulder Bed is also worthy of note. As mentioned above, the evidence points to an influx of fresh, relatively primitive, orthopyroxene-bearing, sulfide-saturated magma at this level over the top of a somewhat viscous magmatic plagioclase-bearing mush. Sulfides and PGE appear to have been absorbed into the host, plagioclase-bearing magma, and Fe-sulfide has been
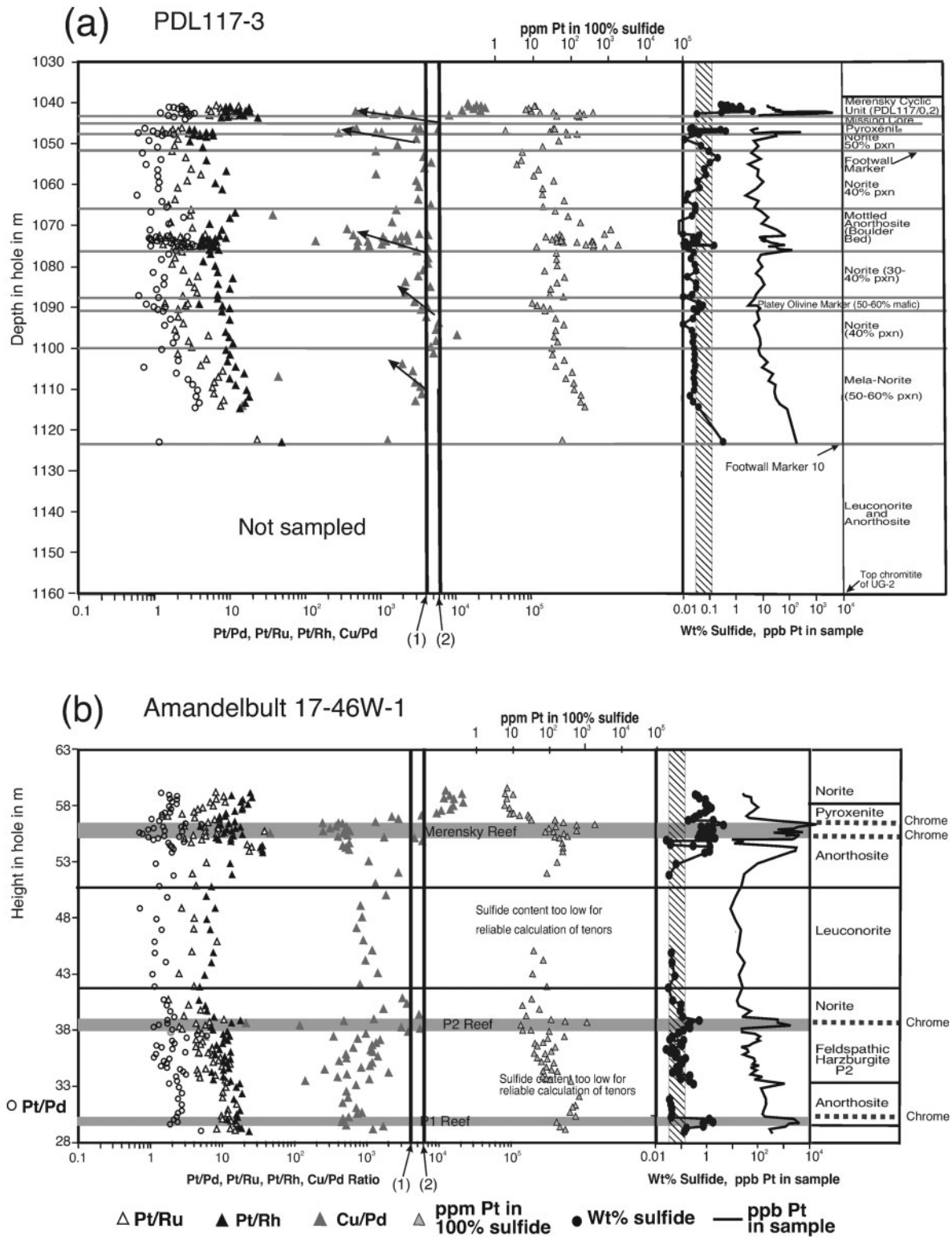
Fig. 10. Pt/Pd, Pt/Ru, Pt/Rh, Cu/Pd, Pt tenor, wt % sulfide, ppb Pt in holes (a) PDLl17-3 and (b) l7-46W-l. The correlation between more mafic intervals in the succession (mela-norite and pyroxenite) along with the Boulder Bed and decreases in the Cu/Pd ratio are noteworthy features.

dissolved and removed, leaving the host magma enriched in PGE in a manner analogous to that proposed to explain variations in TN72 (see Electonic Appendix 3 and discussion below).

Northwestern Bushveld

In the northwestern Bushveld, the Merensky Reef is much closer to UG-2 than in the SW. In hole 17-46W-1, the Reef is immediately underlain by 16 m of anorthosite, leuconorite and norite that have low sulfide and PGE concentrations, and relatively constant metal ratios. In contrast to the southwestern Bushveld profile discussed above, the Cu/Pd ratio is substantially lower (about 1000). This interval is underlain by a chromite layer that is part of the P2 cyclic unit. Two peaks in sulfide concentration occur within the P2 unit, one associated with the chromite at the norite–feldspathic harzburgite contact and the other at the lower contact with the underlying anorthosite. The upper sulfide concentration constitutes the P2 Reef. The P1 cyclic unit, comprising anorthosite and underlying pegmatoidal olivine pyroxenite, forms the footwall to the P2 cyclic unit. A chromite layer and associated PGE-enriched sulfides (P1 Reef) occur within the olivine pyroxenite, just below the anorthosite of this unit. Throughout the interval of the P1 and P2 cyclic units the Cu/Pd ratios are of the order of 500–1500, although samples with immiscible sulfide have ratios of 100 or less.

Variation across the Merensky Reef

Cawthorn *et al*. (2004) argued that the chromite layers that are associated with the Merensky Reef mark divisions between pyroxenite deposited by successive influxes of magma. Each influx deposited chromite followed by orthopyroxenite and sulfide. We accept these interpretations, and refer to the lower chromite and overlying pyroxenite as the Pre-Merensky cyclic unit, and the upper chromite, and overlying pyroxenite, norite and anorthosite as the Merensky cyclic unit.

Southwestern Bushveld

Figure 11 shows data for hole TLU131 from Townlands shaft in the Rustenburg area. Data for samples from this hole, and for a hand sample from Townlands shaft, are given in Table 1. Figure 11 illustrates a 2 m profile across the Reef, with thicknesses corrected for the dip of the strata (10°); thus they do not correspond precisely to the metreage given in Table 1 and in the Electronic Appendix. Figure 11 shows data for the overlying Bastard Reef from the same hole. The hatched area in Fig. 11 and in Fig. 12a–c indicates the sulfide contents within which between 10 and 40% of trapped interstitial sulfide-saturated magma would lie. Sulfide contents lying within or to the left of this zone indicate samples with little or no excess sulfide, and those lying to the right of it are interpreted to contain sulfide in excess of that that could be dissolved in the intercumulus liquid.

The data shown by the lines with a series of small dots are 2 cm samples from a hand sample from the same shaft, but not the same position. They are discussed below.

All of our results for the southwestern Bushveld are shown on plots similar to that of Fig. 11 in Fig. 12a and b. Because disruption to the normal stratigraphy of the Reef is known to occur in potholes, holes within or close to these structures were avoided during our sampling. Where possible, two deflections of a given hole were analysed to provide an indication of the representativeness of our data. It is standard practice in Bushveld exploration to drill a single hole and, a few metres above important horizons such as MR or UG-2, to insert wedges in the original hole to deflect the drill bit once it is reinserted and resumes drilling, so that more than a single intersection through the horizon is obtained. In some cases results from both deflections are shown in the figures, but where no significant differences existed between the two deflections, the results have been averaged on the basis of their position in the stratigraphy.

A number of important observations can be made, as follows.

(1) There is an exponential (the plots of the tenor data are logarithmic) upward decrease in the tenor of Pt in all profiles in the 20–50 cm of pyroxenite immediately above the Merensky Reef. The decrease is of the order of 1·5–2 orders of magnitude, from 300 to 700 ppm, depending on location, to about 10 ppm, at which concentration the upward change in Pt tenor levels out. In some cases (e.g. Imp 2298, PDL60-4, KLG24, TLU131, TRF88, BRPMS443, TN72) high-tenor sulfides extend for several tens of centimetres below the upper chromite layer of the MR. Although only Pt tenor is shown in Fig. 12a–c, all PGE show analogous behaviour.

(2) In all cases the Cu/Pd ratio decreases from a value between 2×10^3 and 2×10^4 well in the footwall of the MR to between 2×10^2 and slightly greater than 2×10^3 in the lowermost samples to carry excess sulfides. TN72 is an exception to this and is discussed below. The Cu/Pd ratio then rises steeply through the sulfides of the MR to a value of about 2×10^4 in the pyroxenites and/or norites that overlie the MR; this increase coincides closely with the decrease in the Pt tenor in the sulfides referred to in (1) above.

(3) As illustrated in Electronic Appendix 2, in most profiles there is an accompanying decrease in the Pt/Pd ratio from 3–4 to 1–2 over the zone within which the Pt tenor decreases (the two examples of contact reef, PDL95 and Imp 2298 are exceptions to this). Examination of the data indicates that there is no systematic trend in PPGE (Pt and Pd) to IPGE (Ru and Ir) ratio over this interval. In some cases the ratio increases, in some cases it does not.

(4) Holes TN72, WP 32 and SD-22, -45 and -46 are exceptions in that the Pre-Merensky pyroxenite is much
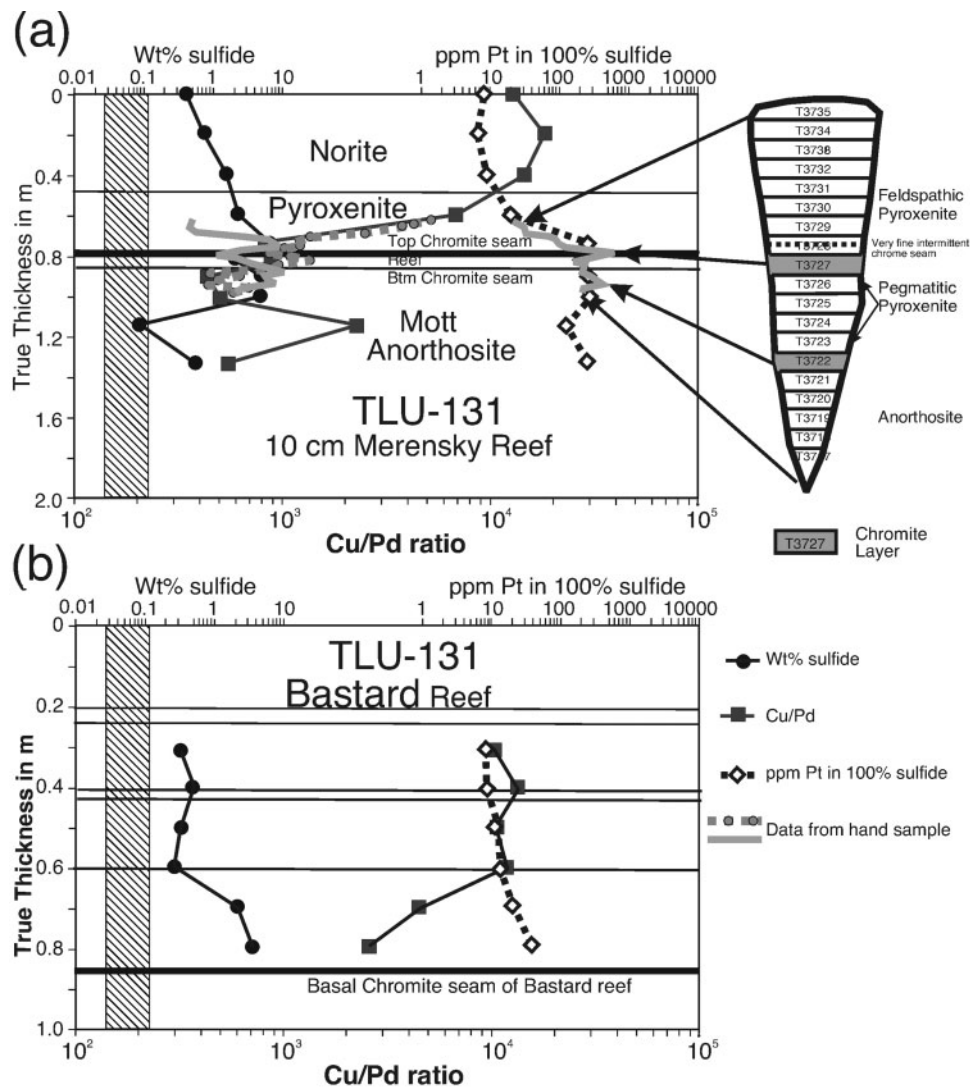
Fig. 11. (a, b) Variation with depth in the hole of total Pt, wt % sulfide, Cu/Pd and Pt tenor in hole TLUl3l. The grey dots and continuous line are data from the hand specimen that was sampled at 2 cm intervals; the black squares, open diamonds and black dots are from our 20 cm sampling of the drill core. The exponential upward decrease in Pt tenor and accompanying increase in Cu/Pd above the top chromitite of the Reef should be noted.

thicker than elsewhere. Holes SD22, 45 and 46 occur in an area that covers a transition from the more primitive, 'thick' Reef characterizing what is referred to locally as the 'Zwartklip facies' of the Union–Amandelbult area to the thinner Reef of the less primitive, so-called 'Rustenburg facies'. They have been discussed by Wilson & Chunnett (2006), who concluded that the Pre-Merensky rocks are the result of complex mingling between a Critical Zone-type (U-type in this paper) and Main Zone-type (T-type in this paper) magma. They noted that the PGE tenors in the Pre-Merensky pyroxenite appear to be partly dependent on the extent of the mingling. Holes TN72 and WP32 show much more systematic

tenor variations, which are discussed in detail in Electronic Appendix 3. The main aspects of these variations are as follows: (a) high-tenor sulfides appear up to 1 m below the chromitite that is regarded as marking the contact between the Pre-Merensky and Merensky pyroxenites, showing a progressive upward decrease in tenor across the chromitite and into the Merensky pyroxenite; (b) these high-tenor sulfides are underlain by a zone up to 2 m thick that is sulfide poor but PGE-enriched; (c) at the base of the Pre-Merensky pyroxenite in both holes there is a 20–30 cm thick sulfide-poor zone also enriched in PGE.

(5) Sulfides in the Bastard Reef show similar upward variations in PGE tenor and Cu/Pd to those in the

Table 1: Representative analyses (the full dataset is given in Electronic Appendix 1)

Sample no.:	T2480	T2481	T2482	T2483	T2484	T2485	T2486	T2487	T2488	T2489	T3735	T3734	T3733	T3732	T3731
From:	103·1	103·3	103·5	103·71	103·91	104	104·07	104·16	104·28	104·45	See Fig. 11				
To:	103·3	103·5	103·71	103·91	104	104·07	104·16	104·28	104·45	104·66	See Fig. 11				
Unit:	MCU	MCU	MCU	MCU	MCU	PMCU	Footwall	Footwall	Footwall	Footwall	MCU	MCU	MCU	MCU	MCU
Rock-type:	Norite	Norite	Norite	Felds Pxenite	Pxenite + Top chr	PegPxenite + Btm Chr	Mot Anorth	Mot Anorth	Spot Anorth	Mot Anorth	Felds Pxenite	Felds Pxenite	Felds Pxenite	Felds Pxenite	Felds Pxenite
S wt %	1505·7	2765·5	5594·7	8529·7	24763·5	7503·3	18487·6	17787·9	283·9	2039·2	1950·6	2007·8	1820·8	2198·1	11221
Ni wt %	418·2	899·3	1785·9	2677·8	5841	2404·5	4927·9	4918·3	266·4	674·3	951·9	940·6	927·7	1064·8	2904
Cu wt %	287·8	535·9	949·8	1635·5	4130·7	1824·6	3150·2	3366·8	135·1	400·7	504·2	544·1	420·8	420·7	2042
Pd ppb	22	29	64	241	4966	2021	7044	6741	59	721	96	124	110	166	1479
Pt ppb	33	52	137	472	17463	4210	14128	13732	112	1466	119	149	155	202	2245
Rh ppb	2	2	9	32	774	346	842	753	7	84	13	16	18	21	116
Ru ppb	3	6	19	70	1648	714	1546	1462	12	158	36	37	35	37	202
Ir ppb	b.d.l.	b.d.l.	4	13	311	118	280	253	3	29	6	6	6	6	37
Os ppb	b.d.l.	b.d.l.	3	9	237	100	219	208	b.d.l.	23	5	6	5	6	30
Au ppb	34	57	98	199	1020	422	958	853	18	116	46	44	41	56	562

| Sample no.:	T3730	T3729	T3728	T3727	T3726	T3725	T3724	T3723	T3722	T3721	T3720	T3719	T3718	T3717
From:	See Fig. 11													
To:	See Fig. 11													
Unit:	MCU	MCU	MCU	MCU	PMCU	PMCU	PMCU	PMCU	PMCU	Footwall	Footwall	Footwall	Footwall	Footwall
Rock-type:	Felds Pxenite	Felds Pxenite	Felds Pxenite	Chromite Top Chr	Peg. Pxenite	Peg. Pxenite	Peg. Pxenite	Peg. Pxenite	Chromite Btm Chr	Mot Anorth	Mot Anorth	Mot Anorth	Mot Anorth	Mot Anorth
S wt %	21659	26755	32847·6	9497	4536·9	8997·8	13330·6	24769	42940	18091·9	23535·1	28648·2	9743·8	8255·3
Ni wt %	5431·5	7000·7	8324·4	2836·5	1467·3	2331·7	3252·2	5811·8	10564·6	5007·7	7228·4	8317·3	2929·2	2332·9
Cu wt %	3599·7	3654·5	4311·7	1991·8	838·8	1654·4	2535·8	4659·6	3892·6	2639·8	3486·3	4590·1	2415·7	1765
Pd ppb	2933	3009	4163	2238	760	1211	2659	4948	8726	4152	7110	10341	3488	2993
Pt ppb	5450	7319	11154	15921	3079	4131	7944	14208	25464	13968	18521	34686	6244	5284
Rh ppb	251	338	543	1022	176	209	401	815	1604	1196	1096	1054	389	326
Ru ppb	463	662	1110	2008	376	415	841	1507	2931	2154	1758	1734	735	637
Ir ppb	86	132	225	375	70	75	148	262	536	410	345	324	130	111
Os ppb	68	103	178	270	53	59	111	210	415	297	252	259	100	85
Au ppb	611	865	557	511	128	214	838	1769	571	633	768	1358	657	558

b.d.l., below detection limit.

Merensky Reef, although the maximum Pt tenor is about 1/l0 of that in the Merensky Reef, and the lowest Cu/Pd ratio is substantially higher.

Northwestern Bushveld

Profiles of Pt tenor and Cu/Pd variations across the MR in the northwestern Bushveld are shown in Fig. l2c in the same way as for the southwestern Bushveld. Because so much of the northwestern Bushveld consists of a regional pothole, the sampling here also included Pothole Reef. As noted above, the pyroxenite and basal chromitite of the Pre-Merensky cyclic unit are not present in the area affected by the regional pothole, and, although a second chromite layer is often present in the zone of mineralization forming the Reef, this is the P2 chromite, and the mineralization associated with it very probably belongs to the P2 Reef, perhaps modified to some extent by mineralization associated with the Merensky (as opposed to Pre-Merensky) pulse.

Looking first at variations close to the upper chromite layer, the same generalized observations made for the
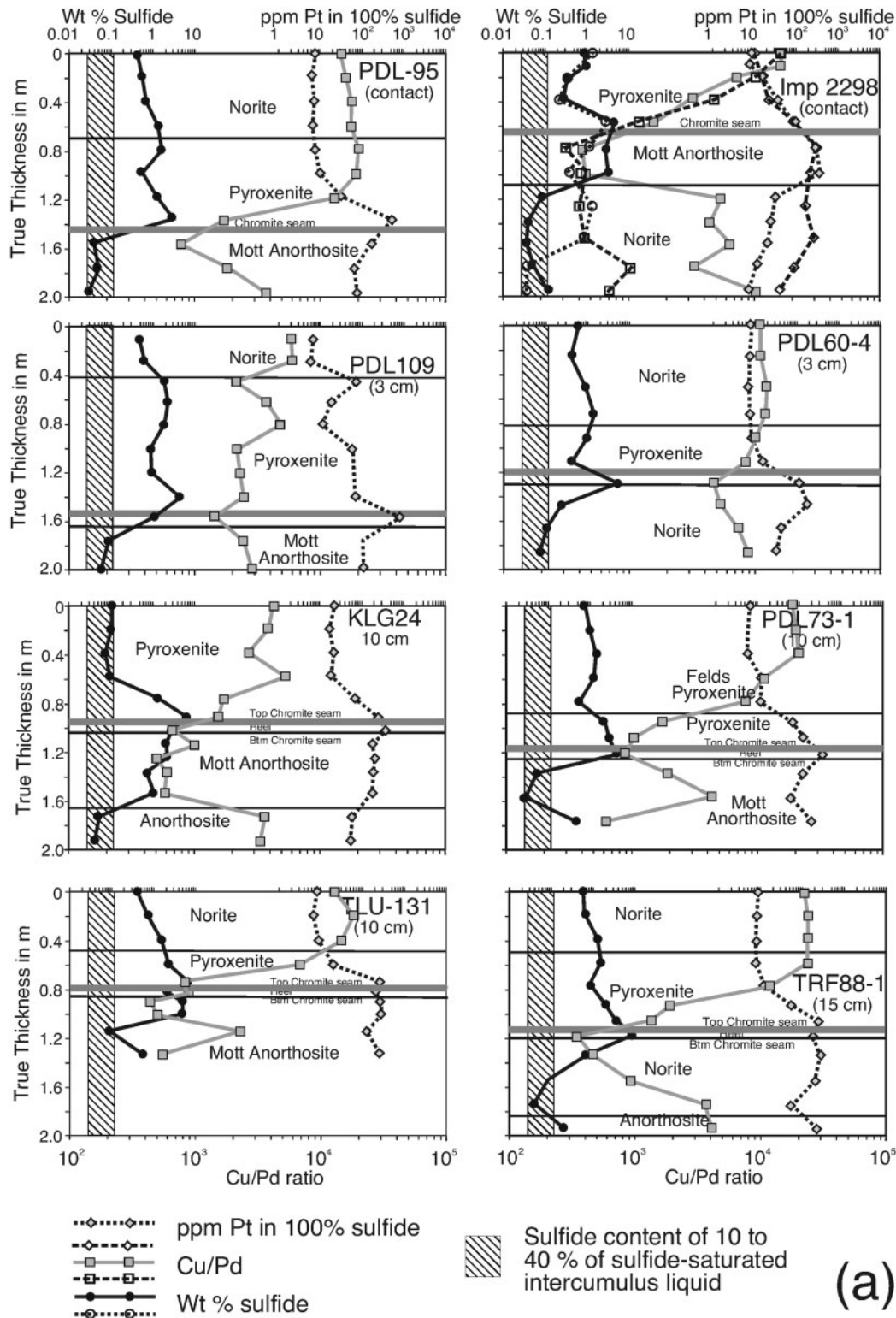
Fig. 12. (a, b) Variation across the Merensky Reef in wt % sulfide, Cu/Pd and Pt tenor in holes from the southwestern Bushveld: (c) similar plots for holes from the northwestern Bushveld. These figures show data plotted in the same manner as in Fig. 11.
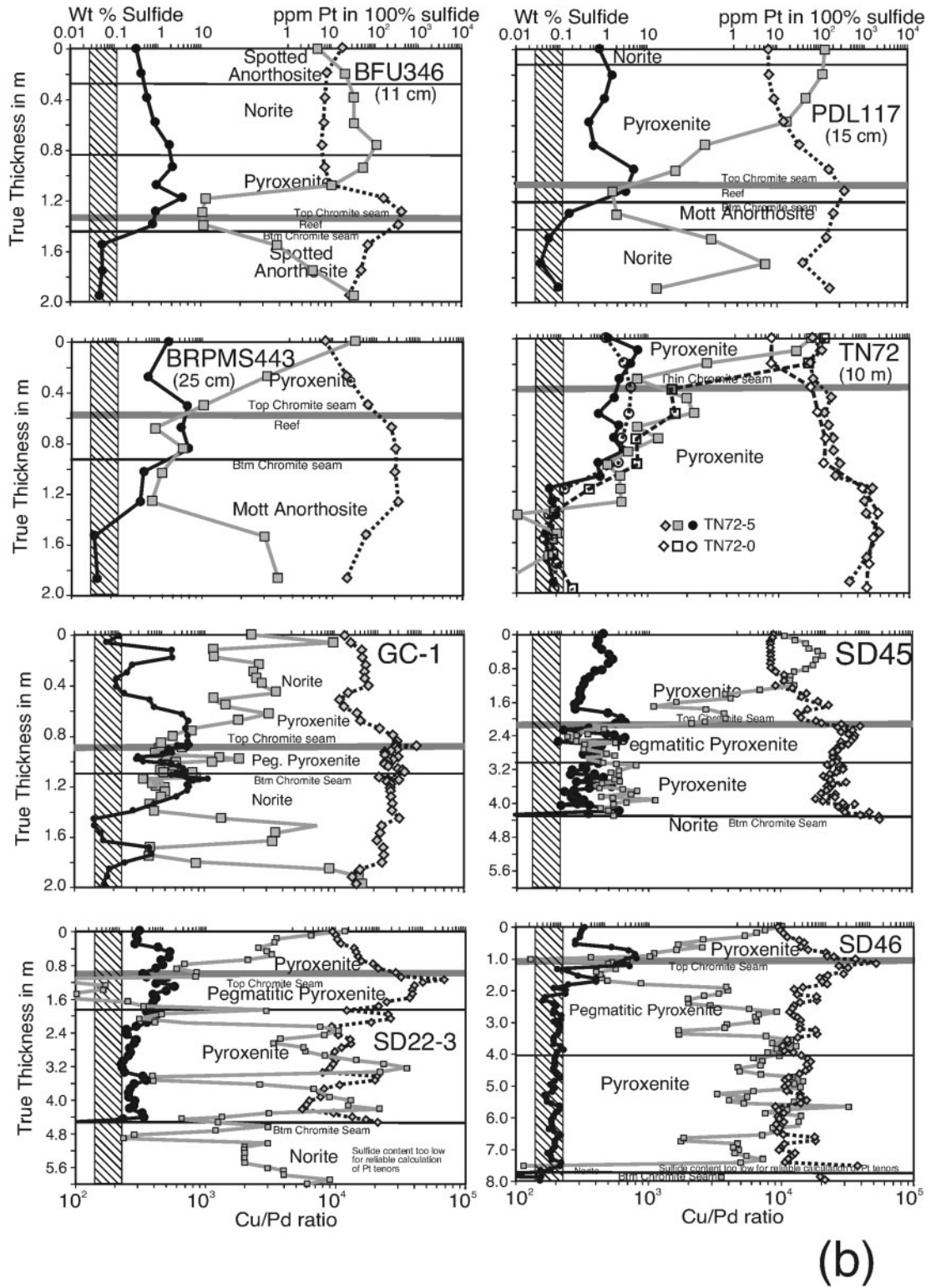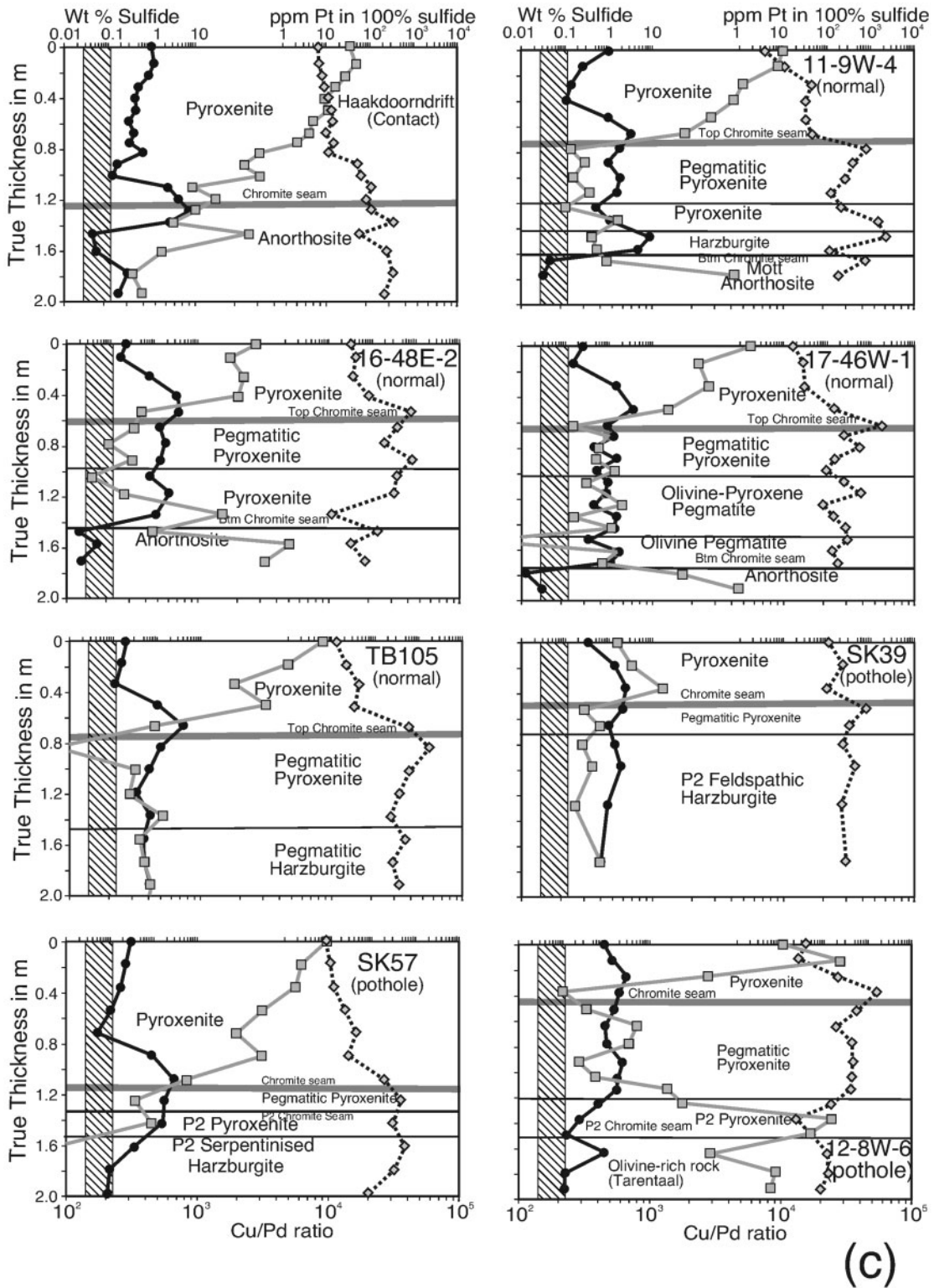
Fig. 12. Continued.

Fig. 12. Continued.

southwestern Bushveld may also be made here; specifically (1) a pronounced decrease in the Pt tenor of the sulfides, (2) a coincident increase in the Cu/Pd and decrease in the Pt/Pd ratio and (3) as seen in Electronic Appendix 2, Fig. 1c, an upward decrease in the Pt/Pd ratio in most profiles. The Reef is significantly thicker in the northwestern Bushveld than in the southwestern, and the spacing of our sampling across Normal Reef should have provided enough resolution to examine ratio and tenor variations related to the bottom chromite seam (Pre-Merensky chromite). However, the four profiles of Normal Reef show no variations analogous to those observed in holes TN72 and WP32. In fact, the interval between the bottom and top chromite in these profiles is characterized by a rather uniform distribution of sulfide with a relatively constant Pt tenor, and oscillating, but overall constant Cu/Pd and Pt/Pd ratio, similar to that observed by Wilson & Chunnett in holes SD22, 45 and 46 (see above).

Comparison of Reef sampled at 10–20 cm intervals with that sampled at 2 cm intervals

Given the necessary coarseness of most of our sampling, and the small distances over which variations in metal tenor and ratio have been observed, it is reasonable to ask whether, if the sampling had been more closely spaced, we would have reached the same generalizations. For this reason we collected some large samples of rock providing profiles across the Reef in a number of localities. These were then sliced at 2 cm intervals to provide more detailed profiles across the Reef. Pt tenor and metal ratio data for hole TLU131 (10 cm Reef, Townlands shaft, southwestern Bushveld) are compared with data for hand samples from roughly the same locations in Fig. 11. Despite the fact that the positions of the hand sample and drill hole are not the same, the trends for the two Townlands locations are very similar.

Interpretation of the data in terms of the genesis of the Merensky Reef

Current ideas on the genesis of the Merensky Reef

The close correlation between the presence of sulfide and PGE enrichment has always dominated ideas about the genesis of the Merensky Reef (Vermaak, 1976, and references thererin; von Gruenewaldt, 1979; Campbell et al., 1983; Naldrett et al., 1986). Miller & Andersen (2002) pointed out that layered intrusions that bear evidence of resulting from two distinct magma types, one U-type and the other T-type, host most of the world's significant PGE deposits, citing the Bushveld and Stillwater complexes, the Great Dyke of Zimbabwe and the Pennikat–Portimo intrusions of Finland as examples. Evidence bearing on whether mixing of a U- and T-type magma occurred at the level of the Merensky Reef has an important bearing on the origin

of the PGE mineralization. Campbell et al. (1983) suggested that sulfide immiscibility was the result of the mixing of U-type magma and more fractionated magma resident in the chamber as a fresh influx of the former rose like a plume through the latter. Naldrett & von Gruenewaldt (1989) showed qualitatively how existing sulfur solubility data supported this hypothesis. Subsequently, as better sulfur solubility data became available, considerable debate developed as to whether the mixing of two magmas with U- and T-type compositions could produce sulfide immiscibility (Li et al., 2001; Cawthorn, 2002). Most recently, Li & Ripley (2005) have shown on the basis of a revision of their earlier 2001 equation for sulfur solubility that a wide range in the proportions of mixing of these magma types can give rise to sulfide immiscibilty, provided that both magmas are close to sulfide saturation at the time of mixing. Cawthorn (2005a) argued that mixing of magmas is not necessary, and that the established negative effect of an increase in pressure on sulfide solubility (Mavrogenes & O'Neill, 1999) provides the best explanation for both sulfide immiscibilty and the formation of the chromite layers.

Boudreau & McCallum (1992) and Boudreau (1999) pointed to the high chlorine/fluorine (Cl/F) ratio of apatites in the Stillwater Complex and argued that any volatile phase separating would contain a high concentration of Cl. Over time, Boudreau has developed the concept of a vapour refining model (Boudreau & Meurer, 1999) in which volatiles released in a cooling pile of igneous cumulates ascend, dissolving amongst other elements, S, the PGE, Ni and Cu. Hanley et al. (2005), in experiments conducted at 1·5 kbar total pressure, $fO_2 = Ni–NiO$, and 600 and 800°C, showed that NaCl brines can dissolve very high concentrations of Pt; for example, their brines containing 20 wt % equivalent NaCl contained typically 1000–3000 ppm Pt. Pt solubility increased with increasing temperature and decreased markedly with increasing NaCl concentration. Wilmore et al. (2000) suggested that vapour refining had redistributed PGE and S throughout the Lower and Critical Zones of the Bushveld Complex, and that the addition of S- and PGE-rich vapour to crystallizing magma at the top of a cumuate pile would cause sulfide immiscibilty and the concentration of PGE within the sulfides.

Ballhaus & Sylvester (2000) found that PGE were widely distributed as micro- (<100 nm) inclusions of Pt ± Au–Pd alloys in olivine and chromite, whose structures were largely free of PGE. They pointed to the experimental work of Borisov & Palme (1997) [since backed up by that of Ertel et al. (1999); see discussion below], which predicted that, at the temperature and fO_2 they calculated for the Merensky Reef, the magma should be incapable of dissolving >10 ppb Pt, and argued that the PGE existed in the magma as 'clusters' of atoms (Tredoux et al., 1995), which
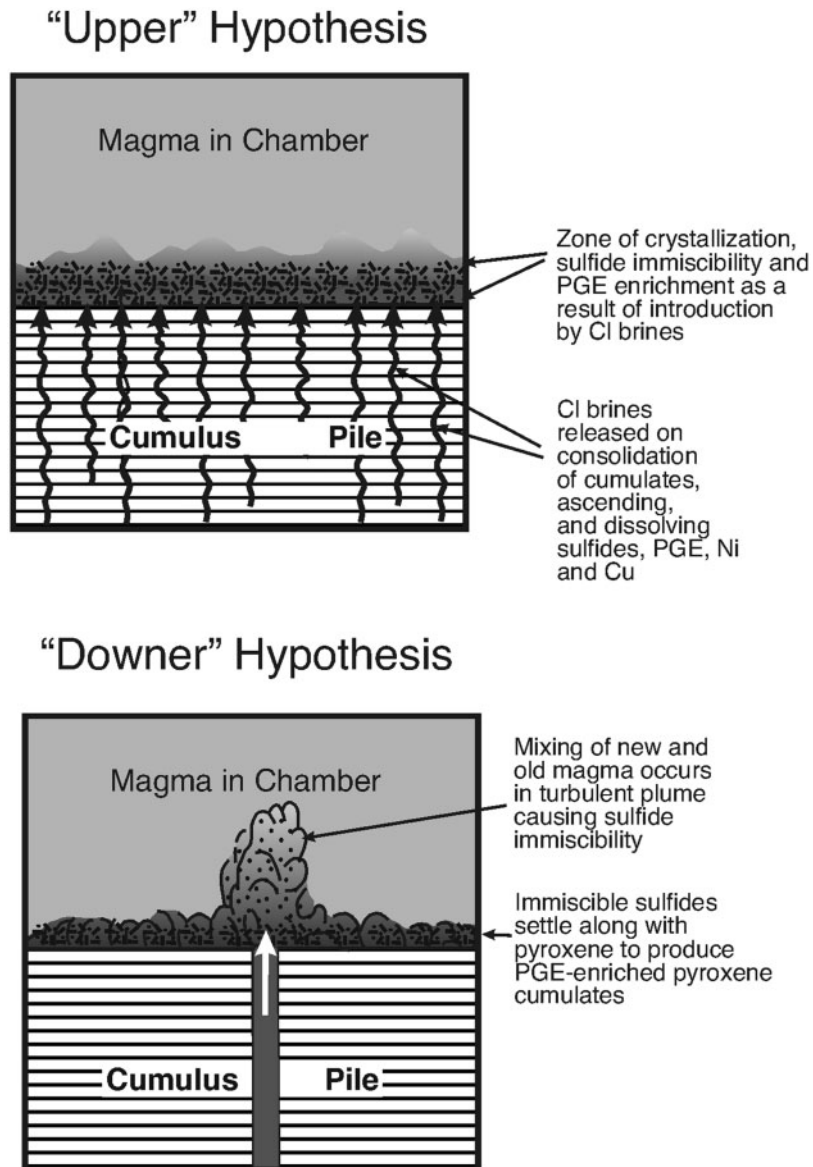
"Upper" Hypothesis

"Downer" Hypothesis

Fig. 13. Models for the origin of the Merensky Reef (from Naldrett *et al.*, 2008).

then dissolved in droplets of sulfide liquid once the magma reached sulfide saturation. Ballhaus & Sylvester (2000) were uncertain as to the provenance of the PGE.

As noted in the Introduction, there are two main schools of thought about the Merensky Reef, which differ in that one school ('Uppers') believe that the PGE have been concentrated from below and the other ('Downers') believe that they have been concentrated from the overlying magma. These concepts are summarized in Fig. 13. Any discussion of the relative merits of these two basic hypotheses would have to be comprehensive, and would be beyond the scope of this paper. We consider that the data provided here provide support for the 'Downer' point

of view and, with all due respect to the 'Upper school', the following interpretation is from this perspective.

As Cawthorn *et al.* (2004) pointed out, and as will become clear from our data, there may have been more than two influxes of magma. The difference in the distance between the upper and lower chromite layers is attributed to the magma responsible for the Merensky cyclic unit variably eroding the pyroxenite of the Pre-Merensky unit. Partial erosion resulted in as much as 10 m of the latter remaining in some areas (Eastern Platinum Mines area), whereas complete erosion, or non-deposition, resulted in none remaining in other areas (contact Reef). The pegmatoidal recrystallization characteristic of the Reef in some

areas is particularly developed where the upper chromite layer is less than 50 cm above the lower layer, suggesting that heat from the later influx is partly responsible for the recrystallization.

Setting of the Merensky Reef

The Merensky Reef occurs in the Upper Critical Zone, which, in the Western Bushveld, is characterized by a series of cyclic units, UG-1, UG-2, P1, P2 (P1 and P2 have been identified only in the northwestern Bushveld), Pre-Merensky, Merensky and Bastard units. It was pointed out above (Fig. 9 and related discussion) that, in the southwestern Bushveld, systematic variations in Cu/Pd ratio from normal values of around 4000 to values of <100 to 400 occur in association with more mafic-rich strata between the top of the UG-2 and the base of the Merensky Reef. The ratios of other PGE vary sympathetically with Cu/Pd. It is impossible to explain these variations in Cu/Pd and other ratios as a result of processes that were occurring in a magma that was unsaturated in sulfide (as is strongly suggested by the S content of the rocks) in terms of closed-system behaviour. Rather, it appears that a resident magma with a Cu/Pd ratio of about 4000 was crystallizing plagioclase and orthopyroxene to form the noritic and anorthositic intervals, and that from time to time there were incursions of fresh magma, with a much lower Cu/Pd ratio, that gave rise to the more mafic layers, and impressed their own low Cu/Pd ratio on the resultant cumulates. The manner in which this fresh magma acquired its low Cu/Pd ratio is thought to be fundamental to an understanding of the origin of the Merensky Reef and is discussed in more detail below.

There is less evidence for the incursion of magma with a low Cu/Pd ratio into resident magma with a normal ratio (4000) in the northwestern than in the southwestern Bushveld. Although the presence of distinct cyclic units such as P1 and P2 suggests that such incursions did occur, the intervening zones of leuconorite and anorthosite have a generally lower Cu/Pd ratio (∼1000) that makes this criterion less diagnostic. It is possible that the rocks found in the northwestern Bushveld were located much closer to a feeder system through which fresh, low Cu/Pd magma was entering the chamber (Eales *et al.*, 1988), and that the new influxes were volumetrically more abundant relative to the resident magma than elsewhere; these mixed with the local resident magma, modifying its composition to a greater extent than in more distal parts of the chamber such as the southwestern Bushveld.

Comparison of observed profiles with those predicted by perfect Rayleigh fractionation

Turning to considering the variations in Pt tenor and Cu/Pd that we have documented across the Merensky Reef, a number of possible scenarios for Pt tenor variation that could have resulted from perfect Rayleigh fractional segregation are shown in Fig. 14. It is assumed that sulfides are settling from an overlying body of magma, and that their settling rate is rapid with respect to the speed with which they are segregating, so that any Pt depletion experienced by the magma as the result of sulfide segregation affects the Pt content of subsequently segregating sulfide.

If sulfides segregate fractionally from a body of magma, one would expect the PGE to become depleted in the magma much more rapidly than base metals such as Cu. This is because although both PGE and Cu partition into a sulfide phase once it develops, PGE do so much more strongly than Cu. The result is that PGE tenors should show a progressive decrease in later segregating sulfides and ratios of base metals to PGE such as Cu/Pd should show an increase. Maier *et al.* (1996) have studied variations of Cu/Pd and Cu/Pt ratios through the stratigraphy of the Bushveld Complex and have shown that variations in the ratio can be used to locate stratiform concentrations of PGE. Rocks from the lower part of the Main Zone above the Merensky Reef and the Bastard cyclic unit have Cu/Pd that are generally >5000 whereas those from the Merensky cyclic unit and below have ratios <5000. Hoatson & Keays (1989) and Naldrett *et al.* (1994) respectively have shown that a similar approach can pinpoint PGE mineralization in the Munni Munni intrusion in the Pilbara, Western Australia and in certain parts of the Fox River sill in Manitoba, Canada.

The variations in both Pt tenor and Cu/Pd ratio that have been observed close to the Merensky cyclic unit chromite layer and that are illustrated in Fig. 12a–c are precisely those that would be expected if fractional segregation of sulfide had been occurring from the Merensky cyclic unit magma. Of the profiles shown in Fig. 12, those of the Contact Reef offer the best opportunity to test whether the Merensky cyclic unit magma carried a bottom load of sulfide liquid when it was emplaced because there is less chance of confusion with sulfides brought in at an earlier stage by the PMCU magma. In profile PDL-95 (Fig. 12a) there is no sign of a layer of sulfide with a uniformly high Pt tenor similar to that illustrated in Fig. 14b; the exponential upward decay continues from the first sample above the basal chromite layer (this sample also included the chromite layer). This is also the case with the Haakdoorndrift profile of Contact Reef (Fig. 12c). In the Contact Reef profile from Impala mine (Fig. 12a), sulfides have settled a variable distance below the chromite layer (35–100 cm depending on the deflection). These sulfides have a uniform, high Pt tenor which suggests that they could have resulted from a bottom load, but, alternatively, could have resulted from mixing during the settling process. In general, it appears that there is little substantive evidence of the
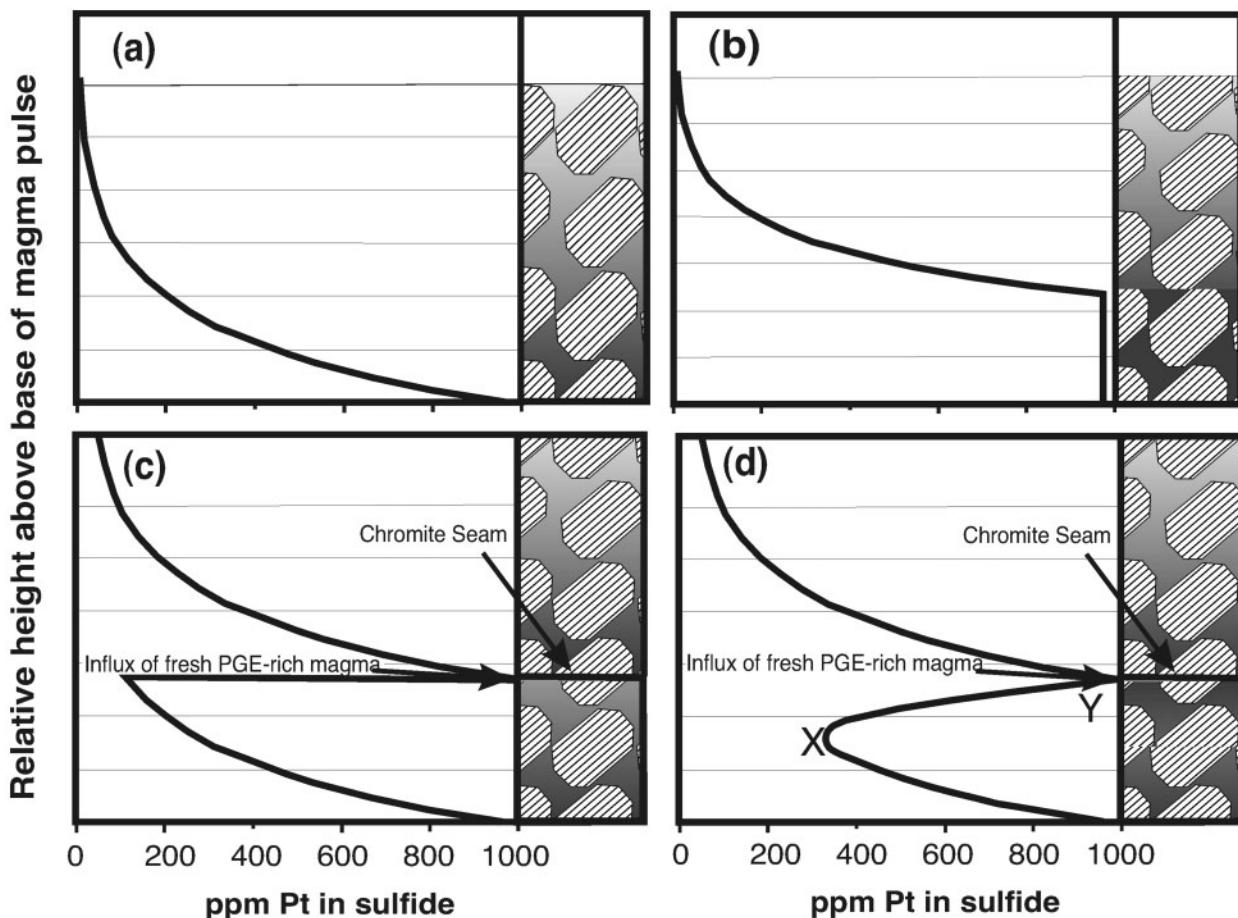
Fig. 14. Theoretical scenarios involving fractional segregation of sulfide. (a) An illustration of the exponential upward decrease in sulfide Pt tenor over a vertical profile as a result of simple segregation. (b) An illustration of the profile to be expected if the magma intruded carrying a bottom load of sulfide of uniform composition and then continued segregating sulfide *in situ*. (c) A scenario involving emplacement of a second pulse of fresh, undepleted magma, as is thought to have happened with the emplacement of the MCU magma after the PMCU pyroxenite formed. (d) Same scenario as illustrated in (c), but modified by the settling of high Pt tenor sulfide associated with the second pulse into the PMCU pyroxenite, and mixing of sulfides from the two pulses.

magma carrying a substantial bottom load of PGE-enriched sulfide.

In many of the profiles shown in Fig. 12a–c sulfides occur in the footwall rocks below the bottom chromite seam, usually concentrated along plagioclase grain boundaries in the anorthosite forming the footwall. Mining operations commonly include rock several tens of centimetres below the lower chromite layer in recognition of this. Godel *et al.* (2006) showed, using X-ray tomography, that the sulfides occupy vertical channel-ways that guided their settling through partially consolidated cumulates.

Considering variations between the top and bottom chromite layers of the Reef, the spacing of the sampling is too large to give much detail of tenor and Cu/Pd ratio variations across the relatively narrow interval between the two layers in most profiles in the Impala to Marikana areas of the southwestern Bushveld.

The exceptions are: the underground sample from Townlands shaft (Fig. 11) that can be related to the profile from borehole TLU13l; TN72 from Eastern Platinum mine, which intersects the Pre-Merensky and Merensky cyclic units where the pyroxenite of the former is 10 m thick; WP32 from Western Platinum mine where the Pre-Merensky pyroxenite is 4 m thick; and SD22, 45 and 46 from the Styldrift area just south of the Pilanesberg. Boreholes TN72 and WP32 are discussed in the following section. In the northwestern Bushveld 'normal' Reef is generally thicker than in the southwestern; all of the profiles studied exceeded 0·6 m in thickness (Fig. 12c). (The reader is reminded that the Pre-Merensky pyroxenite is missing from 'pothole' Reef, and that the strata below the top chromite seam are part of the P2 unit.)

In TLU13l, sulfides have settled ∼20 cm below the bottom chromite layer. These have a low Cu/Pd ratio

(about 420) that increases upward into the pyroxenite between the chromite layers and a Pt tenor of 400, which decreases upward. Thus, in this case, there is evidence that fractional segregation of sulfide also occurred from the influx of Pre-Merensky magma, although this single example is insufficient to claim that this can be considered as a global observation. The sample immediately below the top chromite has a higher Pt tenor and lower Cu/Pd ratio than the immediately underlying samples, which suggests that some mixing of the type modeled in Fig. 14d may have occurred. The Bastard Reef, as seen in Fig. 11b, also shows variations in PGE tenor and Cu/Pd suggestive of fractional segregation of sulfide, albeit sulfide segregating from a magma that was much less enriched in PGE than the Merensky magmas.

There is little systematic variation of Cu/Pd ratio and Pt tenor in the profiles from the Styldrift area. The complexities shown here support Wilson & Chunnett's (2006) conclusion on an inhomogeneous mingling of T- and U-type magmas. 'Normal' Reef from the northwestern Bushveld also shows an irregular variation in Pt tenor and Cu/Pd similar to that observed at Styldrift, although there is always an increase in both parameters in samples immediately underlying the top chromite, which suggests that some mixing akin to that shown in Fig. 14d may have occurred.

Profiles observed in holes TN72 and WP32

Figure 15 illustrates the variations in Pt tenor, Cu/Pd, Pt/Pd and Pt/Ru, across the Merensky and Pre-Merensky cyclic units in TN72 (see detailed description of the profiles of TN72 and WP32 in Electronic Appendix 3). Provided that, as shown in Fig. 15, the intermittent chromite layer at 610·55 m marks the contact between the two cyclic units, the zone of interstitial sulfide above 611·3 m can be explained if the sulfide separated from the Merensky magma and settled into a zone of only partly consolidated Pre-Merensky cumulates. The most primitive sulfides settled farthest, followed by successively more fractionated material. The intercumulus liquid of the Pre-Merensky pyroxenites was probably unsaturated in sulfur, so that as the initial sulfides settled, iron sulfides were partially dissolved, raising the tenor of those elements more chalcophile than Fe. As the settling sulfides penetrated deeper into the unconsolidated Pre-Merensky pyroxenite mush, an increasing amount of sulfide was dissolved, with the result that PGE tenors in the remaining portion of sulfide increased progessively with settling. As this process continued, the pore fluid in the upper part of the PMCU pyroxenite became saturated in sulfide, the dissolution stopped, and lower tenor sulfides entered the zone from above to give rise to the present zone of relatively low-tenor, excess sulfides between 610·6 and 611·3.
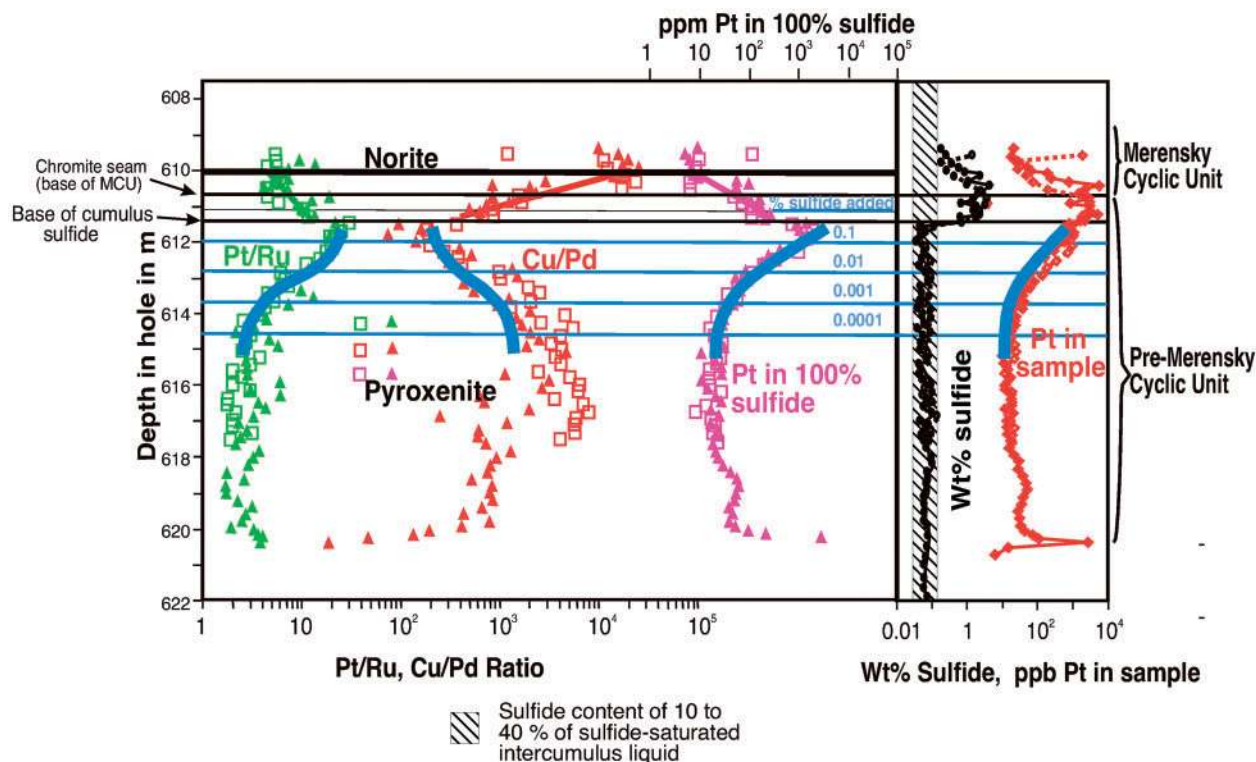

Fig. 15. Variation in Pt tenor, Cu/Pd, Pt/Pd an Pt/Ru across the Pre-Merensky Cyclic Unit and Merensky Cyclic Unit in hole TN72 from Eastern Platinum mine.

The zone below this from 611·3 to 612·0 m is enriched in PGE in comparison with lower parts of the Pre-Merensky pyroxenite, and shows the most primitive ratios (lowest Cu/Pd, highest Pt/Ru and Pt/Rh), but contains only inter-cumulus amounts of sulfide. This is thought to be the consequence of the settling of MCU sulfides, which became progressively enriched in PGE as a result of disso-lution during downward percolation. The amount of sul-fide penetrating into the zone between 611·3 and 612·0 m was insufficient to saturate the pore fluid (it should be appreciated that during the stage under discussion, before compaction had eliminated much of the pore fluid, the amount of fluid was much higher than in the present rocks), so no excess sulfides are preserved, but the metals that they brought with them are a testament to their former presence.

The downward 'tail' of progressively decreasing Pt tenor and Pt/Ru, and increasing Cu/Pd, is thought to be the consequence of progressively decreasing amounts of down-ward percolation of sulfide. Figure 15 also shows model curves (the wide blue lines) that indicate the variations in metal ratios, Pt content of the samples, and Pt content in 100% sulfide that would be the consequence of mixing different proportions of sulfide with 'unmineralized rock'. For the purposes of this modeling, the composition of 'unmineralized rock' is based on the Cu, Pt, Pd and Ru contents of rocks from the lower central part of the pro-file at about 616 m. The Ru, Pd and Cu contents of the settling sulfide used for the mixing model were obtained by assuming that the initial settling sulfide contained 1000 ppm Pt (a reasonable, high value based on our mea-surements along the SW portion of the MR) and then extending the increasing trends in Pt/Ru, Pt/Pd and Cu/Pd shown by the fractionating sulfides 1 m below the base of the present level of excess sulfide, and obtaining the concentrations of Pd, Ru and Cu in this way. The model curves reproduce the observed trends very closely.

Considering the spike in PGE present at the lower con-tact of the Pre-Merensky pyroxenite, as discussed above, this occurs with no spike in sulfide. It is suggested that the first wave of Pre-Merensky cyclic unit magma deposited PGE-enriched sulfides here, but that subsequent Pre-Merensky magma was unsaturated in sulfide (as evidenced by the low concentrations present in most of the Pre-Merensky pyroxenite) and dissolved Fe sulfide away, but not significant amounts of PGE, giving rise to the PGE spike and the very high calculated tenors present at this contact.

The settling of sulfides below the top chromite layer in WP32 is significantly less than has occurred in TN72, although the high tenor of the interstitial sulfides that extends nearly 1 m below the chromite layer is probably due to the resorption of Fe sulfide but not PGE as has

been discussed for TN72 above. WP32 shows the same PGE spike without associated sulfide at the base of the PMCU that is shown by TN72, and it is suggested that the explanation is the same. The profile also shows a small spike in total Pt, wt % sulfide and Pt and Pd tenor 1 m above the basal chromite layer, which can be explained if a surge of fresh, sulfide-bearing magma entered at this stage, suggesting that emplacement of the PMCU was more complex than a single surge of magma. The exponen-tial decay of Pt, and Pt and Pd tenors is also interrupted by a spike in these parameters 50 cm above the top chromite layer, which again can be explained if the MCU magma was the result of at least two surges, the second causing a refreshment in the PGE content of the initial MCU magma.

It is suggested that the movement of PGE by settling sul-fide that becomes progressively dissolved as it settles into or becomes engulfed by sulfide-unsaturated magma is an important process in the distribution of PGE in the Bushveld Complex. It is also likely to be the explanation for the PGE-enrichment shown by the mottled anorthosite that hosts the 'boulders' of the Boulder Bed that is discussed above.

Regional variations in PGE tenor

Data for Pt tenors over 1 m true distance close to and above the top chromite layer of the MR are shown on a non-logarithmic scale in Fig. 16. The maximum tenors found in the Union and Amandelbult areas, and in the profiles of thicker Reef in the Styldrift area, are much higher than those of much of the southwestern Bushveld. Values of the maximum tenor are plotted along with the location of the profile in Fig. 17 (note that data for TN72 are omitted from this figure because of uncertainty as to the tenor of the ear-liest segregating sulfides—see discussion on TN72 above). In the Union–Amandelbult area, there appears to be a decrease in tenor towards the NE (reaching 334 ppm at Haakdoorndrift) and to the SW (reaching 593 ppm) of this area. High values are also found in the holes just south of and closest to the Pilanesberg, with a rapid decrease south of this to values typical of the southwestern Bushveld. Information on more profiles is required before a comprehensive picture of the variation and its possible cause can be developed, but at this preliminary stage it is suggested that the areas with high tenor may be closer to feeder zones than those with lower tenor, and that progres-sive segregation of sulfide from the Merensky cyclic unit magma as it flowed laterally across the underlying cumu-lates caused it to become depleted. The feeders may be related to long-lived, through-going structures such as the Thabazimbi–Murchison lineament and related splays (see Fig. 1) and the zone of weakness that localized the Pilanesberg intrusion.
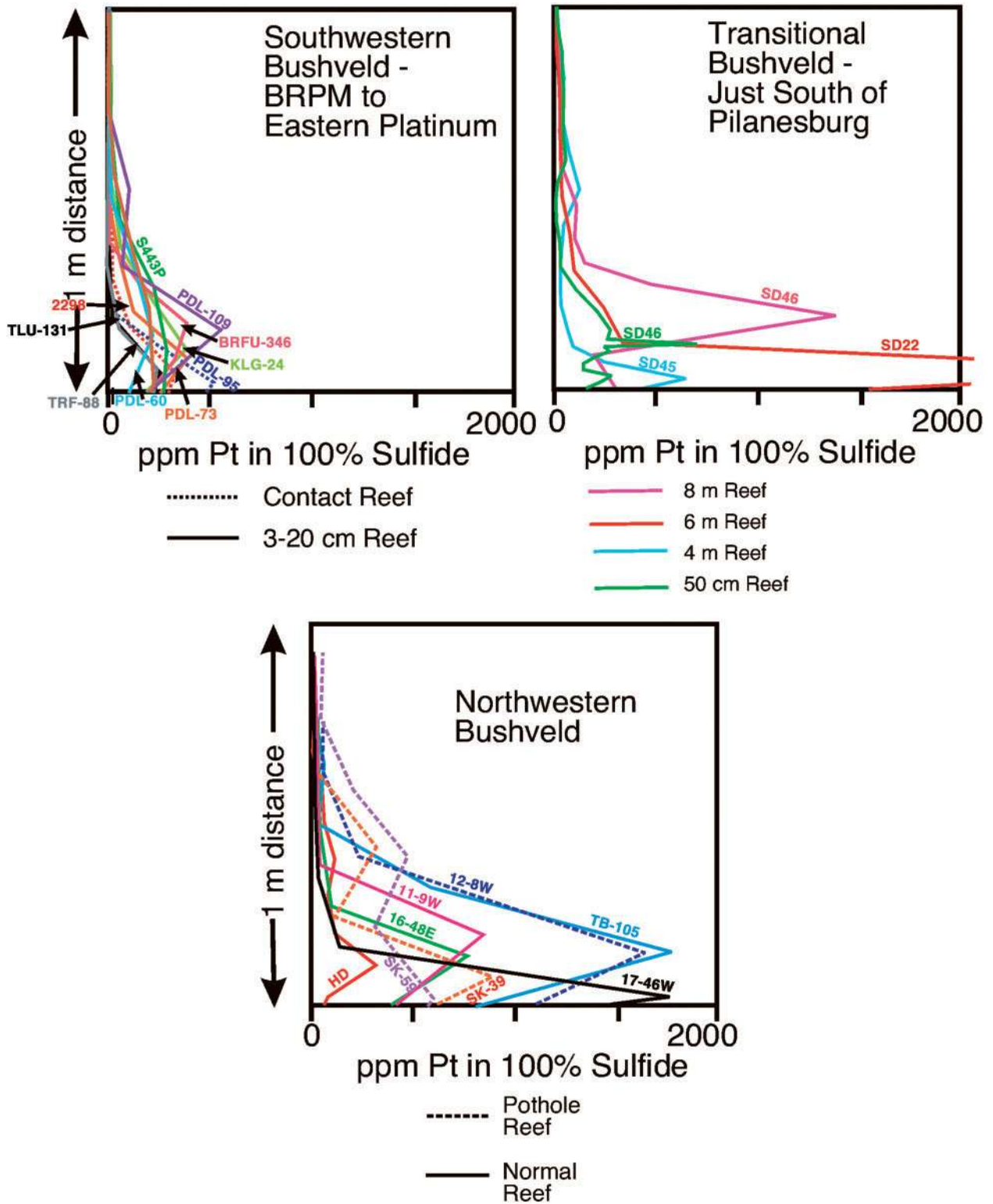
Fig. 16. Variation in Pt tenor (plotted on a non-logarithmic scale) over a 1 m true thickness including, and extending above, the top chromite layer.
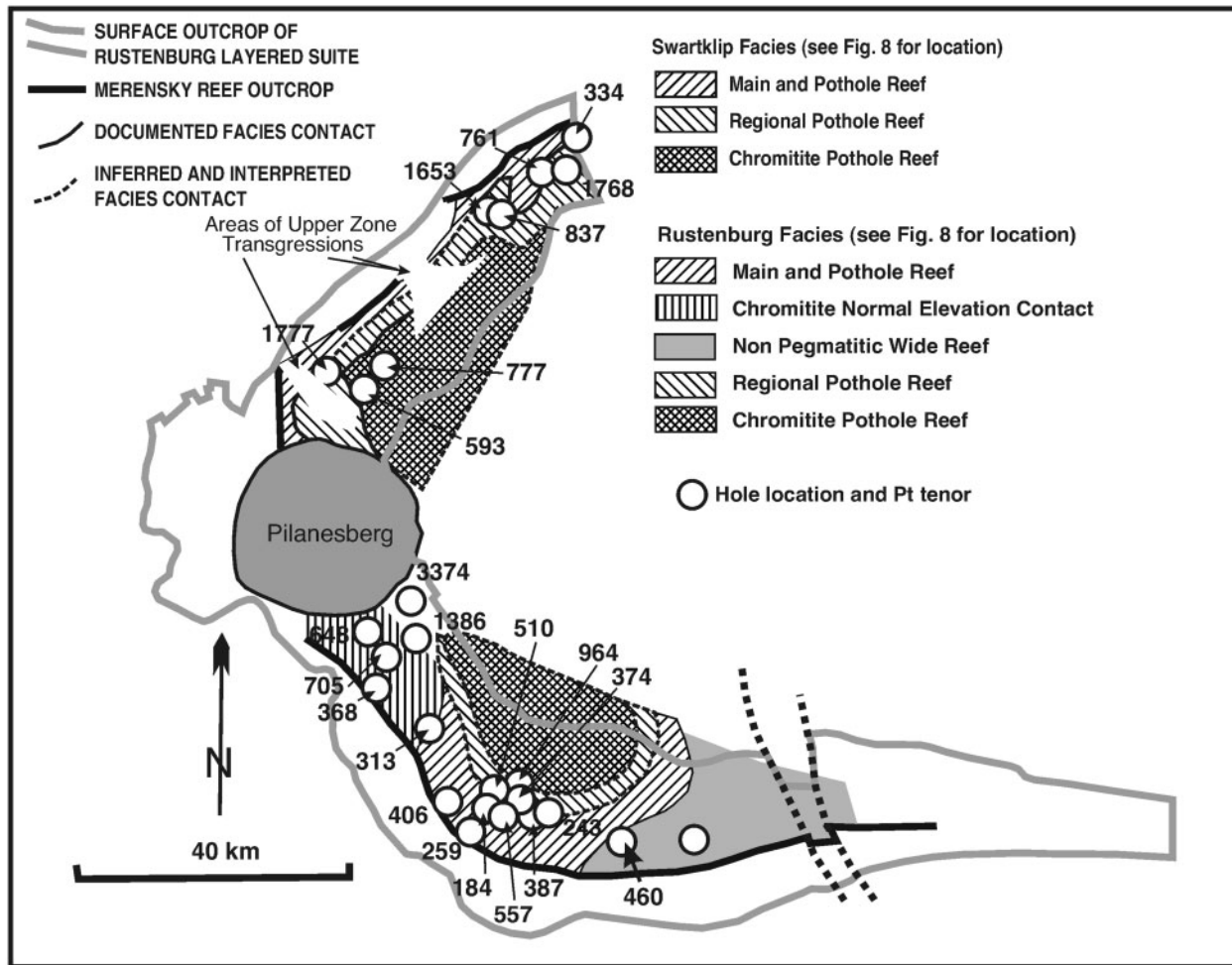
Fig. 17. Plan showing variation in maximum Pt tenor (in ppm) in boreholes in the western Bushveld.

MODEL FOR FORMATION OF MERENSKY REEF

Many recent papers (Ballhaus & Sylvester, 2000; Barnes & Maier, 2002; Wilson & Chunnett, 2006) have addressed the origin of the Merensky Reef. The data of Barnes & Maier (2002), Seabrook *et al.* (2004) and Wilson & Chunnett (2006) indicate that two magmas were involved in the formation of the Reef. It was proposed above that during formation of the Upper Critical Zone, the Bushveld chambers were occupied by a resident magma crystallizing plagioclase and orthopyroxene, and that incursions of more primitive magma, enriched in PGE and with a low Cu/Pd ratio, occurred into this along the top of the succession of cumulates (Fig. 18). The Pre-Merensky and Merensky magmas were particularly energetic examples of these inclusions, mixing with the resident magma (Eales *et al.*, 1988) and causing significant erosion of the cumulates; in some areas this gave rise to potholes or Regional Pothole Reef. It is our contention that in the case of the

Pre-Merensky and Merensky pulses, magma mixing resulted in sulfide immiscibility (Li & Ripley, 2005) and formation of the Reef (Fig. 18). In the northwestern Bushveld, where the magma was closer to its source and had mixed less with the resident magma, it was both hotter and poorer in SiO_2 so that it gave rise to more olivine-rich rocks and caused the troctolitization of the anorthosite footwall as described by Roberts *et al.* (2007).

The question arises as to how and where the two magmas interacted. Seabrook *et al.* (2005) argued on the basis of density considerations that the U-type magma was introduced first and that the T-type magma intruded subsequently beneath the U-type, that sulfide immiscibility developed as a result of pressure increase accompanying the intrusion of the magmas, and that pyroxene and sulfides from the overlying Merensky magma settled through the underlying T-type magma to form the Reef.

Figure 19 is based on the trace element data of Wilson & Chunnett (2006) and shows Th/Nb ratios for both the
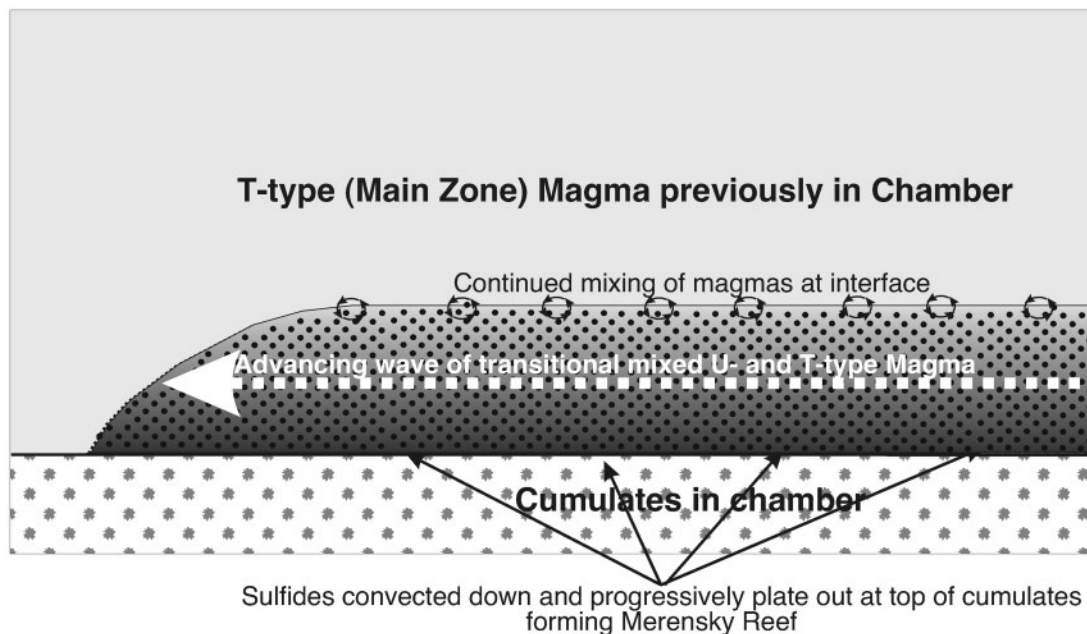
Fig. 18. A lateral mixing model for the genesis of the Merensky Reef. PGE-enriched Critical Zone (U-type) magma was introduced through a number of feeders into the Bushveld Complex where the resident magma was T-type. Some mixing of the two magma types probably took place at the points of entry, but as the magma flowed laterally, continued mixing, aided by convection within the flowing magma, resulted in continued sulfide segregation and depletion of the flowing magma in PGE. On coming to rest, fractional segregation and settling of sulfide gave rise to the observed Pt tenor and Cu/Pd profiles.

norites and anorthosites forming the footwall to the Merensky Reef, and the pyroxenite immediately overlying the bottom chromite layer of the Reef in the Styldrift area. Th/Nb ratios of both groups of rocks are intermediate to those of Wilson & Chunnett's (2006) average Main Zone (T-type) and Critical Zone (U-type) magmas, but the Footwall rocks are closer to the Main Zone magma than are the Merensky pyroxenites. This illustrates their conclusion that T-type magma had already entered the chamber and was in contact with the underlying cumulates prior to introduction and mixing or mingling of the Pre-Merensky and Merensky magmas with the Main Zone magma. It is our opinion that the field relations described above, including the scouring out of potholes, the formation of rolling reef-type structures and the incorporation of blocks of footwall cumulates into the Merensky pyroxenite, the concentration of chromite in footwall irregularities, the 'troctolitization' of footwall anorthosites, and the absence, in the northwestern Bushveld, of the products of Pre-Merensky magma in the local and regional potholes, requires the U-type magma to have been in direct contact with the cumulates at the time of deposition of the Reef. If so, and if, as the trace element data indicate, T-type magma was already in the chamber, the Pre-Merensky and Merensky magmas must have intruded beneath the T-type magma (see section on density below).

It is likely that some mixing between the two magmas took place very close to the points of entry, but we suggest that continued mixing took place at the interface between the two magmas, perhaps aided by turbulance and convection within the new pulse (Fig. 18). This led to continued sulfide saturation and settling as the magma proceeded, with the magma becoming progressively more depleted as it flowed away from the points of entry, and the sulfides thus developing progressively lower tenors. Scoon & Teigler (1994) suggested a similar mechanism for the origin of the Bushveld chromitites, which they referred to as 'lateral mixing'. It is suggested that in the case of the Merensky event, a small amount of chromite developed as the two magmas mixed, and that much of this settled to the floor and was dragged along as a bottom load by the spreading magma, thus accounting for its concentration in sedimentological traps as discussed above. The process acted at least twice, with the second pulse (the Merensky pulse) apparently being the more energetic, as this has cut through and eliminated the Pre-Merensky pyroxenite in the potholes of the northwestern Bushveld.

Problems associated with the proposed model

The above hypothesis raises certain problems in itself. One of these is how did the sulfides settle quickly enough so that the composition of the less PGE-rich sulfides segregating
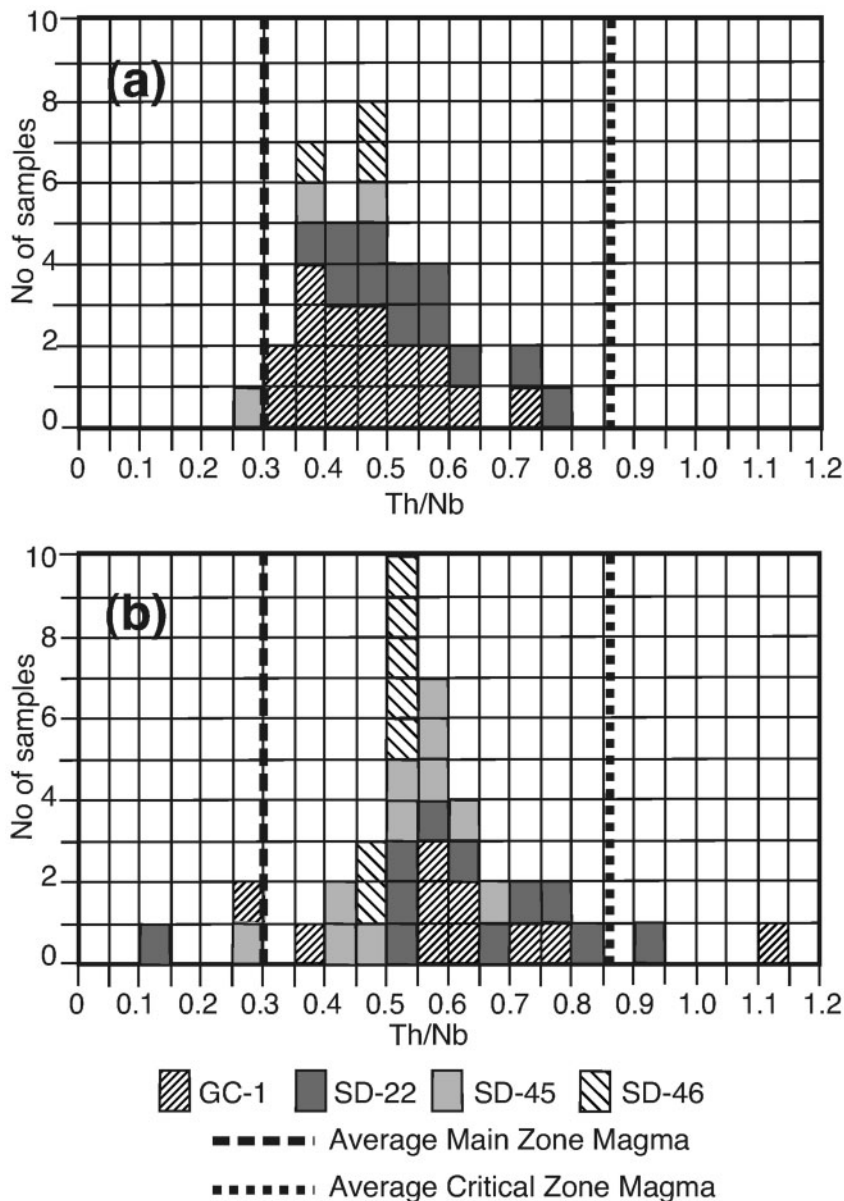
Fig. 19. Histogram comparing Th/Nb ratios in both (a) footwall norites and anorthosites, and (b) pyroxenite immediately overlying the bottom chromite layer in the Styldrift area. Average values for the Main and Critical Zone magmas are indicated [data from Wilson & Chunnett (2006)].

at a later stage near the base of the zone of magma did not get mixed with and enriched by earlier segregating sulfides settling from near the top of the zone? The second, related problem is that of the height of the column of magma needed to provide the PGE found in the Reef. A third problem relates to the relative densities of the U- and T-type magmas, as density calculations indicate that the U-type magma should be less dense that the T-type, and should not have displaced early Main Zone magma.

Mechanism of sulfide settling

Considering the problem of the settling of the sulfides first, El-Rassi (2000) found that the removal of small mica particles suspended in viscous glycerol–water mixtures was greatly enhanced if the mixtures were convecting. Rather than having to settle through the viscous medium, the convection brought the mica particles down to the base of the experimental tank, where they became trapped in the stagnant boundary layer at the base of the tank. It is suggested that a similar process of convectively induced

plating-out operated as the PMCU and MCU magmas spread out across and came to rest above the footwall to the MR, as shown in Fig. 18.

Height of required magma column and Pt solubility in mafic magma

Turning to the question of the height of the magma column required to supply the PGE of the Reef, a reasonable Pt content over a 1 m mining width would be 5 ppm Pt. Extrapolation of the data of Borisov & Palme (1997) and Ertel *et al*. (1999) on diopside–anorthite melts suggests that at 1300°C and an fO_2 of $10^{-7.3}$ [=QFM (quartz–fayalite–magnetite buffer), which is a reasonable value for the magma giving rise to the MR] the maximum solubility of Pt in the magma would be 1–2 ppb. Accepting this solubility range, the thickness of the magmas contributing to the PMCU and MCU phases of the Merensky Reef would be ~2500 m. The problem is how does one concentrate sulfides from 2·5 km of magma into a 1 m thick zone and yet still show profiles indicative of Rayleigh fractional segregation? We can envisage the mechanism of convective plating-out discussed above occurring within a magma column of perhaps tens of metres but not thousands of metres, and are forced to conclude that silicate magma can carry substantially higher concentrations of PGE than the two cited experimental studies would suggest. Tredoux *et al*. (1995) have suggested that the PGE are carried as molecular 'clusters', finely dispersed within the magma. Ballhaus & Sylvester (2000) called upon such clusters to account for the concentration of PGE in the Merensky magmas, concentrations that were subsequently incorporated in sulfide liquid. However, such clusters would not follow the Rayleigh fractionation law that is so clearly demonstrated by our data and we discount this mechanism. Bezmen *et al*. (2008) studied the solubility of Pt and Pd in water-saturated diopside–anorthite–albite melts at 1200°C and 2 kbar total pressure and found that the solubility of Pt was 20 ppm at $fO_2 = QFM$. They attributed these high solubilities to the contribution of Pt and Pd hydroxyl complexes in the magmas; it is also possible that Na might have some effect, although it is difficult to understand why. Sulfide-undersaturated flood basalts of the North Atlantic Igneous Province contain between 1 and 14 ppb Pt (Momme *et al*., 2003), those of the Tuklonsky tholeiitic–picritic suite of the Noril'sk area between 7·4 and 12·1 ppb (Lightfoot & Keays, 2005), and those of the Vaigat formation, Nuusuaq peninsula, West Greenland, between 4·7 and 10·5 ppb, with one sample carrying 39·8 ppb (Keays & Lightfoot, 2007). None of these basalts contained native Pt or Pt alloys with a high Pt activity, so that their Pt content is unlikely to have been the maximum attainable at the fO_2 at which they approached the surface (probably about QFM). Li *et al*. (2003) have shown that the presence of S decreases the partition coefficient of Ni between olivine and sulfur-unsaturated mid-ocean ridge

basalt by a factor of up to two, depending on the S content of the magma, which they attributed to the formation of Ni–S complexes within the magma increasing the affinity of Ni for the magma. PGE are far more chalcophile than Ni, so it is reasonable to expect that the presence of even small amounts of S dissolved in a silicate melt might have a significant effect on their affinity for the melt. Our conclusion is that, for reasons that are not fully understood, silicate magmas can carry much higher concentrations of PGE than experimental work on dry, S- and Fe-free diopside–anorthite melts would suggest. Naldrett *et al*. (2008) have reinterpreted the data of Maier & Barnes (1999) to indicate that the Bushveld Critical Zone magma was capable of dissolving up to 200 ppb Pt and Pd.

Generation of PGE-enriched magma

If the Merensky magmas contained 200 instead of 2 ppb Pt, the thickness of the column of magma required to give rise to the MR is reduced from 2500 to 25 m. Given that the Reef is the consequence of at least two pulses of magma, this reduces the required thickness of each pulse to 12·5 m, within which it appears possible to us that convective fractional plating-out could have occurred. The next question is how could such a PGE-rich magma have been produced? As detailed above, the documented Pt contents of tholeiitic and picritic lavas rarely exceed 20 ppb. The concept of the upgrading of magma in chalcophile metals as a result of interaction with early formed sulfides was proposed by Naldrett *et al*. (1992) to account for the PGE-rich deposits associated with the Talnakh-type intrusions at Noril'sk. Brugmann *et al*. (1993) suggested that PGE-rich sulfides such as those found at Noril'sk would be upgraded by a process of 'zone refining' as they settled through a vertical column of magma and scavenged chalcophile metals from the magma. The concept of the upgrading of early formed sulfides in a magma conduit through reaction with magma flowing through the conduit was proposed by Naldrett *et al*. (1996) for the Noril'sk–Talnaklh ores and Naldrett *et al*. (2000) for the Voisey's Bay deposit. Maier (2005) pointed out that, given the negative effect of increasing pressure on sulfide solubility, if a magma carried entrained sulfides, on rising into regions of lower pressure it would selectively dissolve FeS from these sulfides, enriching the remaining sulfide in more chalcophile elements such as the PGE. Kerr & Leitch (2005) considered the question of the upgrading of sulfides as a result of the dissolution of FeS from pre-existing sulfides through their interaction with sulfide-unsaturated flowing magma. They pointed out that sulfide-unsaturated magma will dissolve sulfide to tend towards saturation, but that, because of the much more chalcophile nature of both the PGE and Ni and Cu in comparison with Fe, the bulk of the dissolved sulfide will be FeS, with the more chalcophile metals remaining with the sulfide until very little of this remains. The equations of Kerr & Leitch (2005) have been used
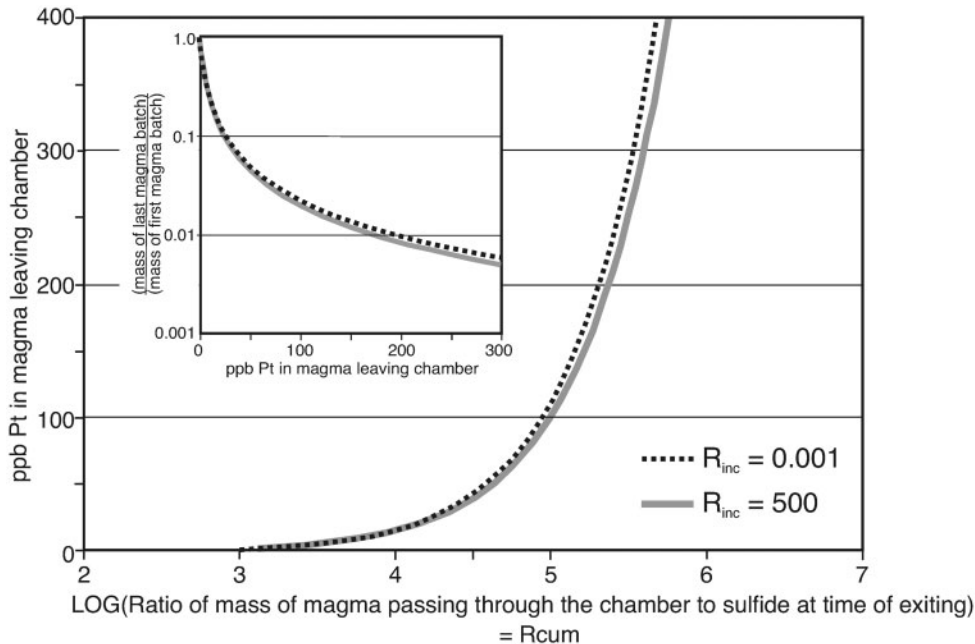
Fig. 20. Enrichment of a magma as a result of multiple upgrading of sulfide along with sulfide dissolution based on the equations of Kerr & Leitch (2005). In the example shown the Pt content of the magma is taken as 20 ppb and the value of $D_{Pt}^{sul/sil} = 10\,000$. It is assumed that a batch of magma had deposited a zone of sulfide and that the R factor of these sulfides was 1000. New, PGE-undepleted and sulfide-unsaturated magma entered the chamber and interacted with the sulfide, enriching it in PGE, and also dissolving some of the sulfide. The ratio of the mass of each successive batch of magma entering the system to the sulfide remaining in the chamber is R'_{inc}, and the sum of all batches of magma to the amount of sulfide remaining in the chamber is R_{cum}. Following the reasonable assumption of Kerr & Leitch (2005), it has been assumed that the ratio of sulfide dissolved to the mass of each successive magma batch is 0·0005 (= their L/R'_{inc} ratio) (thus the mass of each batch of magma entering the system decreases as the remaining sulfide is progressively dissolved). Two situations are illustrated in this figure, one in which R'_{inc} is 500, and the other in which R'_{inc} is 0·001. This second example was chosen because it is likely that in nature this reaction proceeds as a semi-continuous, not a batch process, and by investigating very small batches of magma we are approximating a continuous system. As Kerr & Leitch (2005) pointed out, the sulfides become very enriched in Pt. The figure illustrates how, in addition to enriching the sulfides, the magma leaving the system is also enriched in PGE, in the later stages far above its initial PGE content. In the two cases illustrated, the Pt concentration in the last batch of magma to interact with the sulfides reaches 200 ppb at almost the same value of R'_{cum} of just over 200–000, showing that the enrichment is not strongly related to the relative size of a batch. The amount of PGE-enriched magma produced in this way is very small in comparison with the initial magma depositing the sulfides. As shown in the inset, if the magma is enriched to 200 ppb Pt, its mass will only be about 1% of that initially depositing the sulfides. Despite the small quantities of PGE-enriched magma being produced, this process of 'cannibalization' of pre-existing sulfide can give rise to extremely high PGE concentrations in a magma, provided, as discussed in the text, the magma can dissolve these amounts.

to illustrate the effect of the interaction of sulfide containing a relatively low concentration of Pt with successive batches of sulfide-unsaturated magma in Fig. 20. An explanation of the assumptions underlying the use of these equations is given in the legend to the figure.

It is suggested that the sulfide that was upgraded to produce the PGE-enriched magmas of the Upper Critical Zone was deposited from early batches of magma (perhaps those responsible for the Lower Zone) in a staging chamber (Fig. 21) that subsequently became a conduit for later magma. Successive batches of magma passing through this chamber dissolved FeS, leaving the residual sulfide progressively more enriched in Ni, Cu and PGE. As time progressed, the sulfides developed an unusually low Cu/Pd ratio (because Cu was dissolved by the successive pulses of magma more readily than Pd) and this ratio was impressed on later batches of magma passing through the

system. These batches were not necessarily sulfide-saturated but their Ni, Cu and PGE contents reflected the sulfides with which they had interacted. This model is supported by the earlier demonstration that some sulfide-absent zones in the interval between UG-2 and the MR (Fig. 13) have low Cu/Pd ratios of the order of 100. McDonald & Holwell (2007) have proposed a similar staging chamber model, although their model is directed specifically at the origin of the Platreef.

Density considerations

In the preceding discussion, evidence has been cited that makes it highly likely that the Pre-Merensky and Merensky magmas spread out across the top of the cumulate pile. However, as others have pointed out previously (Campbell *et al.*, 1983; Seabrook *et al.*, 2005) and as calculations using the equations of Lange & Carmichael (1987)
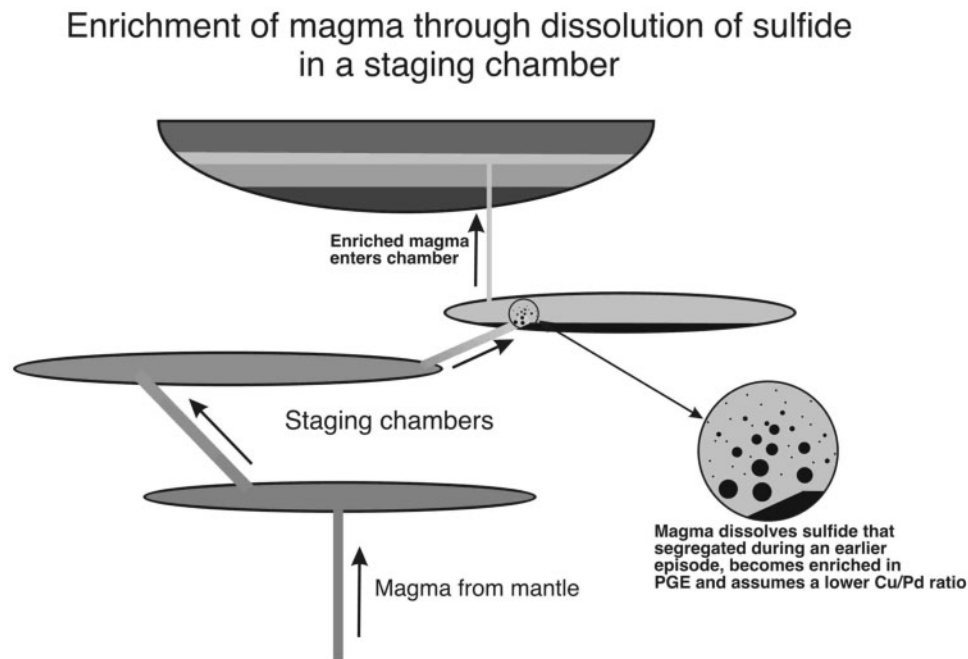
Enrichment of magma through dissolution of sulfide in a staging chamber

Fig. 21. Staging chamber model for the development of PGE-enriched magma with a low Cu/Pd ratio. Sulfides are deposited by an early batch of magma in a staging chamber. Subsequent batches of sulfide-unsaturated magma passing through the system interact with these sulfides, dissolving primarily FeS, with the resultant enrichment of the sulfides in elements more chalcophile than Fe. It is possible that the Merensky magma pulses dissolved the last of the by then very enriched sulfide, becoming very PGE enriched themselves. This would then account for the low tenors of sulfides at the base of the Bastard cyclic unit that overlies the Merensky cyclic unit.

show, the calculated density for the Main Zone magma (at 1200°C, and a molar ratio of $Fe_2O_3/FeO = 0.1$) is 2.707 g/cm^3. This is significantly higher than that calculated for the Critical Zone magma (2.653 g/cm^3) under the same conditions. The conclusion is also true if one uses the equations of Bottinga & Weill (1970) or Bottinga *et al*. (1982) rather than those of Lange & Carmichael (1987). Ochs & Lange (1999) remarked that 'the effect of 1 weight percent dissolved H_2O on the density of a basaltic melt is equivalent to increasing the temperature of the melt by ~400°C'. Using this very qualitative assertion, if the Main Zone magma had contained 1 wt % H_2O, it would have been slightly less dense (2.641 g/cm^3) than dry Critical Zone magma. It must be noted that the rocks of the Main Zone show little sign of deuteric alteration, so that evidence that they formed from a magma that was substantially more hydrous than that responsible for the Critical Zone is lacking. Thus, field relations and densities calculated on the basis of partial molar volumes seem to be in conflict. In the emplacement model presented above, we have chosen to be guided by field relations rather than density calculations for dry magma.

CONCLUSIONS

The overall conclusion of this study is that the Upper Critical Zone of the Bushveld Complex (base of UG-1

to the top of the Bastard cyclic unit) is the product of a body of resident magma in the chamber crystallizing orthopyroxene and plagioclase, into which a succession of more primitive (orthopyroxene ± olivine and/or chromite but no plagioclase on the liquidus) magma pulses were injected along the cumulate–magma interface. These influxes were derived from a staging chamber in which previous bodies of magma en route to the complex had deposited sulfide. The FeS component of this sulfide was selectively dissolved by fresh, sulfide-unsaturated magma passing through the chamber, with the result that the remaining sulfide became steadily enriched in Ni, Cu and particularly the PGE, and developed a low Cu/Pd ratio. These characteristics were impressed on later batches of magma passing through the staging chamber as they approached equilibrium with the residual sulfide or, possibly in the case of the Merensky magmas, dissolved away the last of the residual sulfide. The result was that these later influxes of magma were highly enriched in PGE (≈ 200 ppb Pt as compared with 10–20 ppb). By the time that the Pre-Merensky magma was injected, the resident magma had changed from that responsible for much of the Critical Zone (U-type) to that responsible for the Main Zone (T-type). Possibly this change resulted in a greater amount of sulfide being segregated as a consequence of the Pre-Merensky and Merensky influxes than had

occurred in the case of previous additions of magma, thus accounting for the relatively sulfide-rich nature of the Reef. The magma influxes spread out over the cumulates in the chamber, continuously mixing with the resident magma. Continued sulfide segregation as a result of this mixing resulted in their becoming progressively depleted in chalcophile metals as they progressed away from the feeders, accounting for the lateral variations in maximum PGE tenor observed in the Merensky cyclic unit. On coming to rest, continued fractional segregation of sulfide gave rise to the exponential upward decrease in PGE tenor and major change in Cu/Pd ratio that have been documented as part of this study.

It will be apparent to the reader that our conclusions imply that a very specific set of circumstances operated in the case of the Merensky Reef. The question arises: 'Does this mean that similar circumstances are unlikely to have operated elsewhere, and that the high PGE concentrations of the Bushveld are a one-off?' In this respect, PGE enrichment of magma by selective dissolution of earlier sulfides deposited in a staging chamber has also been called upon (Li *et al.*, in preparation) to rationalize the 'R' values dictated by sulfur isotope and PGE data at Noril'sk, Siberia. The Ni–Cu–PGE deposits at Noril'sk, Siberia, are the most PGE-enriched Ni–Cu–PGE deposits known (Naldrett, 2004). Besides accounting for approximately one-third of the world's known sulfide Ni resources (i.e. excluding Ni contained in laterites), they also contain respectively 24% and 5% of the world's resources of Pd and Pt. We suggest that 'cannibalization' of earlier sulfide, either in a staging chamber or within the crystallizing intrusion itself, may well be an important process in the formation of magmatic PGE deposits in general.

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SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal of Petrology* online.

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