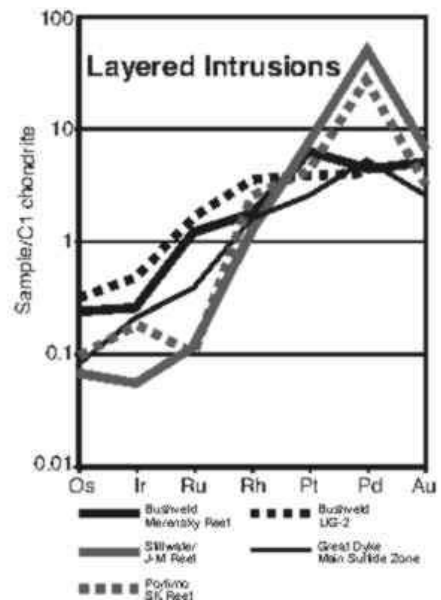
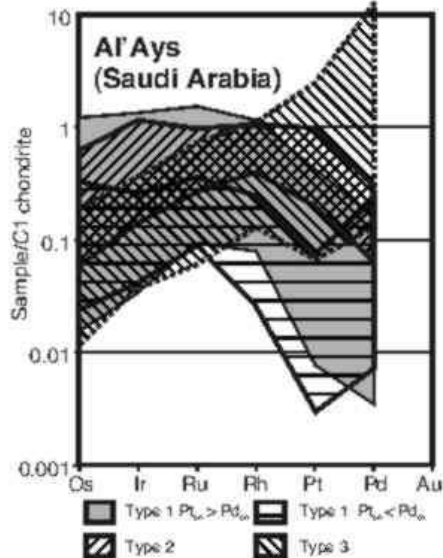
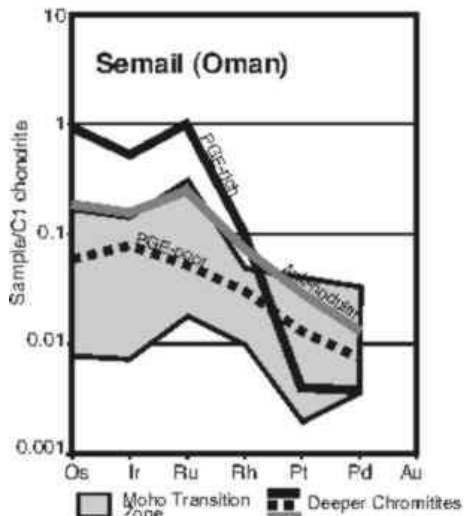
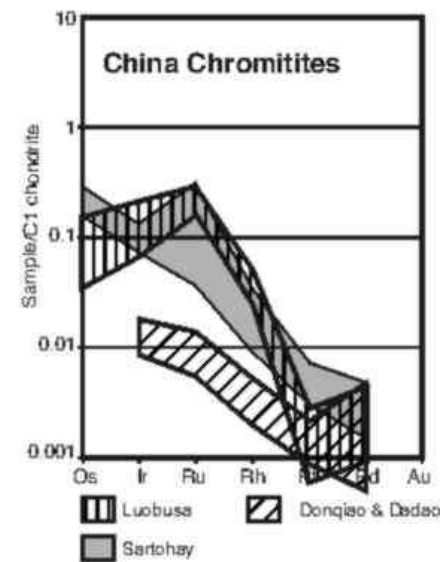
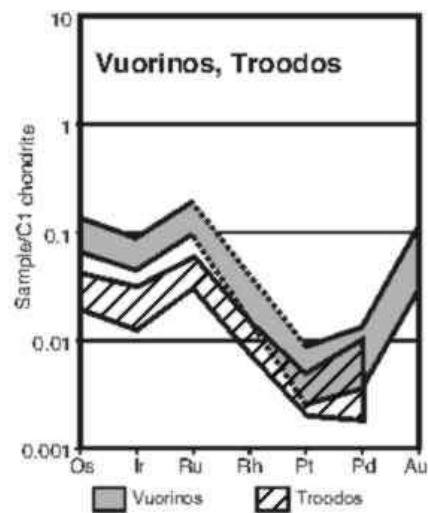
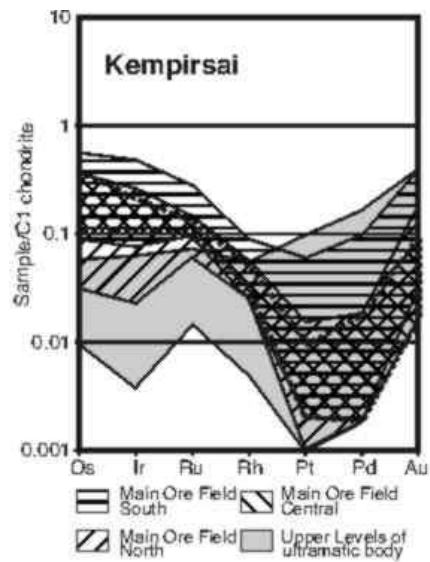


**PGE in the Lower and Middle Group
Chromitites of the Bushveld Complex**

HAPPY BIRTHDAY KEVIN AND LEW

**Tony Naldrett, Judith Kinnaird, Allan Wilson,
Stewart McQuade, Gordon Chunnnett and Chris Stanley**

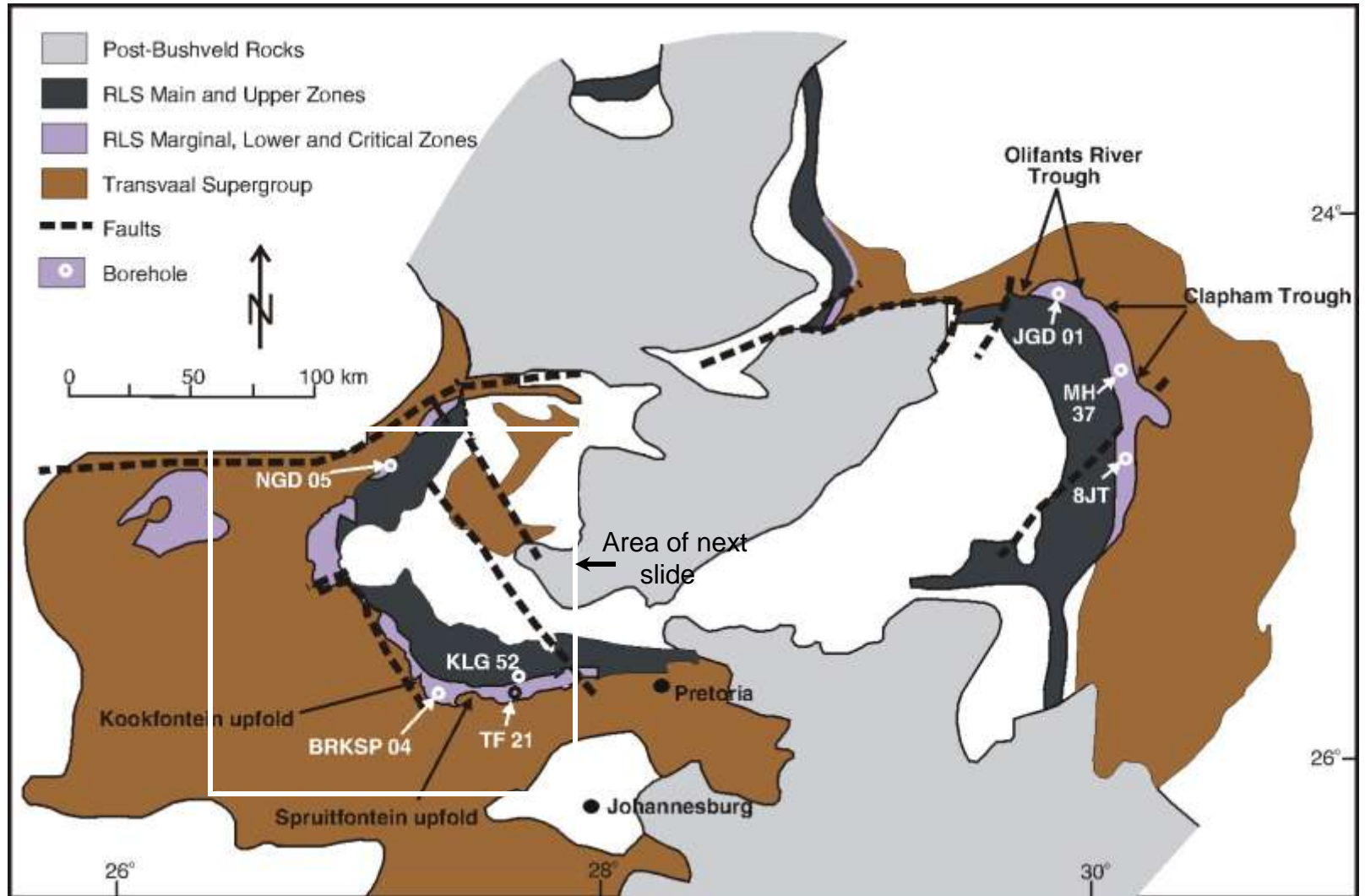


Chromitites from ophiolites generally, but not always, have low Pt and Pd and high Rh, Ru, Ir and Os. Chromitites from layered intrusions show the reverse

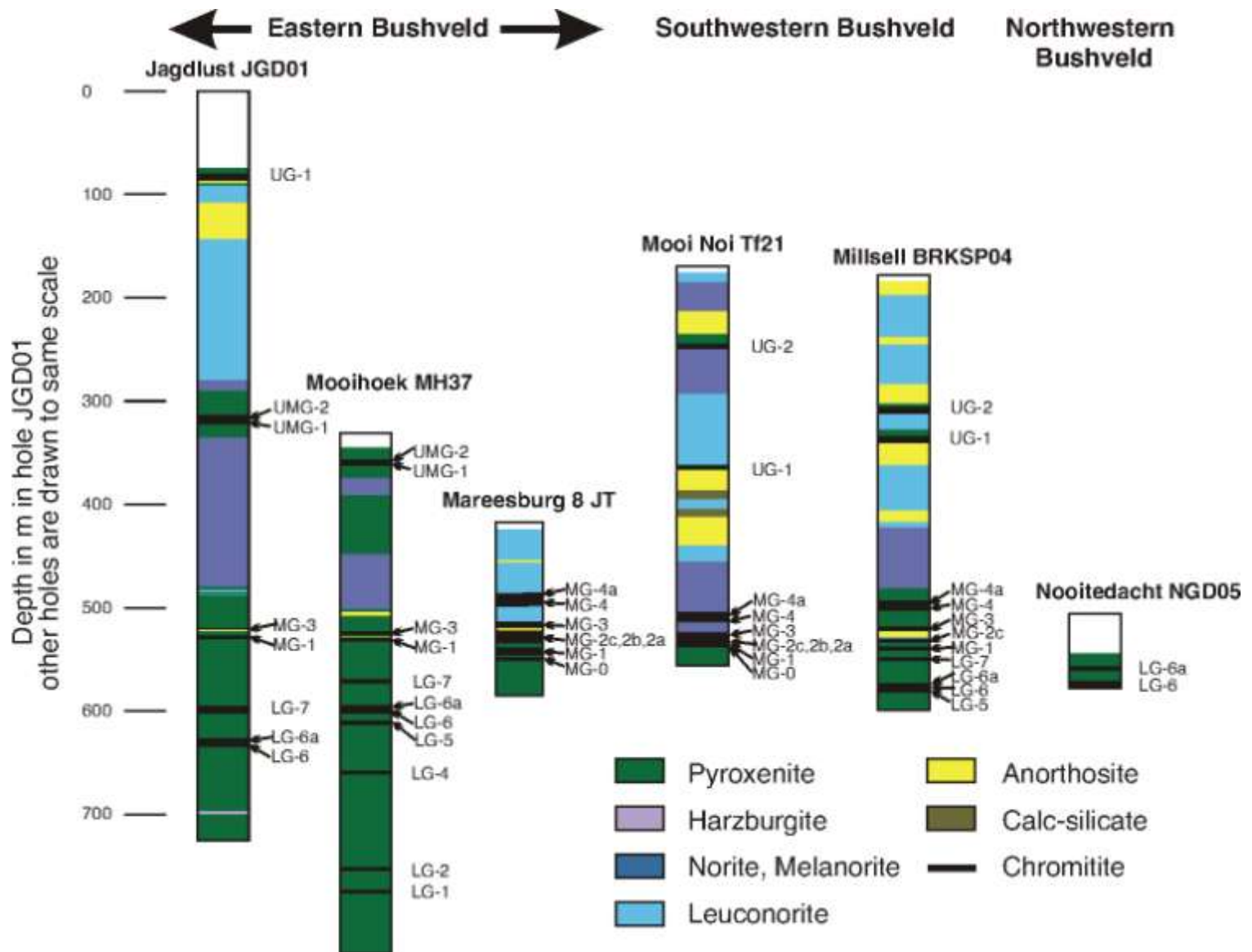
The purpose of this presentation to to explain aspects of the association of PGE with Lower and Middle Group chromitites of the Bushveld complex, and to show the implications of this with respect to PGE in chromitites generally.

Specifically

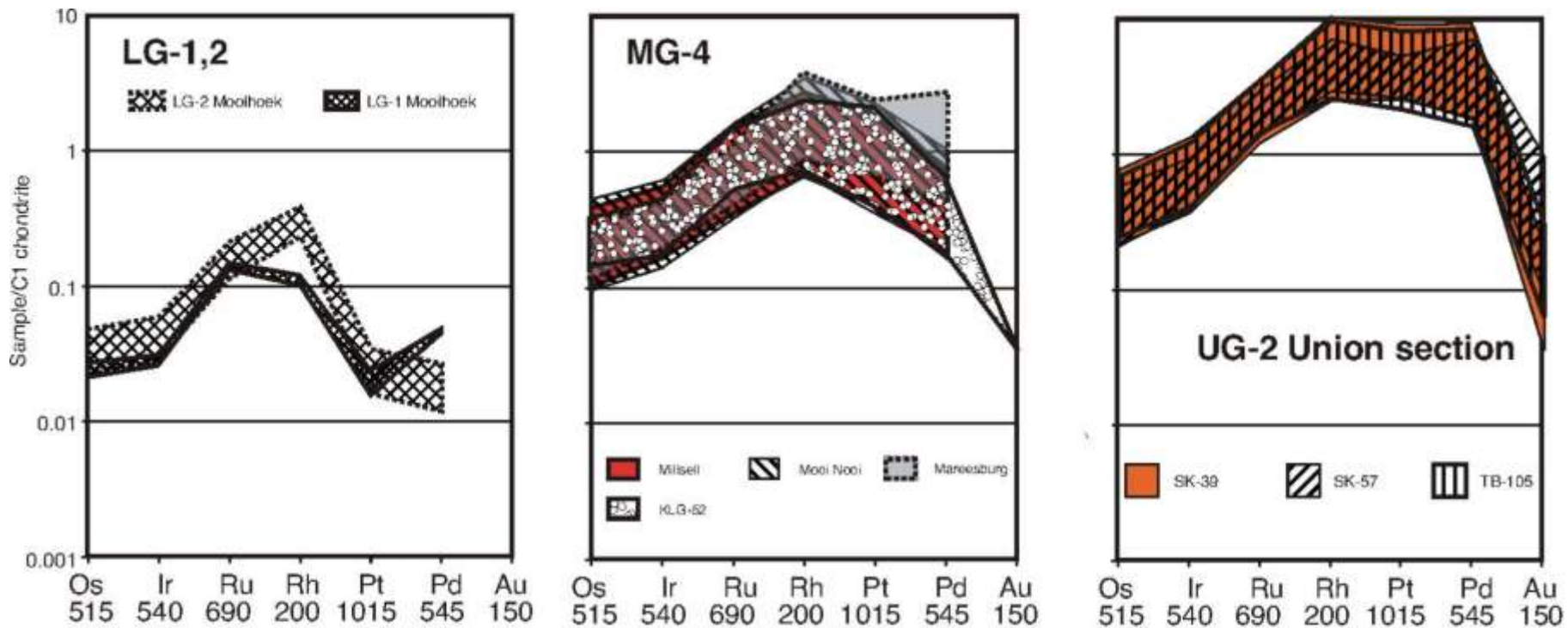
1. The variation in PGE concentrations from the LG-1 to UMG-2
2. The variation in composition of the chromitites with stratigraphy and the implications of this with respect to how the Bushveld magma was changing in composition
3. The fact that high concentrations Pt and Pd in chromitites from the LG-5 upward are due to their having contained sulfide that has largely been destroyed by reaction with chromite
4. That modeling of the magma-mixing hypothesis can explain the presence or absence of sulfide in particular chromitites



Core from drill holes were chosen to reflect the different sector (compartments) of the Bushveld to see if differences existed between them

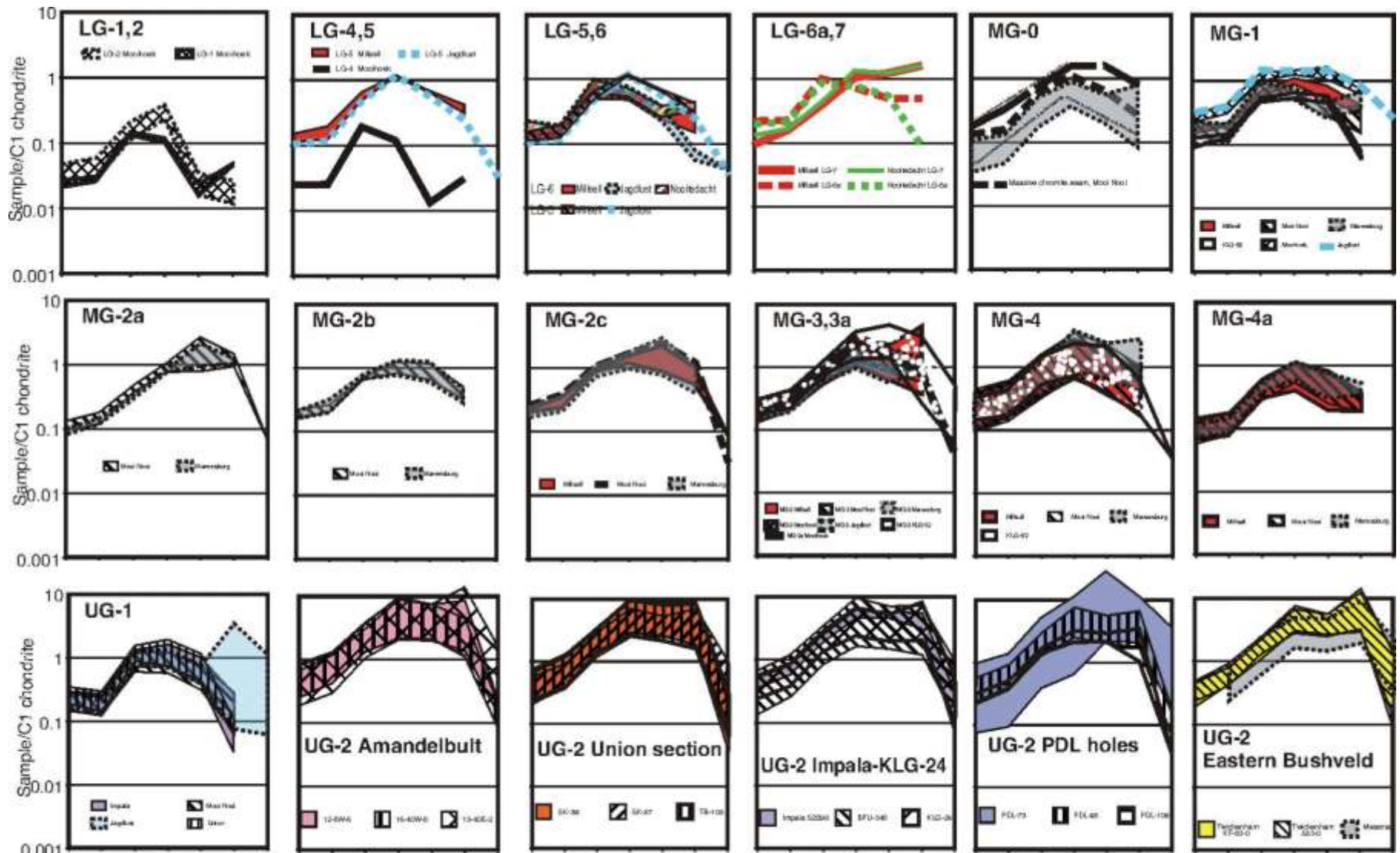


Drill holes sampled. Note that not all chromitites are present in all sectors

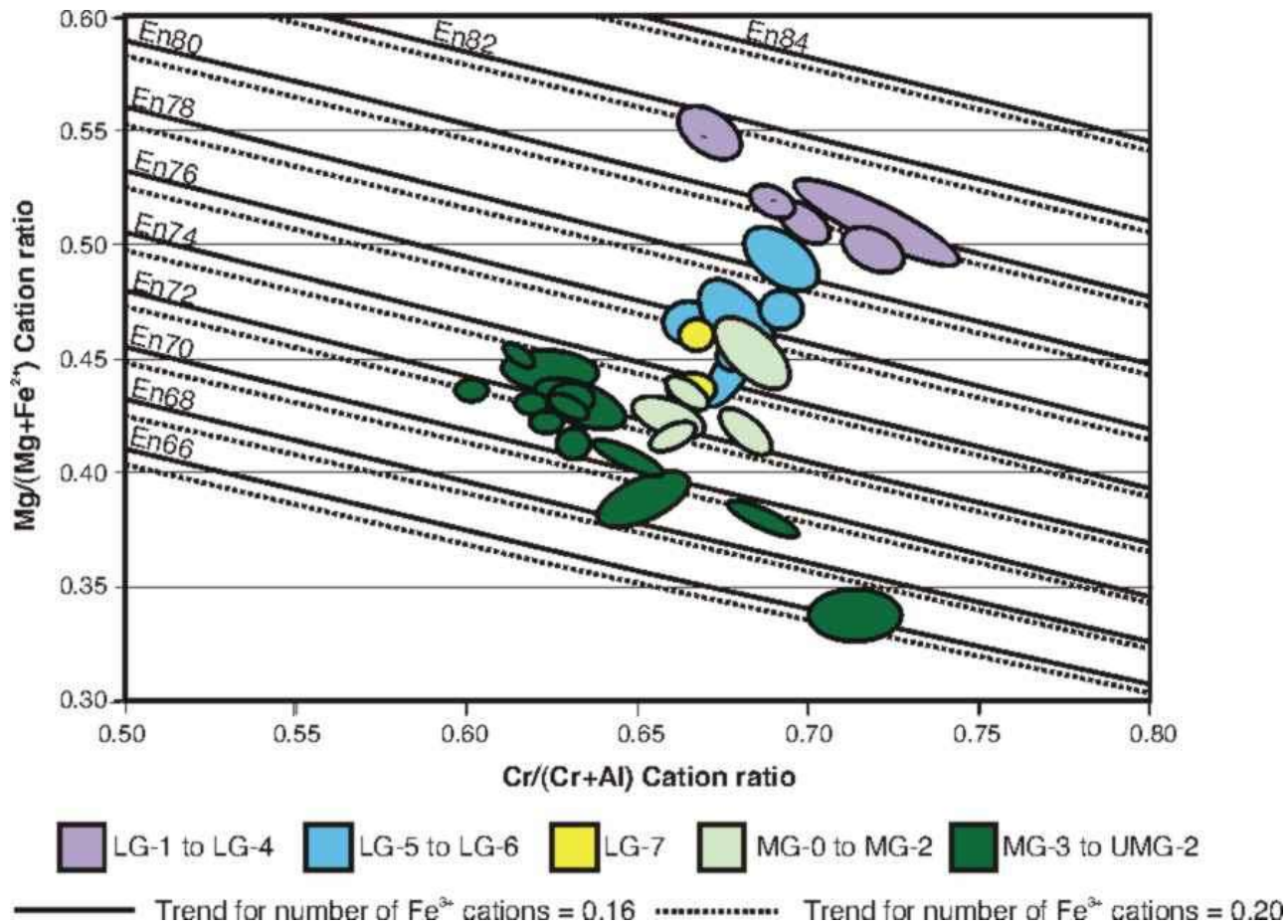


Chondrite-normalised PGE profiles of some Chromitites

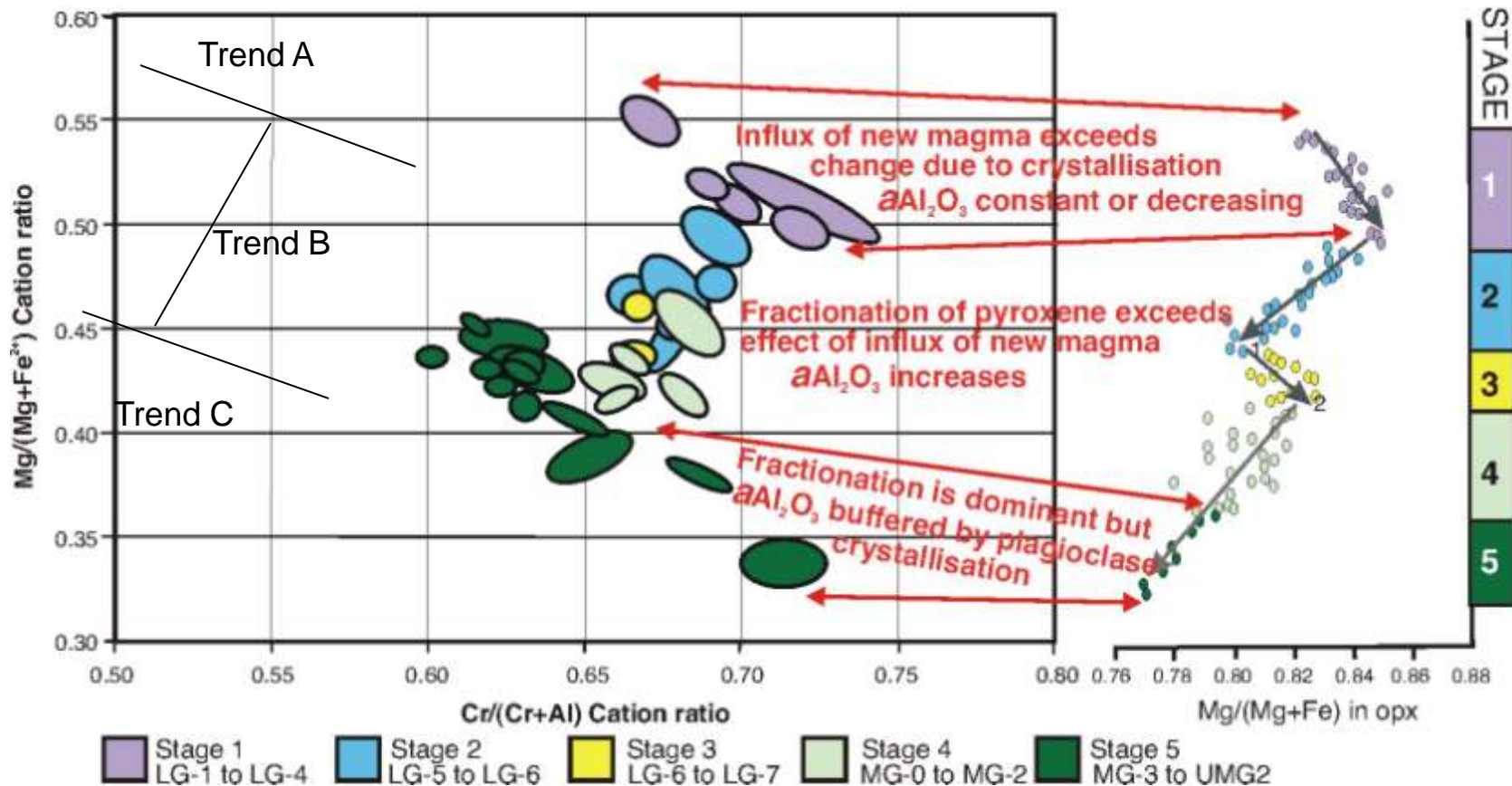
Note: The shaded areas represent the range in PGE concentrations in different samples collected continuously across massive chromitite at each location. The number below each element is the concentration in C1 chondrite in ppb, and is the number with which the concentration in the sample was normalised.



Order of noble metals (left to right): Os-Ir-Ru-Rh-Pt-Pd-Au



The Mg/(Mg+Fe²⁺) vs Cr/(Cr+Al) plot contoured in terms of variation in Mg/(Mg+Fe²⁺) ratio of the spinel that would result from variation in the Cr/(Cr+Al) ratio of the same spinel in equilibrium with a liquid with a constant Mg/Fe²⁺ ratio. The value of this ratio is indicated by the En content of the orthopyroxene that would be in equilibrium with this liquid. The contours are based on the equations of Allan et al. (1988) that show that the reciprocal exchange substitution of Cr and Fe²⁺ for Mg and Al between spinel and liquid will have a major effect on the Mg-Fe exchange partition coefficient between spinel and liquid.

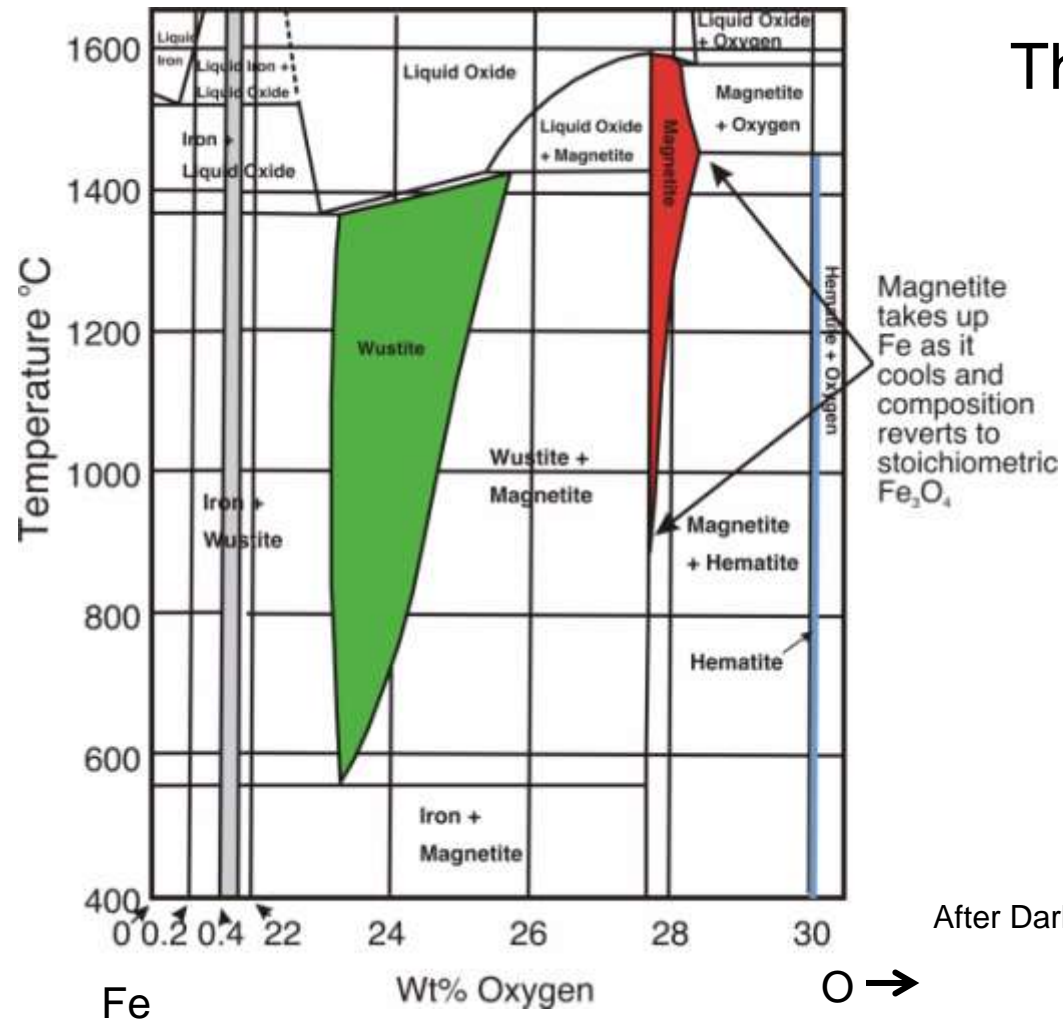


Explanation of trends. Trend A Influx of new magma, as indicated by the change in MgNo of orthopyroxene from Eales et al.'s (1988), over-rode any changes due to crystallisation so ΔAl_2O_3 did not increase. Chromite composition was controlled largely according to Allen et al.'s equations

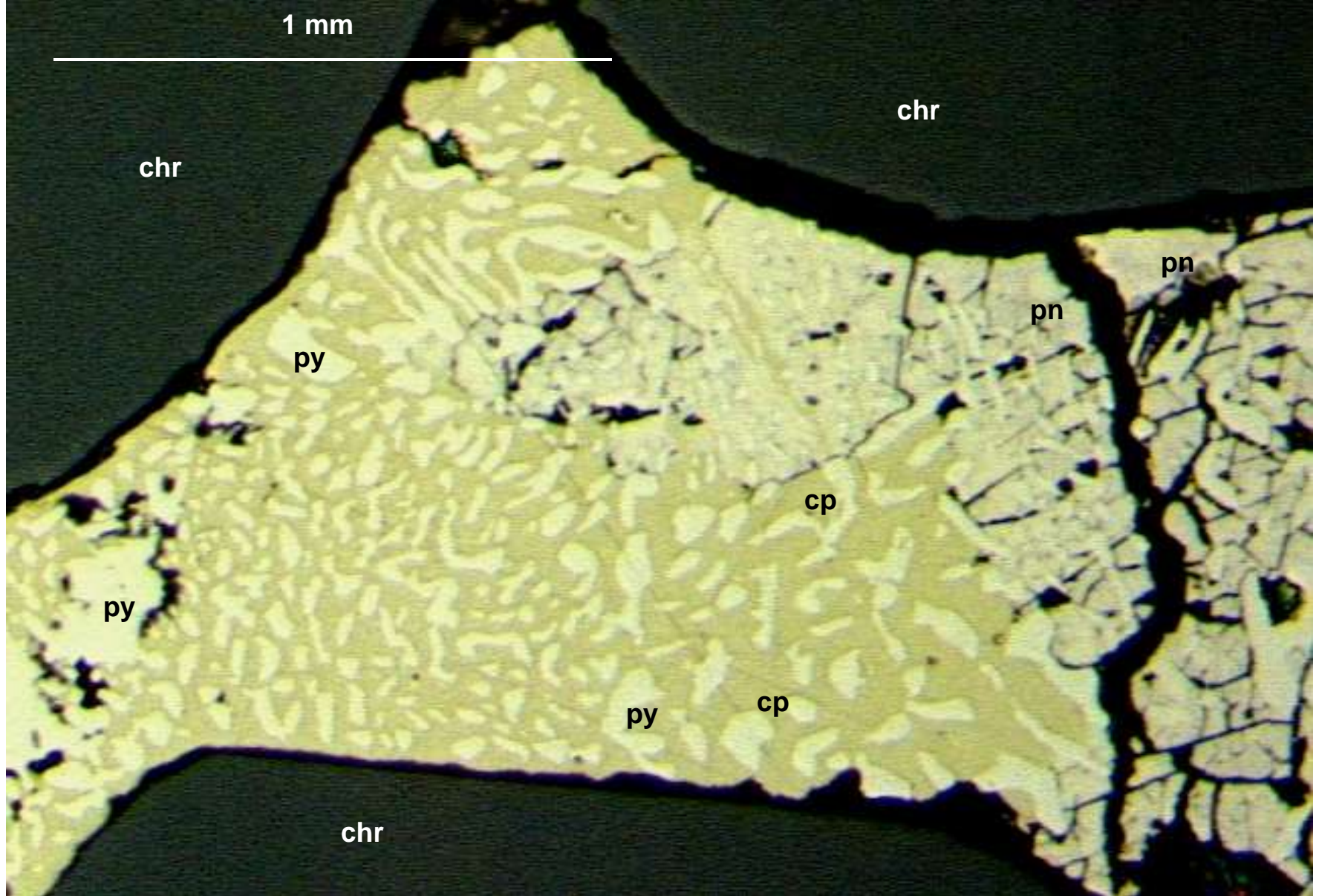
Trend B Here the MgNo data indicate that fractional crystallisation was dominant, and as mafic minerals crystallised ΔAl_2O_3 increased. This is reflected in the decreasing Cr/(Cr+Al) of the chromites

Trend C This sets in above the MG-2. While the orthopyroxene data indicate that fractionation was still dominant, plagioclase appears on the liquidus and essentially buffers Al_2O_3 so that the Allen et al. equation again largely control chromite composition

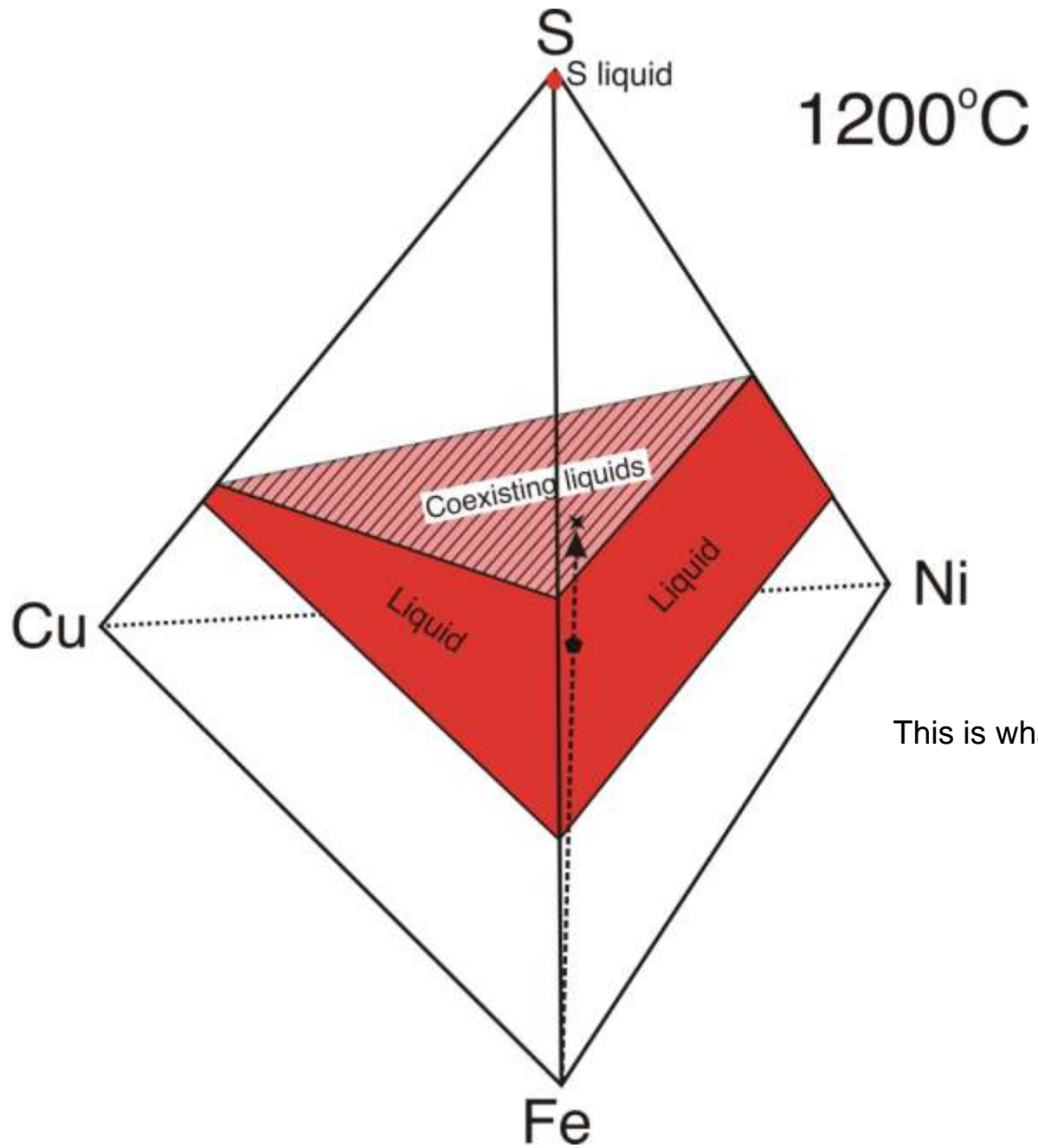
The system Fe-O



Magnetite is non-stoichiometric above 900°C, with a deficiency of Fe atoms, the extent of the deficiency depending on the prevailing fO_2 . Naldrett and Lehman (1987) showed thermodynamically that cooling magnetite will react with pyrrhotite, taking up Fe and increasing the fS_2 and the S content of the sulfide, until the fS_2 is so high that S is lost to the local environment



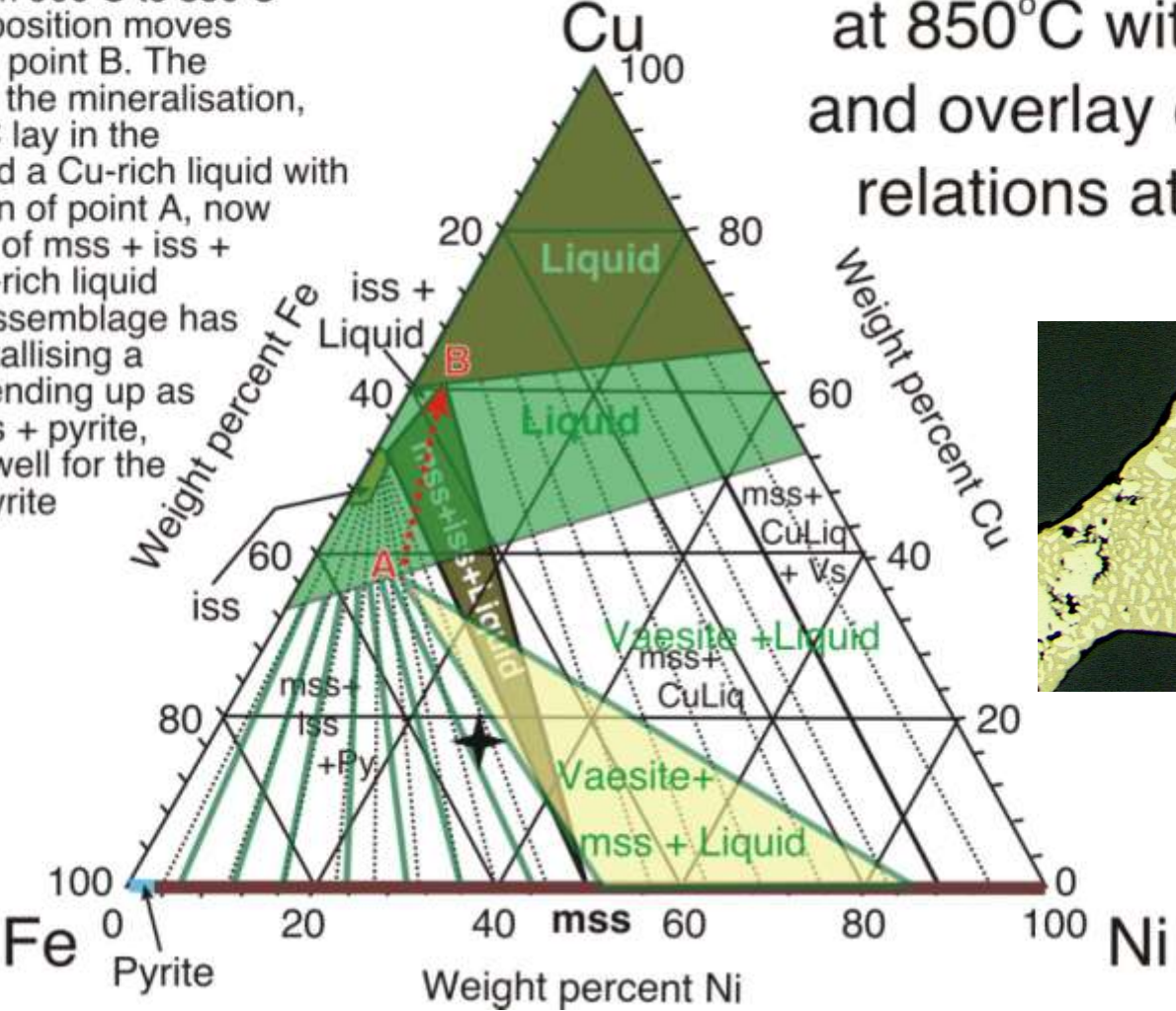
This is a photomicrograph of sulfide in chromite from UG-2 at the Lonmin-Limpopo deposit. The sulfide assemblage consists of chalcopyrite, pyrite and pentlandite. This is taken as evidence that the Naldrett-Lehmann reaction has occurred. Where sulfide are surrounded by silicate, the assemblage is the normal one of pyrrhotite-chalcopyrite-pentlandite.

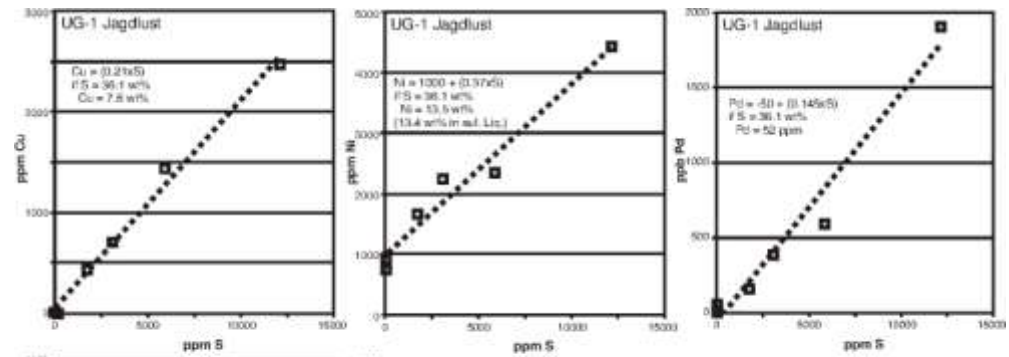


This is what has occurred

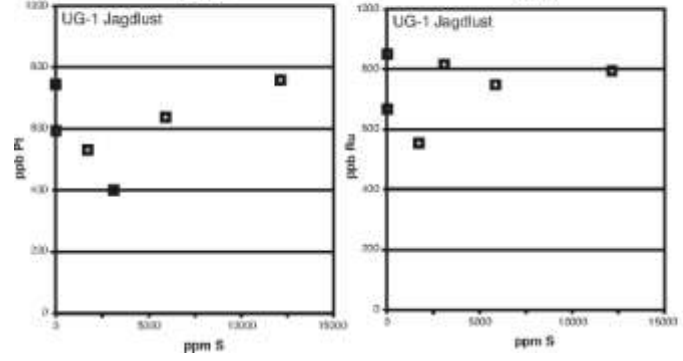
Schematic section through the CuFeNi system at 850°C with pyrite and overlay of phase relations at 900°C

On cooling from 900°C to 850°C the liquid composition moves from point A to point B. The composition of the mineralisation, which at 900°C lay in the field of mss and a Cu-rich liquid with the composition of point A, now lies in the field of mss + iss + pyrite. The Cu-rich liquid of the 900°C assemblage has solidified, crystallising a little mss and ending up as a mixture of iss + pyrite, that accounts well for the chalcopyrite-pyrite symplectite



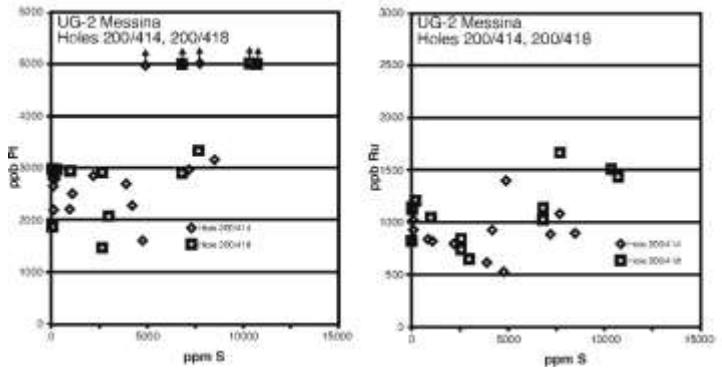
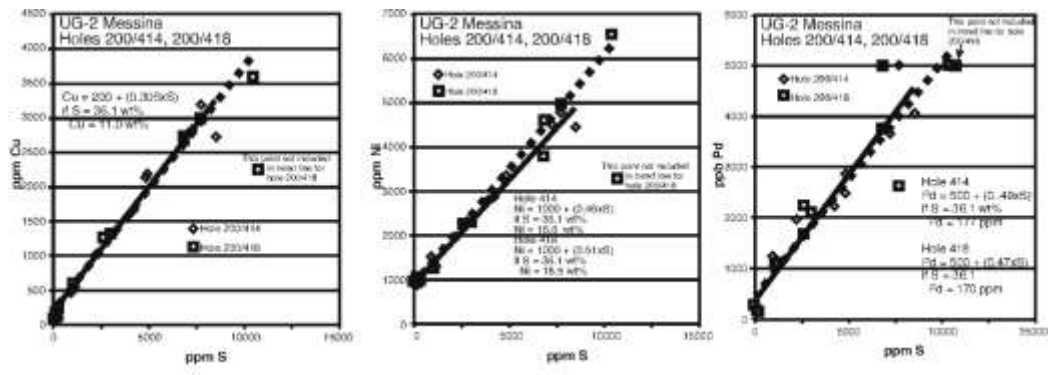


NOTE: In these sulfide-rich environments we see a correlation of Cu, Ni, and Pd with S, but no correlation for Pt, Rh, Ru, Ir and Os with S

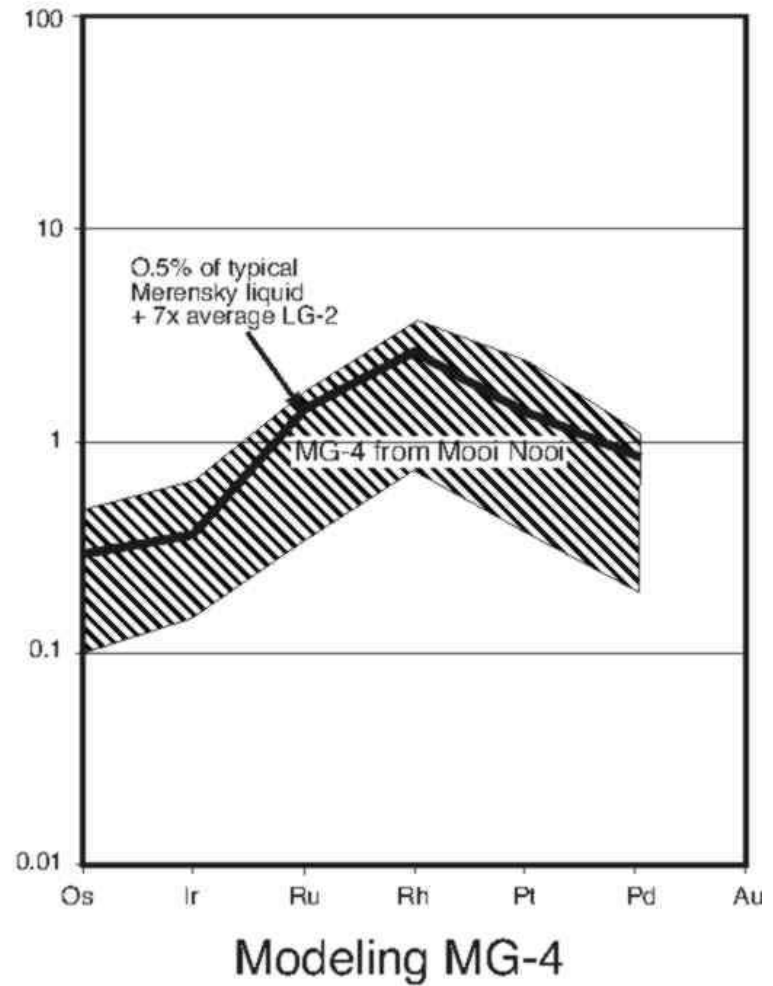
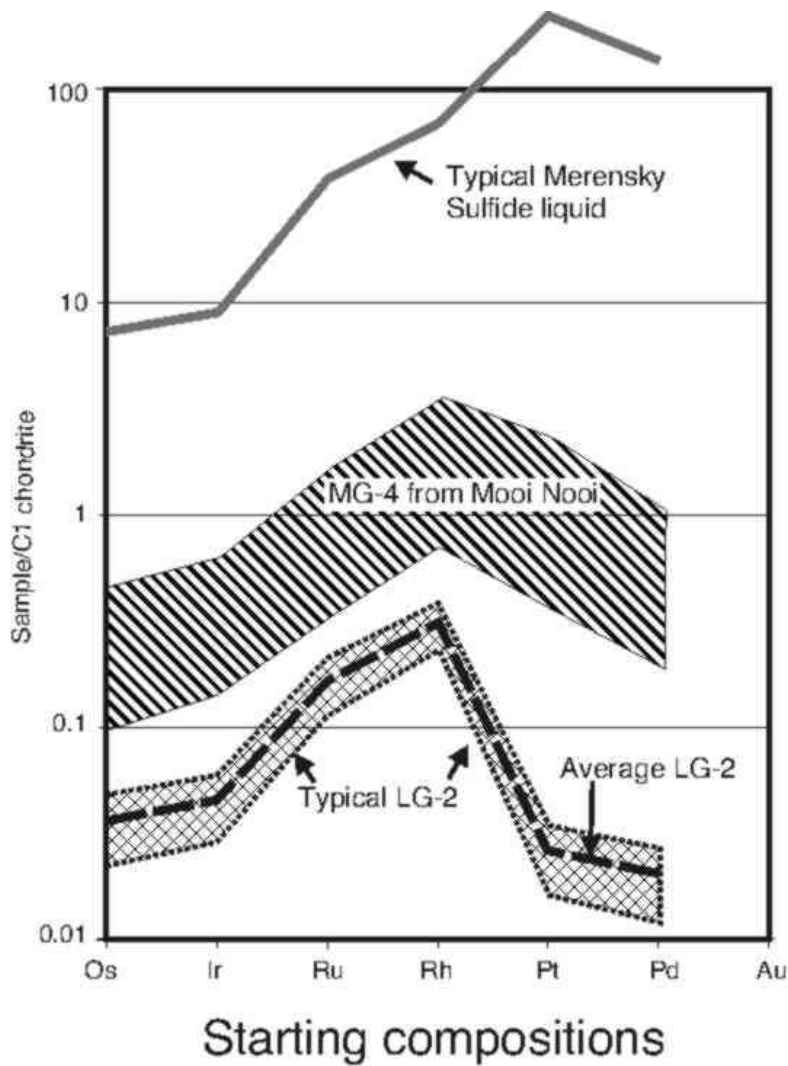


Metal vs S
UG-1 Jagdlust

Interpretation is that Rh, Ru, Ir and Os were included in growing chromite grains (consistent with mineralographic observations) but that the Cu, Pt, Pd, most of the Ni and some of the other PGE were contributed by sulfide that has subsequently been lost, along with the metals in it, EXCEPT Pt which formed as resistant minerals (alloys, As, and others) and some Ni that was in solid solution in chromite



Metal vs S
UG-2 Messina



Accepting this, the chromitites from the LG-5 up can be modeled as a mixture of Ni, Rh, Ru, Ir and Os in chromite in proportions similar to those in the LG-4, plus a contribution of Ni, Cu, Pt, Pd and minor amounts of the other PGE from a small percentage of Merensky-like sulfide liquid

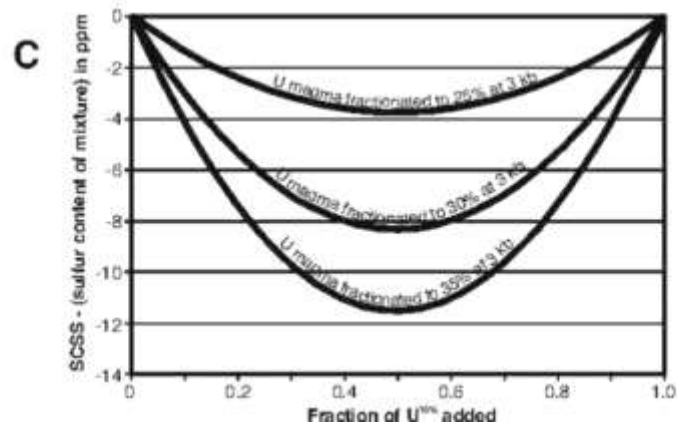
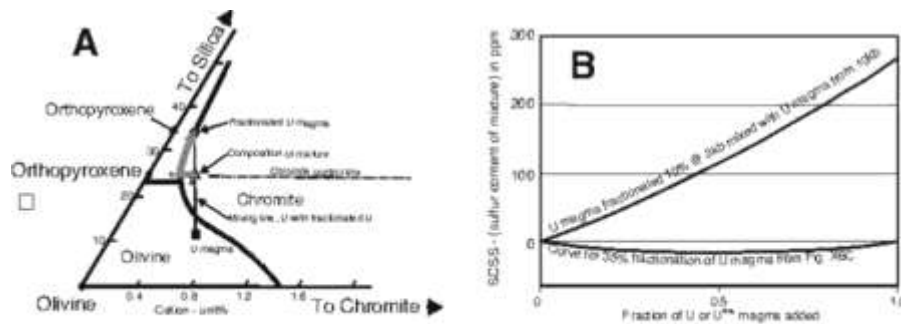
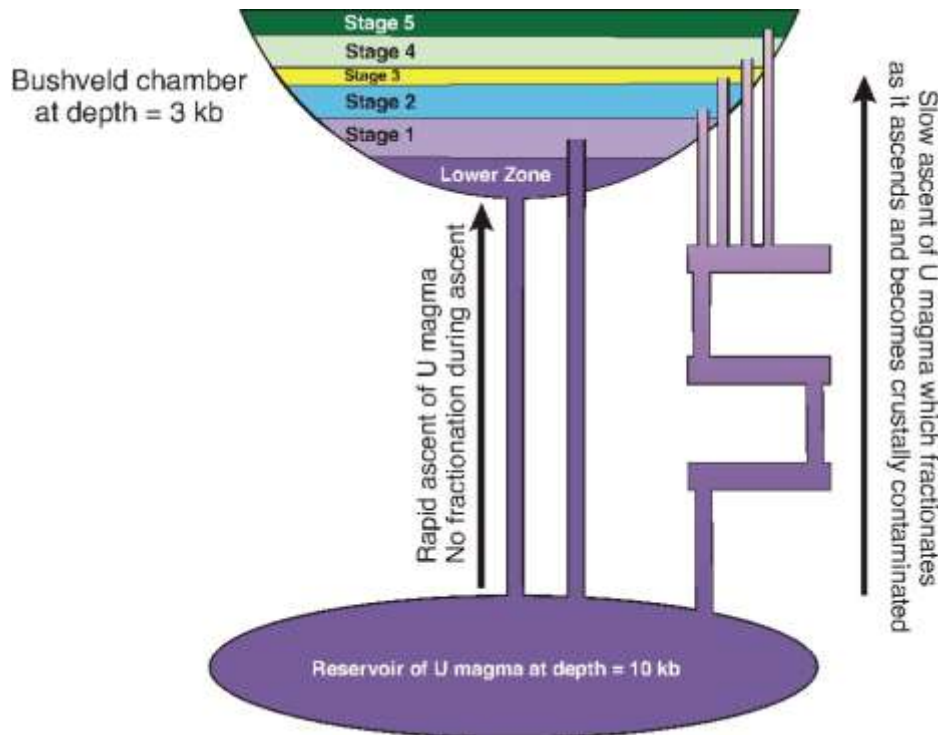
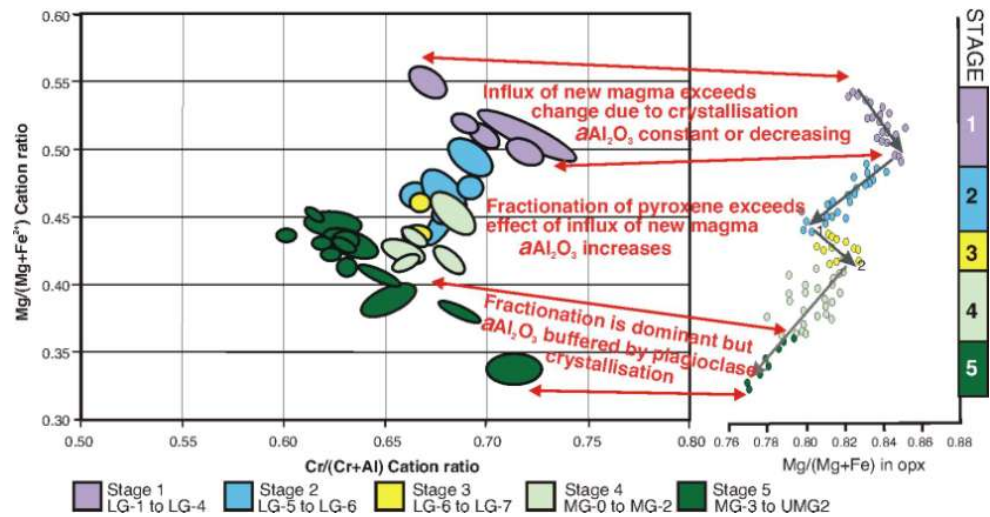


Fig. A is a representation of the Irvine model for Chromite crystallisation as a result of mixing of fractionated magma in a chamber with primitive initial magma.

Fig. B has been modeled using Melts to fractionate an estimate of the Lower Zone magma of the Bushveld assuming that it has risen to a depth equivalent to 3 kb, and has then been mixed at 3 kb with a new pulse of the original primitive magma carrying its original sulfide content. Based on the equation of Li and Ripley (2009), the hybrid magma contains less sulfide than is required to saturate it, so that while chromite will form no immiscible sulfide will develop. This is taken as the situation for the LG-1 to LG-4 when new magma was added quickly

Fig. C shows the result of mixing of the magma in the chamber, fractionated to different degrees (25, 30 and 35%) with the same primitive magma, with the exception that the latter has risen slowly and had crystallised 10% during ascent. Immiscible sulfide will form, and the amount that will form will depend on the degree of fractionation in the chamber. This is taken as the case for chromitites from the LG-5 upward, which formed when new magma was added slowly, as indicated by the Eales et al. orthopyroxene data



This is the scenario envisaged in the previous Slide. In stage 1 (LG-1 to LG-4), magma enters Quickly as shown by the increasing MgNo of the opx. Calculations show that no sulfide will develop as a Result of mixing. Thereafter, stages 2, , 4 and 5 (stage 3 is an exception) the magma enters slowly, and as suggested, fractionates to some extent en route. Modeling shows that mixing in this case will produce sulfide, the greater the fractionation of the resident magma, the more sulfide will form.

SUMMARY

1. Chromitites have been sampled from the LG-1 to UG-2 from locations representing the major sectors (troughs) of the Bushveld complex.
2. On an $(\text{Mg}/\text{Fe}^{2+})$ vs (Cr/Al) plot of chromite composition, 2 trends are apparent, one largely influenced by the effect of the reciprocal exchange of Cr and Al on the Mg-Fe K_D , and the other due to increasing $a_{\text{Al}_2\text{O}_3}$ that is buffered once plagioclase appears on the liquidus.
3. PGE profiles vary little from trough to trough, but show a major difference between the LG-1 to LG-4 and the LG-5 to UG-2, with the former having low and the latter high $(\text{Pt}+\text{Pd})/(\text{Rh}+\text{Ru}+\text{Ir}+\text{Os})$ ratios.
4. This is attributed to the former having developed without immiscible sulfide and the latter with variable amounts of sulfide liquid that concentrated Pt and Pd in particular. The sulfide has subsequently been destroyed as Fe has been lost through reaction with cooling chromite.
5. Modeling using MELTS and the Li-Ripley sulfur solubility equation indicates that if, as suggested by the En content of orthopyroxene, the LG-1 to LG-4 chromitites developed by intermixing of magma in the chamber with rapidly ascending fresh primitive magma, and the overlying chromitites by intermixing with more slowly ascending, slightly fractionated primitive magma, the lack of sulfides in the former and their presence in the latter is explicable.
6. The hypothesis of missing sulfide also provides an explanation for the high Pt and Pd in some podiform chromite bodies in some ophiolite chromitites

Thank You