Chemistry of Cr-spinel and olivine delimits connections with possible Cu, Ni and PGE ore deposits of the Serra Geral intrusions Southern Brazil

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Abstract The Morungava intrusions, SE Paraná Basin, have distinctive shapes and petrological characteristics, grading from dunitic orthocumulates into olivine websterite and olivine-free gabbros, ending in some intrusions with adcumulate anorthosites. The mafic and ultramafic rocks have high MgO (13-27 wt%), Cr (500-3500 ppm), Ni (300-950 ppm), and Co (50-110 ppm), and are the most primitive intrusive bodies in Paraná-LIP. The magma chemistry is interpreted as a combination of magma fractionation inside the crust and crustal contamination in higher-level magma chambers. The investigations of compositions of olivine and Cr-spinel show a strong correlation between mineralized and barren intrusions, explained by crystallization from a Ni depleted magma, resulted from extraction of Ni by a sulfide liquid or from reaction and reequilibration with nickeliferous magmatic sulfide during cooling and solidification due to partitioning of Ni between spinel, olivine and sulfide. The chemical zoning of the two minerals, particularly FeO, NiO, Cr_2O_3, MnO, Al_2O_3 and TiO_2, contrasts with the more homogeneous composition of olivine and spinel from some mineralized intrusions (e.g., Noril'sk). The mineral zoning may be due to the interplay of several processes, particularly the faster cooling of the Morungava magma at shallower position in the crust.

Resumo As intrusões da região de Morungava, SE da Bacia do Paraná, apresentam formas e características petrológicas distintas, variando entre ortocumulados duníticos a olivina websteritos e gabros, chegando a adcumulados anortosíticos. As rochas ultramáficas apresentam alto MgO (13-27%), Cr (500-3500ppm), Ni (300-950 ppm) e Co (50-110 ppm), correspondendo aos corpos intrusivos mais primitivos encontrados na LIP-Paraná. A geoquímica dos magmas é interpretada como sendo uma combinação entre fracionamento e contaminação na crosta superior. Análises minerais foram utilizadas como indicativos para identificação das condições de solidificação e na comparação entre intrusões mineralizadas como Noril'sk - Talnakh e Jinchuan. As investigações sobre a composição de olivinas e Cr-espinélios mostram a existência de uma forte correlação entre ambientes mineralizados e estéreis, possivelmente relacionados a cristalização a partir de magmas depletados em Ni, resultantes da extração do Ni por soluções sulfetadas, e o reequilíbrio gerado pela partição entre o magma sulfetado e a cristalização de espinélios e olivinas. Foram identificadas zonações minerais, relacionadas aos processos específicos como a cristalização rápida dentro de câmaras magmáticas rasas posicionadas na crosta superior.

Keywords: Paraná Basin, Serra Geral mafic-ultramafic, Cu-Ni (PGE), Cr-spinel, olivine.

INTRODUCTION The Paraná Basin, central-eastern South America, is covered by a thick sequence of continental lavas and intrusions of Jurassic age – the Paraná-Etendeka Province (Peat 1997), one of the large igneous provinces (LIP) in the world. The huge amount of magma generated in a comparatively short period of time has long been linked to upwelling of deep, hot mantle plumes (Morgan 1981, Richards *et al.* 1989, White & McKenzie 1989). Mafic and ultramafic intrusions have been identified as part of a feeder conduit system for the voluminous Serra Geral flood basalts. These intrusions may be associated with important sulfide mineralization, as exemplified in the Siberian traps and Noril'sk–Talnakh intrusions, that host first class Ni-Cu (PGE) ore deposits. There is a well-established connection between ore and ultramafic intrusions. These are believed to be comagmatic with some of the Siberian traps (Lightfoot *et al.* 1993, Naldrett *et al.* 1992, Barnes & Kunilov 2000).

This paper concerns the intrusions with the highest magnesium contents in the Paraná-LIP which occur in the Morungava area (Fig. 1). Modern analytical techniques were used to compare Cr-spinel and olivine compositions of the intrusions with those of mineralized intrusions in the Noril'sk - Talnakh and Jinchuan deposits. The compositions are a key factor to understand the solidification conditions of the gabbroic intrusions from southern Brazil. Extensive studies on the mafic-ultramafic intrusions and associated flood basalts have been undertaken by the Geological Survey of Brazil and university researchers in the search for proxies for a world-class Cu-Ni-PGE ore deposit.

Along this line, Barnes and Roedder (2001) reviewed detailed studies on Cr-spinel in mafic and ultramafic rocks, first used by Irvine (1965) 40 years ago as *petrogenetic indicator*. Spinel crystallizes over a wide range of conditions in mafic and ultramafic magmas - magma composition, crystallization temperature and cooling rates, so its composition can be a rich source of information. Even more than cotectic olivine in primitive magmas, Cr-spinel compositions offer the potential to decipher important petrogenetic aspects of such magmas - source, peridotite *fertility*, early stage magma mingling, aggregation of melt batches in subvolcanic magma chambers, and subsequent shallow level magma mixing (Kamenetsky *et al*. 2001).

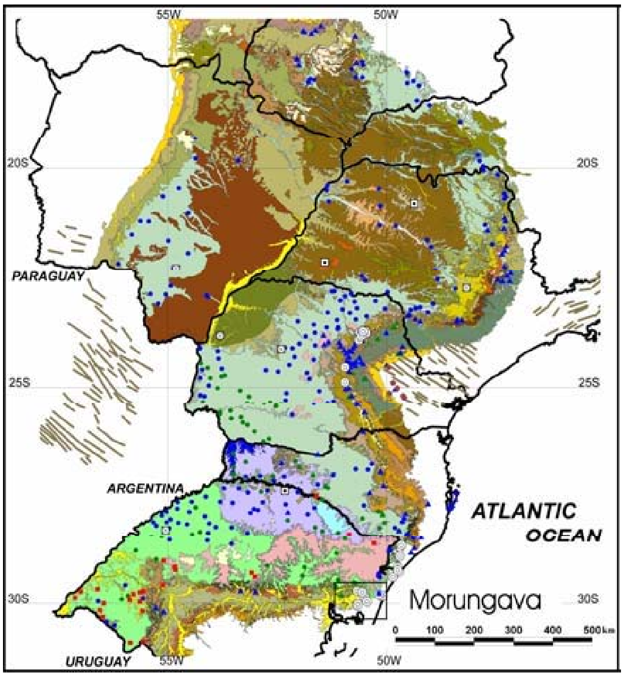

Figure 1. Geological map of the Paraná Basin; the Morungava area is indicated. Dots point to locations of analyzed samples; open dots are drill cores presently evaluated

KNOWN SILLS The Morungava intrusions are of specific interest because of their distinctive intrusive shapes and petrological character. They are composed of mafic and ultramafic rocks with up to 13 wt.% MgO (13-27%), high Cr (500-3500 ppm), Ni (300-950 ppm), and Co (50-110 ppm) contents. Thus, the Morungava intrusions are the most primitive bodies found in the Paraná Basin, as here reported for the first time. The sills were found during drilling for coal seams that were evaluated by Romanini and Albuquerque (1996) and Hulbert *et al.* (1999).

The Morungava sills and lopolith-like bodies ranging in thickness from a few meters to 450 m, are nearly conformable with the host sedimentary rocks. Some have 10 to 25 cm thick layers in cyclic arrangements. Olivine is a cumulate phase, whereas clinopyroxene and plagioclase occur as intercumulate phase; plagioclase and quartz fill the interstices between olivine crystals. Petrographically, the rocks are dark-reddish grey olivine gabbros, olivine gabbronorites with medium-grained, granular ophitic to subophitic texture. The rocks grade in some sills from dunitic orthocumulate layers into olivine websterite and olivine-free microphaneritic gabbro ending some times with adcumulate anorthositic concentrates.

The abundance of olivine phenocrysts and their Fo_{mol} contents are variable. The latter variation is shown by $Mg^{\#}=Mg/(Mg+Fe^{2+})$ from 32 to 88, ranging from hortonolitic compositions to chrysolite-forsterite. The remaining constituents are augite and pigeonite in ophitic to sub-ophitic crystal arrangements, labradorite-bytownite, Fe-Ti oxides (magnetite, ilmenite, Mg-ilmenite and $chromite_{ss}$) and apatite. The olivines are strongly zoned, with rims rich in iron and cores rich in MgO (Fig. 2). This zonation in Fo content relates with strong positive correlation with Cr_2O_3 and NiO, and negative correlation with MnO. The zonation is probably connected with intercumulate, magmatic fluid circulation in these intrusions interpreted as the conduit to the Serra Geral volcanic sequence.

The diagrams Fo_{mol} *vs* MnO in olivine (Fig. 3) show a positive correlation. Two breaks are identified and interpreted as different steps in P-T magmatic conditions. Only olivines with $Mg^{\#}$ numbers higher than 60-70 have spinel inclusions. Two breaks were also identified in regard of the NiO content of olivine. Olivine phenocrysts show higher NiO contents than crystals in the matrix, suggesting a complex evolution for these intrusions. In addition, the studied rocks probably do not represent melt compositions, as pointed out by Kamenetsky *et al.* (2001) for Noril'sk olivines.

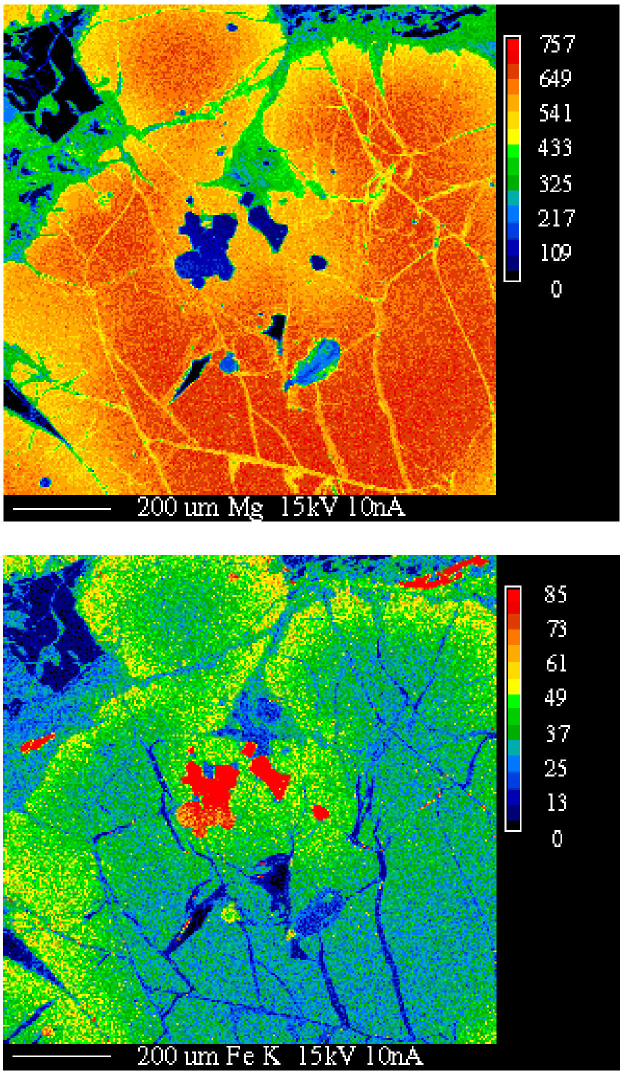

Figure 2. Olivine phenocryst; compositional Fe and Mg zonation shown

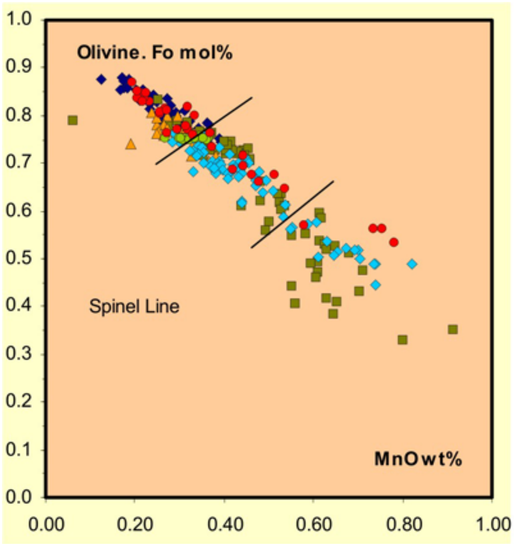

Figure3. Fo versus MnO content of olivine; spinel break lines shown. Each symbol represents a different intrusion

SPINEL CHEMISTRY The occurrence and abundance of Cr-spinels are variable in the Morungava sills; larger abundance would be expected in the high-Mg samples, especially in picritic intrusions, known from the area. The olivine gabbro and the leucocratic rocks contain strongly exsolved Cr-free titanomagnetite as well as magnetite with ilmenite lamellae. Only a few grains of low-Cr and low-Al_2O_3 spinels occur. The spinels are preferentially trapped in olivines. Less commonly they occur in the interstitial spaces between olivine and cpx grains. The size varies from 20 to 70 µm. Lamellae of ilmenite or Mg-ilmenite were not identified in Cr-spinel crystals.

Chromium spinel$_{ss}$, as defined by Haggerty (1981), is used in its broadest sense to denote compositions which are Cr-rich but show extensive solid solution among Al-Cr-Fe^{3+} end-members and limited solid solution with other components. Along this line, spinels from the Morungava Intrusive Complex display a strong compositional zonation (Fig. 4) and a tight and coherent trend of compositions from high temperature aluminium-rich true spinel (hercynite), to Al-chromite, Mg-chromite and chromite, finishing with compositions enriched in FeO, Fe_2O_3 and TiO_2.

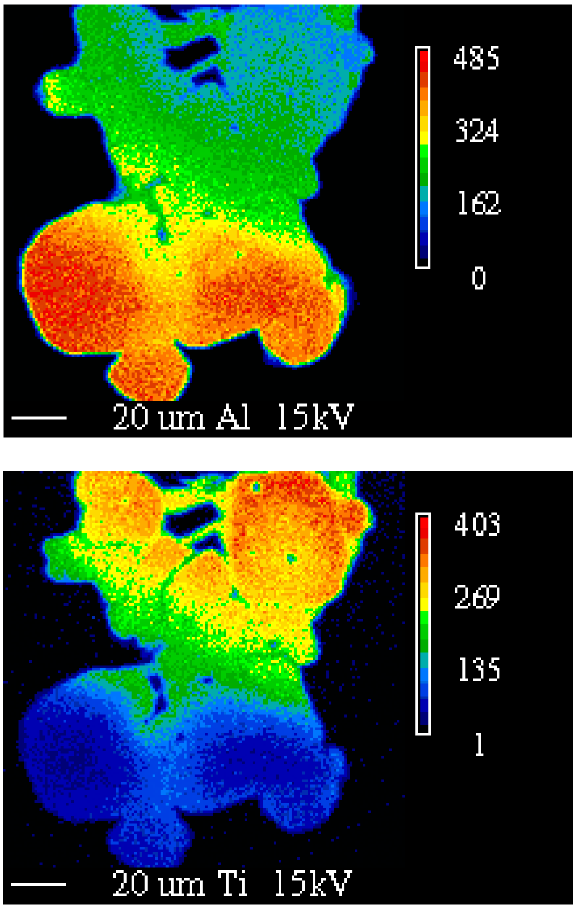

Figure 4. Spinel zonation map showing Al and Ti contents

THE Cr-Al TREND The spinel data set from Morungava shows a trend of widely variable Cr/(Cr+Al) ratios that is strongly correlated to $Fe^{2+}/(Mg+Fe^{2+})$ ratios. This trend was first described by Irvine (1967), who explained this trend as a spinel equilibrated with olivine of constant composition, at constant temperature. The slope is a consequence of non-ideality within the spinel solid solution, and the T dependence is the basis of the olivine geothermometer (Sack & Ghiorso 1991). Different portions of the spinels in the diagram of Fig. 5 correspond to crystallization under distinct magmatic conditions, where the lower Cr values are nearly restricted to the Morungava spinels. Higher Cr concentrations are related to the Noril`sk-Talnack magmatic system. The magma chemistry has been interpreted as a result of a combination of magma fractionation within the crust and crustal contamination at higher-levels of magma chambers.

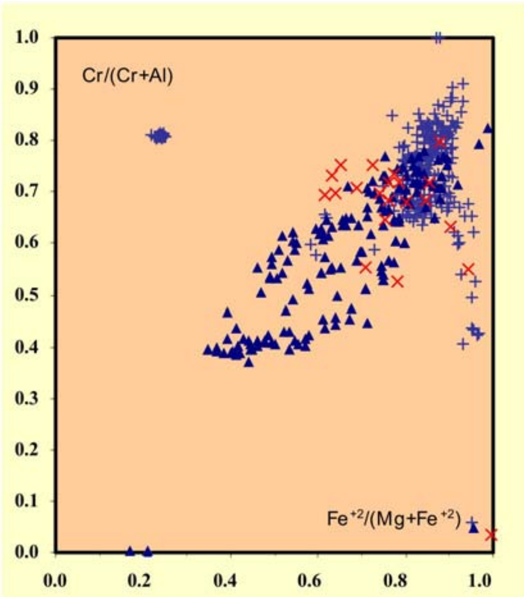

Figure 5. Cr/(Cr/Al) vs $Fe^{2+}/(Mg+Fe^{2+})$ of spinel. Triangles refer to data from this paper, blue crosses from the Noril`sk (Czamanske et al. 1995) and red x from Pechenga (Abzalov 1998)

THE Fe-Ti TREND The spinels from Morungava also show a strong trend of increasing Fe^{3+} and Ti contents and $Fe^{2+}/(Mg+Fe^{2+})$ ratios (Fig. 6), that bends up toward magnetite. This contrasts with the Noril´sk–Talnak trend that splits in two branches - one similar to the Morungava trend that enriches TiO_2 and the other with increasing Fe^{3+}. All these trends can be attributed to the evolution of spinel compositions during fractional crystallization of olivine or pyroxene, resulting in increasing Fe/Mg ratios and Ti contents of the melt (Barnes & Roeder 2001). In many cases, this is accentuated by reaction of spinel in orthocumulate rocks with evolving trapped intercumulate magma.

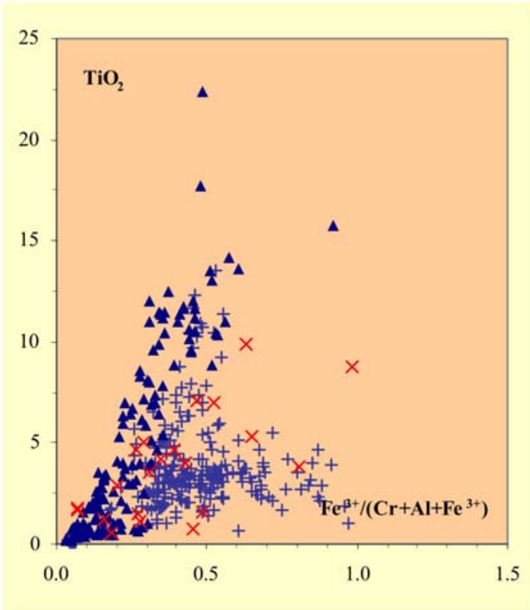

Figure 6. $Fe^{3+}/(Cr+ Al+ Fe^{3+})$ vs TiO_2 of spinel, symbols as in Fig. 5

The variation in $Fe^{2+}/(Mg+Fe^{2+})$ is due to changing magma composition during crystallization, as a result of fractionation within crustal levels, and to exchange of Fe^{2+} and Mg between spinel and coexisting silicates (usually olivine). An additional factor is this exchange between accessory cumulate spinel grains and evolving intercumulate liquid favoring increasing $Fe^{2+}/(Mg+Fe^{2+})$ ratios in spinel with falling temperature and variable degrees of low pressure fractionation (Henderson & Wood 1981, Roeder & Campbell 1985, Scowen *et al*. 1991, Barnes & Roeder 2001). This effect is most pronounced in slowly cooled rocks and particularly evident in those chromite grains situated at the rim of olivine crystals. These chromites have a lower Cr content because they are more susceptible to reactions with trapped liquid.

A specific feature of the Morungava Cr-spinels is their high Ti content. These contents in the final phase of crystallization is taken as evidence that the magma changed composition from a low Ti magma at the beginning in a deep magma chamber to a Ti-rich magma in a higher chamber reflecting the ferropicritic nature of the residual magma.

Ni CONTENTS OF SPINEL AND OLIVINE IN RELATIONSHIP TO MINERALIZATION A feature of spinel from different ultramafic intrusions in the world is the low Ni content of spinels connected with a Ni sulfide ore body as in the Jinchuan (Barnes & Tang 1999) and Noril'sk–Talnakh and Chibacheka river intrusions (Barnes & Kunilov 2000). The NiO and TiO_2 contents plotted against $Fe^{3+}/(Fe^{3+}+Cr+Al)$ demonstrate two distinct groups of samples: **1-** spinel from some mineralized intrusions with higher NiO and TiO_2 values for a given Fe^{3+} content, on a proportion of approximately 2:1 (Fig. 7a), **2-** spinels from Morungava intrusions with higher NiO and TiO_2 (ratio of 3:1) (Fig. 7b), demonstrating a distinct geochemical behavior in between ore rich intrusions (Noril´sk) and Morungava, that have high NiO and TiO_2 values.

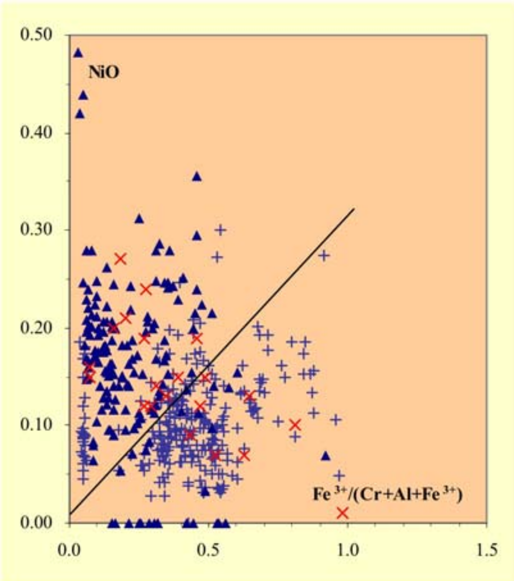

Figure 7a. NiO vs $Fe^{3+}/(Cr+Al+Fe^{3+})$ in spinel; symbols as in Fig. 5

The strong correlation between mineralized and barren intrusions was explained by Barnes and Kunilov (2000) by crystallization from a Ni depleted magma. The depletion resulted either from extraction of Ni by a sulfide liquid or from reaction and reequilibration with nickeliferous magmatic sulfide during cooling and solidification due to partitioning of Ni between spinel and sulfide.

Similar to spinel, the NiO and Cr_2O_3 contents of olivine from Morungava are significantly different to those from Noril'sk-Talnakh and Jinchuan in a plot against forsterite content. In the corresponding diagrams, there is a positive correlation of Fo Mol% and NiO and Cr_2O_3 values. The olivines from the ore zones have a restricted composition compared with the Morungava olivines and a large NiO, Cr_2O_3 range (Figs. 8a, b). The NiO content of olivine from the ore zone does not correlate with the Fo number. In contrast, the NiO depletion of the parent magma seems to be a good explanation in regard of the magmatic evolution and fractionation of the Morungava intrusions.

The ore zone in the mineralized bodies probably had a long period of time to reequilibrate within the magma-host rock system. This seems to be different in the Morungava system characterized by a fast cooling history. The Morungava intrusions are interpreted as part of a high-level conduit for long-lived magmatic eruption, kept hot for a long period of time by flow-through of magma.

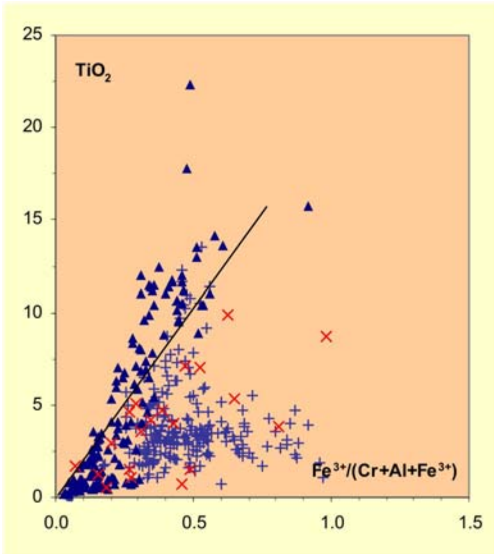

Figure 7b. TiO_2 vs $Fe^{3+}/(Cr+Al+Fe^{3+})$ in spinel; symbols as in Fig. 5

OLIVINE-SPINEL GEOTHERMOMETRY

Magmatic temperatures and the extent of post cumulate reactions can be determined from coexisting mineral pairs such as olivine - spinel, clinopyroxene and magnetite - ilmenite, among others. The geothermometer of Sack & Ghiorso(1991) was used here.

Barnes & Kunilov (2000) described that this thermometer records a blocking temperature only as a function of cooling rate. Thus, rapidly cooled rocks such as basalts record olivine-spinel temperatures close to the liquidus temperature, whereas slowlier cooled rocks record lower temperatures.

One issue of the olivine-spinel method is that both olivine and spinel are chemically zoned. In fact, olivine can be homogeneous from core to rim but spinel crystals can be even asymmetrically zoned. This complicates matching olivine-spinel equilibrium compositions. In addition, the olivine-spinel geothermometer is also pressure sensitive (Stern *et al.* 2006).

The derived temperatures are coherent (Figs. 2-4) with the petrological observation. They decrease from the center to the rim of the crystal, and then to the interstitial crystals compatible with the crystallization descendent line. Cores of the olivine phenocrysts are rich in MgO (46-48 wt.%), Cr_2O_3 (0.3-0.5%), and NiO (0.2-0.3%).

They show relatively low FeO contents (11-14%). Coexisting spinels are rich in MgO (11-14 wt.%), Al_2O_3 (30-32%) and Cr_2O_3 (28-34%) yielding the highest equilibrium temperatures around 850°C. Compared to the corresponding rims, the values drop to MgO contents of 40 wt.% (olivine) and Cr_2O_3 contents of 40% wt.% (spinel) resulting in temperatures around 750°C.

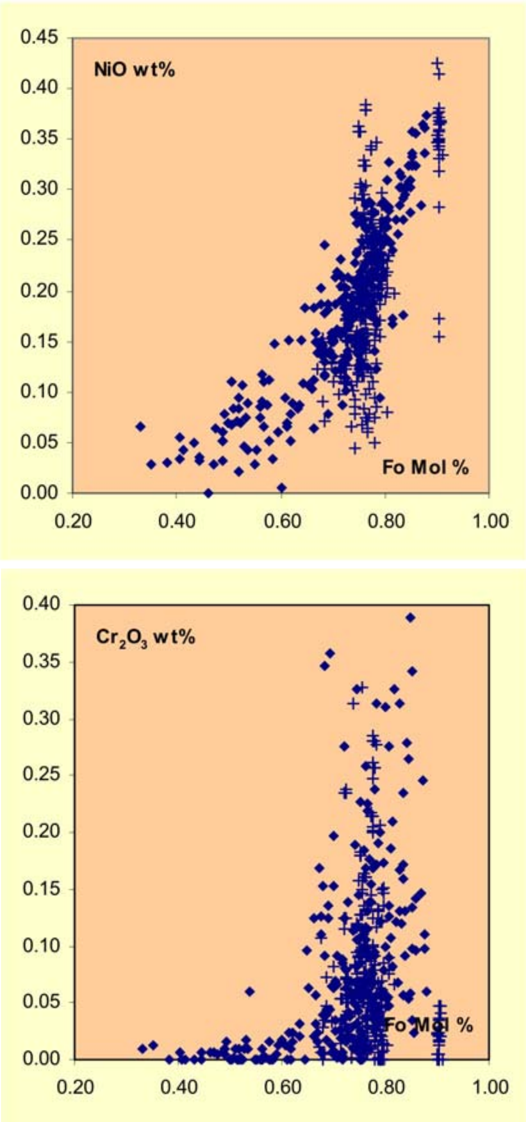

Figure 8. Fo_{mol} vs NiO and Cr_2O_3 of olivine; diamonds: this paper, crosses: Noril'sk-Talnak intrusion from Noril`sk (Czamanske et al. 1995)

The results of calculations using the Sack & Ghiorso (1991) geothermometer are displayed in Fig. 9. In spite of the fact that the temperatures are lower than expected for these types of layered intrusions, the results record temperatures compatible with the interpretation of at least three different steps of crystalization. A longer first step at 815-830°C, a second step at 670-680°C, and a final step at 550-530°C were derived.

This result can be interpreted by cooling temperatures for the intrusions lower than expected. These temperatures are probably related to the mode of emplacement of the intrusions. If the intrusions served as conduit for long-lived, voluminous eruptions, then they should have remained hot for a long period of time during flow-through of magma and as a result of the rapid accumulation of a thick overlying blanket of lava flows.

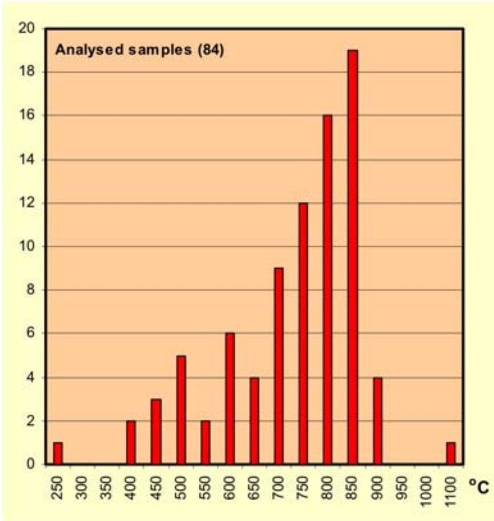

Figure 9. Results of olivine-spinel geothermometer calculations. Individual determination for adjacent crystals

CONCLUSIONS Extensive investigations of compositions of olivine and spinel from the Morungava intrusions show that these minerals are strongly zoned in regard of Fo (olivine) and major and trace element contents. The chemical zoning of the two minerals, particularly in regard of FeO, NiO, Cr_2O_3, MnO, Al_2O_3 and TiO_2, shows correlation with Fo contents of olivine. This is in contrast with the more homogeneous composition of olivine and spinel from some mineralized intrusions (*e.g.*, Noril'sk). In the Morungava intrusions, the zoning may be due to the interplay of several processes, particularly the faster cooling of the magma at shallower position in the crust.

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