## Chemical stratigraphy in the Skaergaard Intrusion

- a study of elemental variations over ca. 66 meters of drillcore from DDH 90-22

Stefan Bernstein & Troels F. D. Nielsen



GEOLOGICAL SURVEY OF DENMARK AND GREENLAND MINISTRY OF THE ENVIRONMENT

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## 1. Summary

A series of elements show large variations in concentration over the interval Pd1-Pd5 in drill core DDH 90-22. Using these variations as stratigraphic markers, it is possible to determine the stratigraphic position to whithin 1m in DDH 90-22. For the intrusion as a whole, the precision depends mainly on the lateral continuity of the chemical markers, which would need to be established. This study further shows that the required data for establishing a chemical stratigraphy within a given interval between Pd1 and Pd5 can be obtained *on site* using hand-held XRF instruments. The material can either be drill core, or rock powder from a fresh rock surface.

## 2. Introduction

This project aims at finding a method by which the stratigraphic position within a mining width of ca. 60 meters can be estimated in a fast way, to the precision better than two metres.

Potential future mining operations in the Skaergaard intrusion will be hampered by the difficulty to determine the exact stratigraphic position relative to the reefs of interest (Pd1-Pd5). In past drilling operations estimation of the stratigraphic position has relied fully on the correct identification of the leucocratic layers L1 and L2. While these layers usually are distinct, and can be recognized visually, they cannot stand alone as stratigraphic markers because:

L1 cannot be distinguished from L2 by macroscopic inspection. This is particularly a problem when working in faulted and heavily dyked areas, where L-layers may be off-set. Pd5 is located at the hard-to-recognize leucocratic layer L0. Allthough the stratigraphic separation between L1 and L0 or the maximum concentration in Pd5 appears very constant, structural distubances could cause displacement of Pd5 and L0 relative to L1. The identification of a geochemical or physical marker for Pd5 and L0 is necessary.

During former drilling campaigns at the Skaergaard Intrusion the routine measurements of magnetic suceptibility has been useful to help determining the location of the L1 and L2. However, in practice it has proved difficult, if not impossible, to rely solely on visual inspection and the measurement of magnetic suceptibility in the determination of the stratigraphic position. The difficulties with the visual identification of the leucocratic layers are only expected to increase in underground workings where rock surfaces are irregular and may be both wet and covered with dust. In order to design a method by which one can estimate the stratigraphich position underground, GEUS has conducted a pilot study of the variation of the bulk rock chemical omposition of the gabbros associated with the precious metal mineralizations. The rationale behind this is that with new improved instrumentation, it should be possible to detect chemical variabilities on a meter scale with a hand-held XRF instrument.

This study consists of three parts:

- 1) Full, high-quality major- and trace element analysis of 25cm segments from drill core DDH 90-22 as basis for detecting chemical markers of stratigraphic position.
- 2) hand-held XRF (XMET) measurements of TiO<sub>2</sub> on DDH 90-22 drill core, to test the feasibility of on-site measurements on drill core.
- 3) XMET measurements of TiO<sub>2</sub> on powders obtained from surface sampling on sawcut channel at Toe of Forbindelsesgletcher to test feasibility of on-site measurements on material from fresh rock surfaces.

### 3. Core DDH 90-22

The core DDH 90-22 is, compared to other cores, relatively poor in cross cutting basaltic dikes and obvious fault zones. This makes DDH 90-22 appropriate for a systematic investigation of the geochemical systematics, and the establishment of a reference in terms of chemical variations with stratigraphy. The core has been selected for detailed mineral chemistry investigations and bulk chemical investigation in a joined research project between GEUS, Århus University and University of California, Davis. The assays from previous investigations (Watts, Griffiths and McOuat, 1991) further show that the Pd, Pt ands Au variation in the mineralised zone in upper MZ has all the charateristics known from other cores (e. g., DDH 89-9).

DDH 90-22 was drilled in 1990 from a location on the north side of Basisgletscher. The collar position was according to the log in Upper Zone b. The drill reached a depth of 1052.47m below collar at an azimuth of 340° and a dip of 70°. The dip is believed to ensure that the core is perpendicular to the dip of the layering in the host rocks. The hole was not logged, but the systematics suggests limited down-hole deviation from the azimut and dip. The core log (see electronic Appendix 1) shows the UZb down to 476m, the transition from UZ to MZ occurs at 930m (masked by dolerite dyke) and the peak of the Pd5 level at 1032m. According to the geological map (McBirney, 1996) and Nielsen (2004) the top of the drill core should be located in UZc, but the boundary between UZc and UZb is not readily identified in core material. Based on the average stratigraphic thicknesses of the zones and subzones in the Layered Series (Nielsen, 2004) it is suggested that the top 75 meters of the core belong to UZc, the following 400 meters down to 476 meters to UZb and the following 450 meters down to c. 930 meters to UZa. UZb is on average assumed to be c. 400 m thick, but no explanation for the possibly somewhat thicker UZa can be given. The Pd5 peak is in accordance with previously observed systematics located app. 100m below the MZ/UZ boundary at 1032m and DDH 90-22 gives a full section of the mineralisation.

### 4. Sample process and analytical techniques

For the measurements of the elemental variation in core DDH 90-22, a section from 978.50m to 1044.75m was selected and cut in quarters or halves, depending on what material was left after the Platinova 1990 core sampling. Sample intervals of 25cm were marked on the core yielding a total of 259 samples. Firstly, the density of each sample was determined by weighing the sample in air and in water. Hereafter, the core was crushed in a standard jaw crusher and subsequently in a tungsten carbide mill. The powder was then analysed for major elements following the techniques outlined in Kystol & Larsen (1999). Trace elements were determined by ICPMS analysis on dissolved glass disks to ensure the dissolution of resistant phases such as spinel and zircon. Approximately 30 grammes of powder from each sample were sent to ActLabs for Au, Pd, Pt analysis. The analytical package (code 1C-research) consists of a fire assay with ICPMS finish, and the detection limits are: Au-1ppb, Pd-0.1ppb, Pt-0.1ppb. All analytical results on bulk-rock material is presented in Appendix 2.

The hand-held XRF (XMET) measurements of  $TiO_2$  were conducted on the core surfaces, with one analysis per 12.5cm. The measurements were done on a cut surface, and the analysed area is about 3 cm<sup>2</sup>. The accuracy and precision were monitored by repeated measuments of two internal powder standards from the whole-rock XRF data collection. One high  $TiO_2$  sample with 11.7 wt. %  $TiO_2$  and one low  $TiO_2$  sample with 3.0 wt.  $TiO_2$  were measured per 20 drill core analyses. The average results on the standards were 10.6 and 2.6 wt. %, respectively, which means that the results are 10-13% lower than the correct values. The standard deviation on the XMET measuments is about 10%.

XMET measurements of  $TiO_2$  on surface powders from channel cut were obtained by electric hand drilling. One sample was taken within each original channel sample from the 2003 channel at Toe of Forbindelsesgletscher. The powder was placed in a plastic cup with a window of X-ray transmitting foil and analysed for 30 seconds with the XMET. Accuracy and precision were monitored using the same standards as described above. Results of average measurements on the standards were 10.7 and 2.5 wt. % TiO<sub>2</sub>.

## 5. Correlation and identification of Pd-levels and Llayers in DDH 90-22

The position of the Pd-levels and the leucocratic marker layers (L-layers) are shown in Table 1. The data has been extracted from previous assays (Watts, Griffiths and McOuat, 1991), drill logs (Watts, Griffiths and McOuat, 1991) and density profiles (GEUS, unpublished). The data from the present investigation are shown in the last three columns. Note should be taken that the assays of earlier investigations are 1m averages and that the earlier density profile is based on 10cm samples collected at 1m intervals. There is in the earlier investigations a 1m uncertainty on the top and base of the Pd levels and the density minima in the leucocratic markers. It should also be noticed that maximum concentrations in the Pd-levels do not necessarily correspond to the peak of Pd as would be identified in, e. g., floating average profiles.

DDH 90-22	Earlier investigations			Present investigation			
	Cut off	top	base	Max. con-	top	base	Max.
				centration			concen-
				and min.			tration
				density			and min.
							density
MZ/UZ bun-				c.930			
dary				(masked by			
				dyke)			
L3		dyke	dyke	dyke	dyke	dyke	dyke
Au (Pd1)	500 ppb	990	994	991 & 993	990.00	992.75	992.50
Pd1	500 ppb	993	994	993	993.25	993.25	993.25
L2 (log)		996.5	1000	998 (av.)			
L2 (density)		997	1001	998	996.25	1002.00	998.00
Pd2a	500 ppb	1000	1001	1001	1000.00	1000.75	1000.75
Pd2b	500 ppb	1003	1007	1005	1002.75	1006.25	1004.75
L1 (log)		1012	1015	1013.5 (av.)			
L1 (density)		1010	1016	1014	1010.00	1017.25	1013.00
Pd3a	500 ppb	1013	1015	1014	1012.75	1016.25	1014.25
Pd3b	500 ppb	1015	1018	1017	1016.25	1017.50	1016.75
Pd4a	500 ppb	1022	1025	1024	1022.50	1024.75	1024.25
Pd4b	500 ppb	1026	1029	1028	1027.75	1028.25	1027.75
L0 (density)		1030	1032	void	1030.25	1032.00	1031.25
Pd5	1000 ppb	1031	1036	1033	1030.75	1035.75	1033.25

#### Table 1.

The stratigraphic thickness between the density minima in L-layers, the stratigraphic thickness between the density minima in L1 and the maximum Pd concentration in Pd5, and the stratigraphic thickness between the maximum Pd concentrations in Pd levels are shown in Table 2.

DDH 90-22	Previously ob- served stratigraphic separation on DDH 90-22	Presently observed stratigraphic sepa- ration on DDH 90- 22	Previously recorded average strati- graphic separation (+/- 1m)
L3-L2	68 (estimated)	void	67.8
L2-L1	16	15.00	14.3
L1-L0	19	18.25	19.1
L2-Pd5	35	35.25	35.7
L1-Pd5	20	19.50	21.4
Pd1-Pd5	40	40.00	40.9
Pd2a-Pd5	32	32.50	32.0
Pd3a-Pd5	19	19.00	19.5
Pd4a-Pd5	9	9.00	9.2
Pd1-Pd2a	8	8.25	8.9
Pd2a-Pd2b	4	4.00	3.9
Pd2b-Pd3a	9	9.50	8.6
Pd3a-Pd3b	3	2.50	3.5
Pd3b-Pd4a	7	7.50	6.8
Pd4a-Pd4b	4	3.50	4.3
Pd4b-Pd5	5	5.5	4.9

#### Table 2.

The results of the present investigation are within error of previous results on DDH 90-22 and previously calculated average stratigraphic separation between Pd-levels and the leucocratic markers for the intrusion. It is accordingly assumed that geochemical correlations developed below are representative, not only for core DDH 90-22, but for the mineralisation as such. A confirmation will require detailed investigations of a number of additional cores.

## 6. Results and discussion

The results of the chemical analysis of the 259 samples are presented in Fig. 1, where all analysed elements (rare earth elements are represented by Ce and Yb), density and magnetic suceptibility are portrayed in alphabetic order as functions of stratigraphy. Note that the element Cr is below detection limit (<10ppm), and therefore not shown.



Fig. 1. Variation in concentration of elements in whole rock, as obtained by XRF (major elements) and by ICPMS (trace elements), arranged in alphabetical order. Also shown is magnetic suceptibility and density.



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## 6.1 Determination of stratigraphic position based on chemical variations

One first assumption to be made is that the chemical variations discussed in the following are concordant, or, at least, semi concordant with the Pd, Pt and Au reefs. This will be briefly discussed in a section below. It is evident from the stratigraphic variations of the elements portrayed in Fig. 1, that the concentrations may be used to identify the stratigraphic position. However, for the potential use in underground workings, one important criterium, which must be fulfilled, is that the key elements have to be present in concentrations that will allow measurement with a portable XRF instrument. Depending on the mass number of the specific element and on the composition of the matrix, this means that the element of interest should have a concentration >>100ppm. In the case of DDH 90-22, this means that the elements of interest are limited to:

Al, Ca, Cu, Fe, K, Mg, Mn, Na, P, Si, Sr, Ti, V and Zn. Since most portable XRF instrument are unable to analyse for elements with atomic numbers lower than 19 (K), this excludes Na, Mg, Al, Si, and P, and the list of potential elements are further reduced to: Ca, Cu, Fe, K, Mn, Sr, Ti, and V.

In the inspection of the element variations in Fig. 1, it should be noted that thin veins of granophyre are present at several levels, mainly at 1022m, at ca 1003m and in the section 994-982m. They are the origin of the anomlous peaks in  $K_2O$ , Ba, Ce, P, Pb, Rb, Th, and Zr, and will not be discussed further.

The element titanium shows the greatest systematic variation throughout the stratigraphic interval of interest. The TiO<sub>2</sub> varies from about 3.0 wt.% in L0 to ca. 13 wt.% in Pd5 (Fig. 1). The peaks in TiO<sub>2</sub> occur with some regular interval through the stratigraphic package with an average distance of ca. 6m. Further, the Ti peaks are unrelated to the occurrence of the leucocratic layers L0-L2. The large variation and the occurrence within as well as outside the leucocratic layers make Ti a powerful element to determine stratigraphic position. In Fig. 2, the Ti peaks have been labeled Ti1 (at about 993m, above L2) to Ti7 (at about 1033m, at base of Pd5 and L0). Ti2 and Ti4 both occur within leucocratic layers (L2 and L1, respectively). L2 may distinguished from L1 by having the Ti peak in the lower third of the layer, while in L1, the Ti peaks towards the top of the layer. L0 may be distinguished from L1 and L2 by the abrupt increase in  $TiO_2$  immediately at the base of the leucocratic layer. While the leucocratic layers are relatively easy to identify by other means (density, visual inspection, magnetic suceptibility) the determination of stratigraphic position in a given interval whithin the mafic layers between L2, L1 and L0 and below L0 is hampered by the lack of any markers other than the chemical variation described here. Since a given interval, either supplied by drill core, or by underground rock surface, is likely to contain at least one Ti peak, the challenge is to distinguish between the individual Ti peaks, Ti1 to Ti7. The absolute level of  $TiO_2$  in a given Ti peak is not a reliable criterium, because, apart from Ti3, all other Ti peaks have TiO<sub>2</sub> at about the same level, and because the absolute values depends strongly on geometry of the sample to XRF-probe, and lastly, because of the short wavelength variations (tens of cm) in concentrations in the rocks. Element ratios should be more reliable, and in Fig. 2 are displayed the variations in the ratios Ti/Ca, Ti/V, Ti/Sr, Ti/Fe, Ti/Mn, and Ca/Sr. Note that these are presented in terms of molar ratios, not oxides. Considering variations in these parameters together, the titanium peaks can be identified in the following way:

- Ti1: low Ti/V (40-50), intermediate Ti/Fe (0.4) and Ti/Mn (20-25), high Ti/Sr (600), and Ca/Sr (900)
- Ti2 and Ti4: high Ti/V (80-100), high Ti/Fe (0.6-0.7) and Ti/Mn (40-45), low Ti/Sr (200) and low Ca/Sr (200)
- Ti3: low Ti/V (35-40), low Ti/Fe (0.3-0.35), and low Ti/Mn (15-20), intermediate Ti/Sr (250-300) and Ca/Sr (450-500)
- Ti5 and Ti6: intermediate Ti/V (55-60), intermediate Ti/Fe (0.4-0.45) and Ti/Mn (25), and intermediate Ti/Sr (350-450) and Ca/Sr (450-550)
- Ti7: low Ti/V (40), intermediate Ti/Fe (0.4-0.45) and high Ti/Mn (30-40), and intermediate Ti/Sr (300-350), and low Ca/Sr (200-300)

With the use of these characteristics, and provided that at least one Ti peak is identified within the stratigraphic interval of interest, it should be possible to determine the stratigraphic position wihtin the nearly 70 meters as analysed in DDH 90-22 drill core. The accuracy of the determination will eventually depend on how well the chemical variations correlate over lateral distances. Given that the data presented by our study of the DDH 90-22 drill core represent 25cm sections, and given the wavelength of the chemical variations, the resolution of the variations in e. g. Ti is about +/- 0.5m.

While the five classes of Ti peaks as stated above (Ti1, Ti2&4, Ti3, Ti5&6, Ti7) can be distinguished with confidence, the Ti2 and Ti4, and Ti5 and Ti6 are not easily distinguished from each other. This would, under normal circumstances, probably not present a big problem, if one just has a reasonable control on the location of the stratigraphic interval of question, which would be the situation underground. However in the case of deep drill holes, with heavily dyked or faulted intersections, or poor core recovery, one may stand with say, 8m of drill core with only one Ti peak. If this Ti peak is either Ti2 or Ti4, or Ti5 or Ti6, the chemical variations in Fig. 2 cannot provide the ultimate answer. Additional data such as density may be helpfull in such a case. For instance, the Ti2 occurs near the base of L2, while Ti4 is located near te top of L1. Continuous measurements of density, which identify L1 and L2, may therefore help distinguishing between Ti2 and Ti4.



Fig. 2. Variation in key element ratios for the titanium peaks Ti1 to Ti7, as defined by variations in TiO<sub>2</sub>.



## 6.2 Results from measurements of $TiO_2$ on DDH 90-22 drillcore by hand-held XRF.

The content of TiO<sub>2</sub> was measured by XMET as one spot analysis per 12.5cm. The results are shown in Fig. 3 (blue curve). There is a larger range in the TiO<sub>2</sub> contents as measured by the XMET than in the 25cm intervals analysed by bulk rock XRF (red curve), with values ranging from 1.9 to 17.7 wt. % TiO<sub>2</sub>. In general, the values obtained by the XMET are repoducible to +/- 0.2 wt. %, so the values reported in Fig. 3 are considered real. Comparing the XMET data with the 25cm bulk-rock data, there is a good overall correlation between the two curves. All peaks and troughs are easily recognizable, and the levels are also approximately correct, with the XMET values consistently being lower by some 10-15%. The XMET data show many short wavelength variations that introduce some noise to the overall pattern. In order to filter out some of this short wavelength variation, the 12.5 cm measurements are recast in terms of average value over 25cm and shown as the green curve in Fig. 3. The result is a very tight fit to the bulk-rock data (red curve).



Fig. 3. TiO2 obtained by hand-held XRF instrument (XMET) on cut surface of core from DDH 90-22. Data was collected with 12.5 cm interval (blue line) and averaged into 25cm interval (green line). Compare with data obtained by 25cm bulk XRF (red line).

The conclusion from the XMET measurements of  $TiO_2$  on drill core shows that the Ti variations can be recognized precisely and with ease, using a hand-held instrument. In the given case, each XMET measurement took 30 seconds and allowing for shift to a new position, measurement of a full 60 meter of drill core can be completed in the order of about 3 hours.

## 6.3 Results from measurements of TiO<sub>2</sub> on rock powder from rock surface

The samples for this study represent one drill 'site' per chip section (usually 0.5m) along the channel cut from point 444 down to Pd5 in 2003 at Toe of Forbindelsesgletscher. The results from the XMET measurements of  $TiO_2$  in the drill powder are compared to the bulk-rock XRF data obtained from the chip samples in Fig. 4. The variations in bulk-rock  $TiO_2$  are very well picked up by the XMET measurements and considering the consistently lower values (about 10-15%), the absolute levels are also approximately correct. The measurement of all ca. 90 samples took only a little over one hour for two persons. In the case of a true underground operation, one would probably go for a more detailed profile over a shorter distance, perhaps 90 samples over maybe 10 meters, and the time required for obtaining data for such a profile will therefore be limited mainly by the time it takes to drill the material from the rock surface. With a trained crew, such data should be available within few hours.



Fig. 4.  $TiO_2$  data for channel sample line at Toe of Forbindelsesgletsher obtained by wholerock XRF on chip samples (red line). The green line and data points show TiO2 obtained by hand-held XRF instrument (XMET) on drill powder from the same profile.

## 7. Conclusions and recommendations

This study shows that within the interval from 10 m below Pd5 to 10 m above Pd1, the stratigraphic position can be determined to within about one meter on the basis of chemical variation in the bulk rock. The main parameters to be used are Ti (or TiO<sub>2</sub>), and the ratios Ti/Fe, Ti/Mn, Ti/V, Ti/Sr and Ca/Sr, which can all be measured by hand held XRF instruments. Measurements of TiO<sub>2</sub> variations obtained by a hand held XRF instrument on the cut surface of a drill core shows very good correlation with bulk-rock XRF data, and shows that the method may prove powerfull during core logging. Similarly, measurements of TiO<sub>2</sub> by hand held XRF on rock powder drilled out from fresh rock surface show very good correlation with bulk rock data acquired on chip samples.

The study proves that it is feasible to obtain reliable chemical data from a stratigraphic sequence with the required resolution in terms of stratigraphy in the matter of a few hours.

The robustness of the use of the 'chemical stratigraphy' in this part of the layered series of the Skaergaard intrusion to identify stratigraphic position requires that the lateral variations of the chemical markers are firmly established. Given the short wavelength of the chemical variations, it is recommended that several drill cores are analysed with sample sections being no longer than about 0.25 cm. Such analyses could be carried out by standard XRF methods on powder pellets.

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## 9. Appendix 1 Core log

Core DHH 90-22 is not described in detail in Watts, Griffis and McOuat (1991). The only description is in the form of a diagram. The diagram has been scanned and is included on the CD-ROM as a TIFF file.

# 10. Appendix 2 Table of analytical results (bulk-rock XRF and ICPMS)

File "9022alldata.xls" on the accompanying CD-ROM contains all the analytical data collected in this project on samples from DDH 90-22.