Study of opaque phases in carbonatites of the Grønnedal-Íka alkaline complex, Southwest Greenland

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Abstract Opaque phases from carbonatites of the Grønnedal-Íka alkaline complex (1299±17 Ma) of Southwest Greenland were analyzed in terms of their mineralogy and microstructure. The analysis demonstrates that a later intrusion by a 55 m wide dolerite dyke of unknown age has prompted the mineralization of magnetite by activating hydrothermal fluid convection. The fluid has interacted with the carbonatite, replacing siderite and ankerite by magnetite, which at places constitutes over half of the rock volume. Magnetite is shown to have become partly replaced by hematite at a later stage. A paragenetic sequence is suggested for the opaque phases that comprise major magnetite and hematite, accessory pyrite and trace amounts of sphalerite, chalcopyrite and galena.
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1 Introduction

Oxides and sulfides are sensitive to changing chemical environments even at low temperatures and pressures and can thus preserve a record of past fluid alteration events in their mineralogy and microtexture (Barton Jr., P.B, 1970, Haggerty, 1976; Rumble, 1976; Andersen, 1983; Shi, 1992; Craig and Vaughan, 1994). For example, the ferrous iron ($\text{Fe}^{2+}$) in magnetite or pyrite can lose an electron to form ferric iron ($\text{Fe}^{3+}$) in hematite under oxidizing conditions, which can imply a supergene alteration environment with groundwater-rock interaction (see reaction (V) in section 7.1).

The aim of this thesis is to study the opaque phases in carbonatites from the Grønnedal-Íka alkaline complex, Southwest Greenland, to add to our understanding of the subsolvus evolution of the carbonatites of the area. This can in turn help to unravel questions about the formation of the world-unique Ikka Column Garden (ICG) in the adjacent Ikka Fjord (Buchardt et al., 1997) (see Fig. 1).

The subjects of opaque phase mineralogy and fluid-rock interaction are touched only briefly in previous research on the complex, which have focused on its structure and petrology (Emeleus, 1964; Bedford, 1989), geochemistry (Gill, 1972; Bedford, 1989), petrogenesis (Pearce et al., 1997; Halama et al., 2005), economic potential (Bogvad, 1951; Morteani et al. 1986; Bondam, 1992) and age (Blaxland et al., 1978). The layered syenites of the complex have been studied more extensively than the carbonatites, partly because of better outcrop exposure (Emeleus, 1964).

This problem has been overcome in this study by preparing samples from a 200.84 m long drill core drilled by the Danish mining company Kryolitselskabet Oresund A/S in 1950 (Fig. 2; Bogvad, 1951). The drill core penetrates through carbonatites with a diverse mineralogy that in addition to at least five different carbonate minerals includes silicates, REE minerals and sometimes more than 50% magnetite. The core profile transects a 55 m wide dolerite dyke that is shown in the following sections to be a major cause for the mineralization of magnetite in the carbonatite by ankerite and siderite replacing reactions.

2 Background

This study is undertaken as a 15 ETCS Bachelor Thesis in Geology at Stockholm University as part of the Bolin Centre for Climate Research associated project Low-temperature geologic sequestration of carbon by ikaite formation (2014-). Apart from this study, the project includes research on non-opaque alteration minerals and fluid-rock reactions in the Grønnedal-Íka alkaline complex and laboratory experiments to unravel the processes leading to the formation of the ikaite columns. Hence, it is a continuation of the work originally started by Buchardt et al. (1997).

3 Geological setting

3.1 Ikka Column Garden

Ikka Bund, the shallow end of the Ikka Fjord, cuts through the Grønnedal-Íka complex (Fig. 3). It is the only globally known location where the hydrated carbonate mineral ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) forms submarine columns (Buchardt et al., 1997). The columns form where submarine springs seep into the seawater through
cracks in the impermeable glaciofluvial clay layer in the fjord bottom (Seaman and Buchardt, 2006).

Because the spring water is less dense, it rises vertically towards the surface. Ikaite precipitates at the top of a growing column where carbonate ions from the alkaline, fresh spring water join with calcium ions from the cold seawater (always <6°C). The growth speed is astonishing: 50 cm overgrowth was observed during one year in a cut column (Buchardt et al., 2001). This is the main reason for investigating the carbon sequestration potential of this process.

In the Ikka Bund, ikaite forms at least 657, up to 18 m high columns that serve as conduits for the spring water from the fjord bottom up to the halocline (Seaman and Buchardt, 2006).

Several factors that are required for the formation and preservation of the ikaite columns coincide in Ikka Bund and are summarised by Buchardt et al. (2001). Of importance for this study is that the occurrence of the ikaite columns is tightly confined within the outlines of the adjacent and underlying Grønnedal-Ika alkaline complex (Buchardt et al., 1997).

Buchardt et al. (2001) provided isotopic evidence for the column water originating from rain falling on the alkaline complex, where it enters fractures and cavities to eventually flow into the fjord in submarine springs.

Composition of the spring water sampled from the ikaite columns shows a high carbonate, bicarbonate, phosphate and Na content (Buchardt et al., 2001). Because the Grønnedal-Ika complex lies within the catchment area of the Ikka Bund area and because of the correlation of the ikaite columns with the alkaline rocks (Seaman and Buchardt, 2006), the peculiar column water composition is ascribed to hitherto unknown alteration processes where ground water interacts with the rocks of the Grønnedal-Ika alkaline complex (Seaman and Buchardt, 2006). The high concentration of Na is puzzling because no easily dissolving sodic carbonates have been found in the carbonatites. However, the reason for the absence of sodic carbonates could be that they are generally highly soluble.

Fig. 1. (a) The Ikka Fjord seen from the top of the Grønnedal-Ika complex. Photo by Lena Lundqvist. (b) Ikaite columns in the Ikka Column Garden. Photo by Richard Martin.
The R-core

The R-core is one of six cores drilled in 1950 in the Grennedal-Ika alkaline complex. Kryolitetskabet Orsund A/S contracted the Swedish company Svenska Diamarinbergborning AB, who were specialized in iron ores, to conduct the drilling and evaluate the mining potential. The iron ore, although high grade, was deemed unprofitable because of a low tonnage and logistical challenges.

Coordinates:
61°13'10"N 48°02'15"W

Dip / dip direction:
050 / 160

Length:
200.84 m

R1, R2... Polished samples
- Carbonatite
- ...w. hematite
- ...w. siderite
- ...w. magnetite
- Magnetite
- Diabase
- ...w. xenoliths
- Greensch. essexite
- Essexite
- Microsyenite
- Nepheline syenite
- Syenite w. calcite
- Orthoclase syenite

Fig 2. R-core lithology. Modified after Bøgvad (1951).
Fig. 3. Simplified geological map of the Grønnedal-Íka alkaline complex, showing the distribution of the ikaite columns. Modified after Pearce (1987) and Buchardt et al. (2001).
3.2 Gronnedal-Íka alkaline igneous complex

The Gronnedal-Íka alkaline complex is dated at 1299±17 Ma (Blaxland et al. 1978), which makes it the oldest of the 15 hitherto found alkaline intrusions in Southern Greenland (Upton, 2013). More are likely to be buried beneath the close-by continental ice sheet. The alkaline intrusions are part of the Gardar rifting period at 1300-1140 Ma that was part of a global rifting episode during which the supercontinent Columbia was broken up (Upton, 2013). The extended crust allowed for extensive rifting related magmatic activity comparable to the modern East-African rift zone (Upton, 2013).

The petrological evolution of the Gronnedal-Íka complex is well described by Emelius (1964) and Bedford (1989) based on petrological and structural field observations. Two suites of layered nepheline syenites intruded the bedrock that comprises Archaean gneisses (Bedford, 1989) and Proterozoic metasediments (Emelius, 1964). They show an igneous cumulate layering (Emelius, 1964) which is a distinguishing feature of the alkaline complexes of the North Atlantic alkaline igneous province (Vartiainen and Woolley, 1974).

The syenites were later intruded forcefully by porphyritic syenite bearing xenoliths of the layered syenites and finally a central plug of carbonatite (Emelius, 1964). The entire complex had an original ovoid form that was deformed by several faulting events into its present form (Emelius, 1964).

The faulting is partly coeval with several generations of dykes that post-date the carbonatites. The dykes have not been dated, but seem to be connected to the Gardar episode (Emelius, 1964) which would make them no younger than 1140 Ma (Upton, 2013). The earliest dykes are lamprophyres, cut by trachytes and phonolites. A genetic link between the former and the carbonatites was demonstrated by Coulson et al. (2003). They are followed by olivine dolerite dykes that intrude the complex in at least four stages (Emelius, 1964).

![Geologist P. Graff Petersen studying one of the Gronnedal-Íka cores, 1950-51](image1)

![The drilling site on the magnetite carbonatite body. The house was built for the workers. Photo by Richard Bøgvad, 1950.](image2)
After this, the area has been virtually free of tectonic activity for over 1100 Ma until this day (Upton, 2013). The rocks finally surfaced through glacial erosion by the Quaternary glaciations that probably are responsible for the carving of the Ikka Fjord (Seaman and Buchardt, 2006). This lack of tectonic activity leaves the rocks of Southern Greenland a uniquely well-preserved dissection through the interiors of an ancient rift zone (Upton, 2013).

The mode of petrogenesis for the Gronnedal-Ika complex hasn’t been conclusively demonstrated. Two different petrogenetic models have been suggested. Pearce (1997) argued that the two rock types have formed by fractional crystallization of a primary magma, while Halama et al. (2005) used partly the same isotopic data to show that the nepheline syenites and carbonatites were separated from the same parent magma by liquid immiscibility.

3.3 Lithology of the R-core

The carbonatites of the complex vary from almost pure calciocarbonatite to iron-rich ferrocarbonatites, with a third group of samples falling into an intermediate composition (Bedford, 1989). The pure calciocarbonatites are not represented in the R-core (Fig. 5), either because of the locality, or because the intruding dyke has altered the carbonate mineralogy. Both siderite and ankerite are variably present. Bogvad (1951) reports that the carbonatites in the R-core carry some xenoliths of the bedrock gneisses and the syenites of the complex, but none were observed in the studied samples. The mineralogy of the carbonatites will be discussed further in section 6.

The 55 m wide dyke that cuts the carbonatite, striking roughly NE-SW, belongs to the latest olivine dolerite dykes that intrude the Gronnedal-Ika complex (Emeleus, 1964). The appearance of the dyke is variable along the core profile, exemplified by Fig. 6 that shows R16 (greenschist facies diabase), R17 and R20 (essexite) and xenolithic diabase (R23). No sample from the pure diabase part was available. Table 1 shows the only chemical analysis available on the dyke. It was made from an essexite part of the T-core, 30 meters north of the R-core (Bogvad, 1951) and shows that the dyke is silica-undersaturated and has an alkaline basaltic composition, with relatively high amounts of potassium and volatiles.

The other rock types present in the core constitute a minor part and were not taken into account in this study.

| SiO₂ | 45.77 | Na₂O | 2.38 |
| TiO₂ | 1.64  | K₂O | 1.78 |
| Al₂O₃ | 16.77 | P₂O₅ | 0.19 |
| Fe₂O₃ | 3.89 | H₂O⁺ | 2.51 |
| FeO | 8.31 | H₂O⁻ | 0.09 |
| MnO | 0.14 | CO₂ | 1.7 |
| MgO | 7.37 | Rest | 0.17 |
| CaO | 7.52 |

Table 1. Chemical composition of the dolerite dyke from 64.5-64.6 m in the T-core in % oxides.

From Emeleus (1964).
Fig. 5. 1.2 x 3.4 cm scanned sections of polished carbonatite samples from the R core.
4 Methods

4.1 Sample preparation

A total of 25 drill core samples from the Grønnedal-Íka alkaline complex were prepared at Stockholm University. The samples were ground with a silicon carbide (SiC) abrasive in four grit stages (180, 400, 600 and for some samples, 1200) before receiving a 2 µm diamond solution polish. This method was chosen alongside manufacturing of thin sections to produce a larger and more representative study area of each sample for reflected light microscopy. In addition, 12 polished thin sections were prepared at Vancouver Petrographics Ltd. and two at Stockholm University.

4.2 Optical microscopy

Petrographic study of the samples was conducted at Stockholm University and University of Helsinki using standard petrographic microscopes (Leica and Nikon) with transmitted and reflected light sources and a cross polarizing inset. The microscopes were equipped with regular lenses enabling 25x, 100x and 200x magnification and oil-immersed lenses enabling 400x or 500x magnification. Photomicrographs were taken with a Leica EC3 digital color camera mounted on the microscope and processed by Leica Acquire 1.0 software.

4.3 Environmental scanning electron microscope (ESEM)

A FEI Quanta FEG 650 environmental scanning electron microscope (ESEM) was used to acquire back-scattered electron (BSE) images and the equipped energy dispersive X-ray spectrometer (EDS) to acquire element X-ray spectra from polished
thin sections. The thin sections were placed in the ventilated chamber of the ESEM which was pumped to low vacuum (~0.9 mbar).

No carbon coating was applied to the thin sections in order to make analysis of the carbonates possible. AZtec software by Oxford Instruments was used to control the EDS and to construct line scans and element maps.

4.4 Raman spectrometer

Raman spectra were taken using a confocal laser Raman spectrometer (Horiba instrument LabRAM HR 800) equipped with a multichannel air-cooled (~70°C) 1024 x 256 pixel CCD (charge-coupled device) array detector. Acquisitions were obtained with an 1800 lines/mm grating. The laser light source was the emission of an Ar-ion laser (λ=514 nm). Spectra were recorded using a laser power of 5 mW at the sample surface.

A confocal Olympus BX41 microscope was coupled to the instrument. The laser beam was focused through a 100x objective to obtain a spot size of about 1 micron. The spectral resolution was ~0.3 cm$^{-1}$/pixel. The accuracy of the instrument was checked by repeated use of a silicon wafer calibration standard with a characteristic Raman line at 520.7 cm$^{-1}$. The Raman spectra were achieved with LabSpec 5 software.

5 Opaque phases

5.1 Overview of opaque phases

Magnetite ($\text{Fe}^{2+}\text{Fe}^{3+}\text{O}_4$) and hematite ($\text{Fe}^{3+}\text{O}_3$) are the two oxides identified in the study. They appear in most samples in one- to three orders of magnitude higher abundance (by visual estimation) than the identified sulfides pyrite ($\text{Fe}^{2+}\text{S}_2$), sphalerite (ZnS), chalcopyrite (Cu$^+\text{Fe}^{3+}\text{S}_2$) and galena (PbS).

Ulvöspinel ($\text{TiFe}^{2+}\text{O}_4$) and ilmenite ($\text{Fe}^{2+}\text{TiO}_3$) were identified by Halama et al. (2005) in exsolution lamellae in magnetite in the layered syenites, but were not found in the carbonatites of the R-core during this study. It is however possible that they are present in the trellis-type lamellae typical of magnetites in the essexite, that contains more titanium.

All estimates of abundance in this section are made by visual estimation using standard abundance charts.

5.2 Oxides: Magnetite and hematite

Magnetite is the most abundant opaque phase in all of the carbonatite samples and prominently appears in clusters of sub- to euhedral octahedral and roughly equigranular crystals that fill irregularly shaped forms 0.5-5 cm in diameter, confined within crystals of ankerite, siderite or both.

Two types of clusters are identified on the basis of their texture and the \((\text{magnetite}+\text{hematite})/(\text{siderite}+\text{ankerite})\) ratio within the clusters: In Type 1 clusters (Fig. 7) the ratio is 80-95% and dominated by euhedral magnetite; in Type 2 clusters (Fig. 8) the ratio falls to 20-50% and is distinguished by sub-to euhedral hematite in up to equal abundance with magnetite in which it sometimes forms oxy-exsolution lamellae.
Fig. 7. Photomicrographs of magnetite in Type 1 clusters. (a) Magnetite crystals fill irregular forms. A medium grey zone on the outside of the cluster marks the edges of ankerite. Pyrite (bright white) characteristically grows in the periphery of the clusters. Reflected light, plane polars. (b) Same view in crossed polars. Magnetite and pyrite are isotropic and thus appear black. A typical association with iron oxide inclusions (red) in the milky white carbonate is seen on the outskirts of the cluster. (c) The apparent irregularity of the magnetite crystals in reflected light is an effect of the polishing and the contrasting hardness between magnetite and the interstitial carbonate mineral. Reflected light, plane polars. (d) Same view in transmitted light, crossed polars. The individual crystals become clearly visible in transmitted light. (e) The octahedral magnetite (light grey) stands in high relief above the interstitial carbonate mineral (medium grey) and shows polishing scars and pits and fractures of which some are filled with residual polishing liquid. Reflected light, plane polars. (f) Same view in crossed polars.
In the Type 2 clusters hematite is often pseudomorphic after magnetite, retaining its original octahedral crystal form. The abundance of magnetite within these clusters varies from ~20% (Type 2) to >90% (Type 1) but is relatively uniform within any single sample. The clusters are frequently flanked and cross-cut by veinlets filled with iron oxides, chlorite, pyrite, barite and unidentified silicates and carbonates (Fig. 9).

Magnetite and hematite are also present in the rims of ankerite and siderite crystals in R3, R24 and R25 (Fig. 10), where both minerals appear in sub- to euhedral crystals. Hematite forms needles (Fig. 11), needle swarms (Fig. 13c-d) or needle flowers, often preferably within a siderite part of the crystal (Fig. 11).

Hematite is also seen crystallizing in microveins (Fig. 9c) but the crystal structure is burnt by the 5 mW laser during Raman spectroscopy making definite determination difficult. Concentrations of red inclusions are seen in carbonates around the microveins and are thought to be dust-sized hematite.

The appearance of the magnetite and hematite (dark grey) in the samples above the dolerite-essexite dyke (R1-R14, Fig. 5) differs from the magnetite and hematite in the samples below (R22b-R29, Fig. 5). Above the intrusion the magnetite preferably forms Type 1, grading towards Type 2 clusters higher up, but at a similar distance below the dyke the iron oxides form rims around siderite and ankerite, exemplified by R24 and R25 (Fig. 10). A similar variation is also seen in the bulk iron content of the rocks (Fig. 12).

Magnetite is present in dolerite (R16b) and essexite (R17 and R18), where it forms single crystals evenly spread and highly altered, with rugged edges and parallel and trellis-type lamellae of an exsolved higher reflectant oxide (possibly ilmenite, ulvöspinel or hematite).

5.4 Pyrite

Pyrite is found in almost all of the samples usually sub- to euhedral, variable in size (10 µm-2 mm), abundance (although always < 2 vol.%) and associations. It is often found close to the boundaries of Type 1 clusters where it is typically peripherally overgrown by magnetite (Fig. 13a-b).

In R25, two large (2 mm) pyrite crystals are partly replaced and infiltrated by hematite needles (Fig. 13c-d) that form a swarm emanating from the pyrite.
Fig. 9. Different vein types. (a) Two veins of sub- to euhedral pyrite (light yellow) in a vein crossing Type 1 magnetite. Reflected light, plane polars. (b) A vein filled with unidentified inclusions of iron oxide, carbonate mineral and silica cuts through a Type 1 magnetite cluster in R15. Transmitted light, crossed polars. (c) A Type 3 network of microveins of a soft iron oxide, possibly hematite. Reflected light, plane polars. (d) A calcite vein cuts through the R15 sample and has dark rims against the surrounding siderite. Type 1 magnetite cluster (dark grey) is seen in upper center. Scanned polished core sample. (e) A vein filled with barite (white, left) cuts through an ankerite crystal partly occupied by a Type 2 magnetite-hematite cluster. BSE image. (f) Chamosite (Fe$^{2+}$ end member of chlorite) filling veins in R15. Scanned thin section in plane polars.
**Fig. 10.** (a) Rims of magnetite and hematite (light grey) around siderite and ankerite. Reflected light, plane polars. (b) Same view in crossed polars.

**Fig. 11.** Type 2 magnetite-hematite cluster is pseudomorphic after original ankerite and siderite. The surrounding matrix (black) is relatively pure calcite. Between the Fe-rich ankerite and calcite there is a zone of Fe-poor ankerite (dark grey). The smaller hexagonal grains (light grey) around the margins are magnetite and the larger needles (light grey) in the interior are pure hematite. BSE image in black and white and EDS plots of single elements in false color.

**Fig. 12.** Iron content (in wt.%) along the R core. Only the plotted sections have been analysed. Modified after Bondam (1992).
Fig. 13. Alterations of pyrite. (a) and (b) Former rectangular pyrite crystals (pale yellow) are replaced peripherally by magnetite (medium grey). Replacement is indicated by a convex-inwards growth by magnetite. In (b), small (< 5 microns) crystals of chalcopyrite (brassy yellow, centre right) grow in proximity of the pyrite. Reflected light, plane polars. (c) Hematite needles (bluish grey) are replacing and infiltrating a large pyrite crystal (pale yellow). Suboctahedral magnetite crystal (grey-brown) is seen in lower left with exsolving hematite; Reflected light, plane polars. (d) Same in reflected light, crossed polars. The altered pyrite and hematite show yellow and red internal reflections respectively. (e) Small (< 20 microns) euhedral pyrite crystals (pale yellow) group close to Type 1 magnetite (medium grey, right centre); Reflected light, plane polars. (f) Euhedral pyrite (white) in various sizes is found in a dark areas of a soft, unidentified mineral that takes polishing poorly. Reflected light, plane polars.
Fig. 14. Sulfides. (a) Sphalerite in an altered form in a carbonate matrix. Reflected light, plane polars. (b) Same view in crossed polars. Sphalerite shows red-brown internal reflections. The crystal with bright red internal reflections is an REE-carbonate mineral. (c) Pyrite (Py) and barite (Brt) intergrown with sphalerite (Sp) with a small inclusion of galena (Gn). Surrounding matrix is siderite and ankerite. Reflected light, plane polars. (d) Same view in crossed polars. The opaque minerals showing red internal reflection are iron oxides (Iox). Sphalerite shows translucent yellow internal reflections.

Euhedral pyrite is seen together with Fe-chlorite filling a vein that cuts through a Type 1 magnetite cluster in R15 (Fig. 9a). Pyrite also occurs as unaltered, euhedral crystals not associated with magnetite (Fig 13f) and as groups of small euhedral crystals in the vicinity of Type 1 magnetite (Fig. 13e).

5.5 Sphalerite, chalcopyrite and galena

Sphalerite is present in some samples and always in low abundance although the abundance can be slightly understated due to its similar reflectance and color to magnetite under reflected light. It is found in altered anhedral crystals close to magnetite, associated with chalcopyrite and also in association with barite and pyrite (Fig. 14a-d).

The copper content in the carbonatites is below detection limits in previous geochemical analyses (Bedford, 1989; Pearce, 1997). However, chalcopyrite is found in trace amounts in some samples, associated with magnetite, sphalerite and/or pyrite and always in small (< 5 µm) sub-to euhedral crystals. In Fig. 13b, a group of chalcopyrite crystals are seen outside a pyrite crystal that has been partly replaced by magnetite. Galena was found from a single location in R3 by EDS analysis (Fig. 14c-d). The low Pb content in surface carbonatite samples (2-4 ppm; Pearce, 1997) shows that galena can be present in no more than trace amounts.
A Co-Ni-Fe sulfide was reported by Bedford (1989) in the carbonatites. Cobalt and nickel are present in trace amounts, and it is possible that such sulfide mineral host exists in the carbonatites although not found during this study.

6 Non-opaque mineralogy

This section is a brief collection of observations on carbonates, silicates, sulfates, phosphates and fluorides made during the study. The section is included here because members of the aforementioned mineral groups are often found systematically associated with the opaque phases. Previously the non-opaque mineralogy has been studied by Emelius (1964), Gill (1972) and Bedford (1989). All groups include REE minerals, especially rich in Ce, La and Nd.

Full description of the non-opaque mineralogy of Grønnedal-Ika and its subsolvus history will be covered in future papers within the project.

6.1 Carbonates

The carbonatites in Grønnedal are classified as calcio- and ferrocarbonatite by Bondam (1992). A versatile array of carbonate minerals is observed, including at least calcite (CaCO₃), siderite (FeCO₃), ankerite (Ca(Fe,Mg,Mn)(CO₃)₂), strontianite (SrCO₃) and synchysite (Ca(Ce, La, Nd, Y)(CO₃)₂F). All of the five are present in R25. The last four are all shown in Fig. 16. No dolomite (CaMg(CO₃)₂) was found conforming to the classification by Chang et al. (1996):

Dolomite: Fe / (Fe + Mg) < 0.2
Ankerite: Fe / (Fe + Mg) > 0.2

All the sampled ferrous calciocarbonates fell well within the ankerite range.

6.2 Silicates

Following primary silicate minerals have been reported in the carbonatites as secondary alteration minerals by Bedford (1989): Sodalite (Na₆(AlSiO₄)₆Cl₂), giesekite (KAl₂AlSi₆O₁₆)(OH)₂, chlorite (Mg,Fe²⁺)₅Al₂Si₄O₁₀(H₂O)₉ close to its Fe end member chamosite, cancrinite (Na₆Ca₂Al₆Si₆O₂₄)(CO₃)₂, and zircon (ZrSiO₄) (Emelius, 1964; Bedford, 1989; Halama, 2005).

6.3 Non-opaque alteration minerals

Following minerals have been reported in the carbonatites as secondary alteration minerals by Bedford (1989): The silicates sodalite Na₆Al₂Si₆O₁₆Cl₂, giesekite (KAl₂AlSi₆O₁₆)(OH)₂, chlorite (Mg,Fe²⁺)₅Al₂Si₄O₁₀(H₂O)₉ close to its Fe end member chamosite, cancrinite (Na₆Ca₂Al₆Si₆O₂₄)(CO₃)₂, and the fluoride fluorite (CaF₂), which was also found during this study in a single location.

In sample R15, chlorite is found filling veins and associated with pyrite and a Type 1 magnetite cluster (Fig. 9f), recognized by a characteristic green color in hand sample. The vein filling species is chemically close to chamosite.
Fig. 15. A BSE image (upper left) from R3 showing barite (Brt) intergrown with strontianite (Str), ankerite (Ank), siderite (Sd) and synchysite (Syn). The colored maps show single element distributions from an EDS scan.

Fig. 16. BSE images from R25 of microfractures transporting iron. (a) Shows a transect over a microfracture that has carried iron that has diffused a short distance into the surrounding siderite. (b) An ankeritic (Ank) zone lies between calcite (Cal) and siderite (Sd), in which iron oxides (lox; hematite-magnetite) have formed. Siderite is cut by several iron-bearing microveins (light grey). An iron-rich zone (light grey) is also seen on the margins of siderite. (c) The diagram shows Fe (wt.%) between A and B.
6.3 Sulfates, phosphates and REEs

The studied samples are enriched in rare earth elements (REE). High content of Nb, Nd, Ce and La is reported by Pearce (1997) and Morteani et al. (1986). The REEs in the carbonatites are accommodated mainly by synchysite-Ce (Ca(Ce,La)(CO$_3$)$_2$F), monazite ([La,Ce,Nd]PO$_4$), pyrochlore (Na$_{1.5}$Ca$_{0.5}$Nb$_2$O$_6$(OH,F), apatite (Ca$_5$(PO$_4$)$_3$(OH,F,Cl)) and columbite (Fe,Mn)[Nb,Ta]$_2$O$_6$ (Morteani et al., 1986).

High barium content of up to 20,000 ppm is reported by Bedford (1989) in surface samples in the carbonatite area of this study. Barium is found accommodated mainly by barite found filling veins (Fig. 9e) and in anhedral crystals associated with synchysite and strontianite (Fig 15). A similar strontianite-barite-REE association is reported for Ce-calcioanlyte by Al-Ani and Sarapää (2014) in Jammi and Kaulus carbonatite veins in Sokli, Finland.

REE minerals are also found within Type 1 and Type 2 clusters, in veins and in the interior of carbonates (Fig. 14a-b).

7 Discussion

7.1 Formation of the opaque phases

7.1.1 Formation of the magnetite and hematite

The observations that the Type 1 and Type 2 magnetite-hematite clusters are confined within former ankerite or siderite crystals (Fig. 11) or forms where the two are found intergrown (Fig. 17 and Fig. 18), and that the oxides form rims around both ankerite and siderite is are used to infer two things: That the clusters are pseudomorphic after ankerite and siderite, and that the rims represent an early stage in this replacement process. The following type of oxidation and decarbonation reactions are suggested for the replacement of siderite:

(I) Siderite (s) + O$_2$ (g) → Magnetite (s) + CO$_2$ (g)
(II) Siderite (s) + O$_2$ (g) → Hematite (s) + CO$_2$ (g)

This is in line with Emeleus (1964) and Bedford (1989) who postulated that magnetite in the carbonatites is a secondary alteration product after siderite.

The example in Fig. 17 is interpreted as an early stage in the replacement process that eventually leads to the Type 1 and Type 2 magnetite-hematite clusters. Intergrown ankerite and siderite are being replaced peripherally by magnetite and hematite, but also within the form. The abundant iron-rich microveins give evidence of the transport of iron by a fluid. It is unclear whether the intergrown texture between ankerite and siderite is primary or part of the secondary magnetite-hematite forming processes.

In Fig. 18, the replacement process is seen in a more evolved stage, but the original intergrown ankerite and siderite is still present in the interior of the crystal form. That the hematite needles in Fig. 11 and Fig. 18 grow almost exclusively in siderite and not in ankerite indicates that reaction (II) dominates over (IV) in the formation process of hematite. Because also magnetite is seen replaced by hematite in the same clusters, the formation of hematite is deduced to postdate the formation of magnetite.
A second type of replacement reaction is suggested because the clusters are observed being similarly pseudomorphic after ankerite.

Mg- and Mn enriched zones around Fe-rich ankerite crystals coincide with zones of Fe-poor ankerite and rims of magnetite and hematite (Fig. 11, Fig. 17 and Fig. 18). This indicates a peripheral replacement of the Fe-rich ankerite by the oxides. Following type of oxidation and decarbonation reactions are suggested for the replacement:

\[ \text{(III)} \quad \text{Ankerite (s)} + \text{O}_2 (g) \rightarrow \text{Magnetite (s)} + \text{Calcite (s)} + \text{Mg}^{2+} + \text{Mn}^{2+} + \text{CO}_2 (g) \]

\[ \text{(IV)} \quad \text{Ankerite (s)} + \text{O}_2 (g) \rightarrow \text{Hematite (s)} + \text{Calcite (s)} + \text{Mg}^{2+} + \text{Mn}^{2+} + \text{CO}_2 (g) \]

These reactions imply a H\textsubscript{2}O fluid phase providing the oxygen and a high oxygen fugacity (Andersen, 1984). Because neither hematite nor magnetite can accommodate Mg or Mn in their crystal lattice, they are rejected and left to either form impurities, oxides or Fe-poor ankerite. A reaction similar to (IV) was proposed by Andersen (1984) for the formation of hematite inclusions in the rödberg of the alkaline Fen complex in Norway, and is thought to account for some of the red inclusions observed in the samples.

The replacement of magnetite by hematite produces, in a premature stage, a texture resembling exsolution in the Type 2 clusters (Fig. 8b), but is sensu stricto not exsolution, which is caused by unmixing of a one-phase assemblage upon cooling. Instead, the texture is termed oxyexsolution in the terminology of Haggerty (1976), which is an oxidation reaction in which a higher oxidation state oxide (e.g. hematite, ilmenite or titanomagnetite) preferentially replaces a lower oxidation state oxide (e.g. magnetite) along crystallographic orientations producing either parallel lamellae (one crystallographic orientation) or trellis-type lamellae (two orientations; Haggerty, 1976), with accompanying change in bulk composition. The hematite-magnetite buffer is a univariant phase transition line in the f\textsubscript{O2}-T space that buffers the oxygen fugacity, and represents reaction (V) (Shi, 1992).

\[ \text{(V)} \quad 4\text{Fe}^{2+}\text{Fe}_2^3\text{O}_4 + \text{O}_2 \rightarrow 6\text{Fe}_2^3\text{O}_3 \]

7.1.2 Formation of pyrite

The observation that pyrite is seen peripherally overgrown by magnetite convexly inwards (Fig. 13a-b), shows that pyrite is being replaced by magnetite instead of the two forming coevally. The following oxidation reaction is suggested for the replacement (Shi, 1992):

\[ \text{(VI)} \quad 3\text{Fe}^{2+}\text{S}_2 + 2\text{O}_2 \rightarrow \text{Fe}^{2+}\text{Fe}_2^3\text{O}_4 + 3\text{S}_2 \]

Reaction (VI) is suggested for the oxidation of pyrite to form hematite and sulfate. This reaction is also supported by the presence of secondary, vein filling barite (Fig. 9e). As this reaction requires high oxygen fugacities on or above the magnetite-hematite buffer (Andersen, 1993) it is interpreted as a supergene alteration reaction in an environment with groundwater circulation.

\[ \text{(VII)} \quad 2 \text{Fe}^{2+}\text{S}_2 + 4\text{H}_2\text{O} + 7.5\text{O}_2 \rightarrow \text{Fe}_2^3\text{O}_3 + 4\text{SO}_4^{2-} + 8\text{H}^+ \]
Fig. 17. A form with iron-rich ankerite (Fe-Ank) and siderite (Sd) is separated from the surrounding calcite (Cal) by a zone with magnesium-rich ankerite (Mg-Ank) and iron oxides (Iox). Fluorite (Ft) is found within a single iron oxide crystal. BSE image in black and white and single element maps in color.

Fig. 18. A form with siderite and ankerite surrounded by calcite has an outer rim enriched in Mn and Mg and an inner rim of hematite-magnetite (Iox). Hematite forms needles in siderite within the crystal form. Anhedral strontianite (Str) is found in the calcite matrix. BSE image in black and white and single element maps in color.
Relics of suboctahedral magnetite in Fig. 13c almost entirely replaced by hematite indicate an initial replacement of pyrite by magnetite by reaction (VI) superseded by reaction VII.

These observations demonstrate that pyrite predates both of the oxides and the additional assumption that the initial crystallizing conditions of the carbonatite magma have been favorable, possibly has a primary origin. This model is supported by the notion that unaltered pyrite crystals are often euhedral and that even partly replaced pyrite crystals display remnants of former euhedral forms.

7.1.3 Formation of sphalerite, chalcopyrite and galena

Because of the scarcity of sphalerite, its spot in the paragenetic sequence is uncertain. It is placed together with pyrite as a primary mineral on following premises: The carbonatites include up to 2000 ppm zinc (Bedford, 1989) and sphalerite is a plausible mineral host; it is relatively resistant to P-T changes and is thus more likely to persist than most other sulfides (Barton Jr., 1970); its texture is altered and shows a likeness to an original euhedral form (Fig. 14a-b).

On the basis of the spatial association with pyrite-replacing magnetite, chalcopyrite is interpreted to have formed coevally with the replacing magnetite in the oxidizing environment, possibly using the sulfur that is released from pyrite in reaction (VI).

On the basis of similar associations (Fig. 14c-d) and oxidation states (S$^{2-}$), the formation of galena is suggested being coeval with the formation of chalcopyrite. Because the carbonatite is poor in both copper and lead (below detection limit and 2-4 ppm respectively (Bedford, 1989)), magmatic fluids originating from the mafic dyke are suggested as the source for the copper in chalcopyrite. This makes sense if the magmatic fluids have mixed with more oxidizing hydrothermal fluids needed for the oxidation of pyrite to magnetite.

7.2 Paragenetic sequence

7.2.1 Primary crystallization

The primary oxide and sulfide mineralogy is determined mainly by the pressure-temperature conditions (with pressure playing the minor part; Barton Jr., 1970), bulk chemistry and oxygen fugacity of the crystallizing magma (Haggerty, 1976).

A thermodynamical evaluation of the P-T and $f_{O2}$ conditions have not been made for the carbonatites of the complex, but a comparison can be made with other carbonatites in the world. As an example, Friel and Ulmer (1974) evaluated that the Oka carbonatite reached solvus at $\sim$710°C, and thus halted the $f_{O2}$ equilibration at $f_{O2} \approx \log(17)$, which should be in the region of pyrite formation given the right bulk composition (Shi, 1992). It is thus plausible that the crystallization conditions allow primary pyrite formation even in the carbonatites of the Grønnedal-Íka complex. That the textural analysis points towards pyrite being primary can be reversely used to suggest relatively low oxygen fugacities in the crystallizing carbonatite magma.

In the context of this study, the origin of ankerite and siderite is assumed to be primary, but no evidence for the assumption is provided. Relevant for this study is that they both have been shown to predate the mineralization of the oxides.
7.2.2 Hydrothermal events

Postmagmatic opaque phase mineralization events are given a place in the paragenetic sequence by the following textural observations: Because only magnetite is found replacing pyrite and not vice versa (Fig. 13a-b), and because only hematite is found replacing magnetite and not the opposite (Fig. 8b), the redox conditions in the carbonatites are interpreted as evolving generally from lower to higher oxygen fugacities, which is equivalent to saying that the system has gone from less oxidizing to more oxidizing conditions.

Both magnetite and hematite are found replacing siderite and ankerite in Type 2 clusters (Fig. 11, Fig. 18), but magnetite predates hematite because the latter replaces the former (see section 7.1).

Evidence for a second hydrothermal event is provided by the presence of hematite which is shown in previous sections to post-date the mineralization of magnetite. Coexistence of magnetite and hematite points towards equilibrating conditions along the hematite-magnetite buffer, which implies higher oxygen fugacities during the second hydrothermal event.

7.3 Origin and composition of the hydrothermal fluids

The presence of a fluid is inferred from the necessity of oxygen transport in the oxidizing reactions, from the reaction zones along grain boundaries of ankerite and siderite (Fig. 11) and from diffusion along microvein boundaries (Fig. 16, Fig. 17). That the fluid has been heated and convecting is inferred from the observation that siderite and ankerite oxidation has been most intense closest to and above the dyke.

Fluids are thought to infiltrate the carbonatites in channeled flux through fractures and faults in the alkaline rocks of the complex. Apart from flowing through fractures and cavities, there is also pervasive flow through the rocks concentrated along grain boundaries as shown by the secondary iron oxide rims (Fig. 10) with associated reaction zones (Fig. 11, Fig. 17, Fig. 18). Some diffusion has taken place across vein boundaries, indicated by zonation of Fe over across Fe transporting microveins (Fig. 16).

For the first hydrothermal event it is suggested that the magnetite forming reactions were catalyzed by an oxidizing hydrothermal fluid convection with rising heated fluids, driven by the heat of the intrusion. This would also set the cooling rate of the dyke as the limiting factor for the grade of replacement. Indeed, it is
noted that in no observed case has the replacement of ankerite and siderite by magnetite been complete and instead the Type 1 texture is produced. If the limiting factor of the replacement reactions is the cooling rate of the dyke, which can be calculated, a time span and equilibration rate for the mineralization process would be possible to evaluate, although not attempted here.

The composition of the fluid during the first hydrothermal event is essentially water (meteoric or basinal), but also CO$_2$ derived from the decarbonation reactions. Magmatic fluids from the dyke are not likely to play a major part because they are generally more reducing than allowed for the observed reactions (Haggerty, 1976; Shi, 1992).

The mafic dyke is likely to be a source of some of the iron, because the bulk iron content in the rocks above the intrusion is higher than below it (Fig. 12). It is also a possible source for the copper and lead in chalcopyrite and galena respectively, as discussed in section 7.1.3. It is thus suggested that some elements are supplied by the dyke and transported by magmatic fluids that upon rising mix with the heated groundwater. The origin of the second, more oxidizing hydrothermal event that is linked to the formation to hematite cannot be deduced from the results of this study.

7.4 Remobilization of carbonatite?

Apart from R15, which is interpreted to be part of a piece broken off from the carbonatite wall rock while the dolerite-essexite dyke was still partly molten, R12, R13 and R14 are the samples closest above the dyke (Fig. 5) that have been subjected to the highest temperatures for the longest time. The carbonate matrix in the samples has a fine-grained, fluidal texture and a visible continuous bilateral zoning from milky white, adjacent to Type 1 magnetite, to dark grey towards the interior. The 2mm thick bands of dark and light minerals in R13, and the fluidal structure in the three samples is interpreted to have formed as heat and upwards escaping volatiles from the volatile-rich dyke (Table 1) have partly melted and remobilized the nearby carbonatite.

7.5 Is there still ongoing metasomatism?

The composition and isotopic signatures of the submarine spring water sampled from the ikaite columns (Buchardt et al., 2001) and discovered thermal springs in the area with steady temperature of 3-4°C during the winter months (Hansen et al., 2011) indicate that some metasomatism of the rocks in the alkaline complex is taking place today in an exothermal reaction. No mineralogical or textural confirmation for such a process was found in this study.

7.6 Sources of uncertainty

Textural analysis and optical petroscopy relies on making visual interpretations. This always involves a degree of subjectiveness, which can lead to false interpretations.

A study of the other drill cores from the area would have made the results more rigorous, but even within the single core studied there is a source of uncertainty. Although samples are carefully picked to be representative of the entire core, it is never possible to completely represent an entire formation as diverse as
the one studied. It is thus possible that crucial exceptions have been missed due to the limited time frame and material available.

Neither the petrogenesis nor thermodynamics of carbonatites are completely understood by geologists and the available research on the Gardar episode is relatively limited. New discoveries in these fields can thus lead to pieces supporting some of the conclusions of this research to fall.

The mineralogy of the non-opaque phases has not been covered by this study, which is a major source of uncertainty because, as shown by the results of this study, it is closely connected with the opaque phase mineralogy.

The place of sphalerite, chalcopyrite, and galena in the crystallization sequence relies on only a few observations of the two minerals and is therefore not as corroborated as for the more abundant oxides and pyrite.

8 Conclusions

Geochemical data, textural observations and opaque phase mineralogy outlined in the previous sections provide support for two postmagmatic hydrothermal fluid events postdating the initial crystallization of the carbonatite. The carbonate mineralogy of the rocks has been altered by these fluid events through the replacement of siderite and ankerite by magnetite and hematite as the minerals have re-equilibrated in the changed chemical and thermal conditions as oxidizing fluids have infiltrated the system. Following conclusions are made:

1. Magnetite in the cumulate-like clusters is shown to be an alteration product of siderite, in concert with the conclusions of previous research (Emeleus, 1964; Bondam, 1989; Halama et al., 2005), but also of ankerite.

2. Reactions (I) and (III) are suggested for the replacement of siderite and ankerite respectively by magnetite and reaction (VI) for the replacement of pyrite by magnetite.

3. Reactions (II) and (IV) are suggested for the replacement of siderite and ankerite respectively by hematite although (IV) is seen to dominate over (II), and reaction (VII) for the replacement of pyrite by hematite.

4. A 55 m wide dolerite-essexite dyke is shown to have stimulated the mineralization of magnetite by supplying iron and by driving hydrothermal fluid convection.

5. The carbonatites are shown to have been altered by fluids in at least two separate hydrothermal events: One oxidizing hydrothermal fluid event during which siderite and ankerite were replaced by magnetite and a second, more oxidizing hydrothermal fluid event during which magnetite and siderite were replaced by hematite.
9 Acknowledgements

I am most thankful to my supervisor Gabrielle Stockmann for giving me the opportunity to work with this project, to my co-supervisor Iain Pitcairn for introducing me to ore microscopy and to both for always taking their time with me.

I thank Elin Tollefsen for many a good discussion and for having me around. I am very grateful for the week spent with Dan Zetterberg preparing samples and the two days with Marianne Ahlbo and the ESEM. A special thanks to Curt Broman for helping me with Raman on his spare time. I owe thanks to Kirsi Larjamo at Helsinki University for letting me work in her microscope lab. I am also grateful to professor Alasdair Skelton for his infectious passion for geology during numerous undergraduate courses.

I thank the Ranta-Kuusela family for always supporting me in my endeavors. Finally, I thank my significant other Pauliina and our son Neeme, who was born into the project, for having patience with me and for showing me that life is not only rocks. Without these people I could not have done this.

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Rumble III, D, 1976, Opaque mineral oxides in terrestrial igneous rocks: Mineralogical Society of America, Short Course Notes, Vol. 3, Ch. 8
Appendix A
An illustrated list of the R-core samples with descriptions of the opaque phases.
This list is a collection of visual observations made during the petrographic study of the R-core samples. It is by no means conclusive and is instead aimed to provide a short overview of the opaque mineralogy of each of the studied samples, as a complement to the thesis. A mineral key is provided for the identification of the opaque phases, as well as a characterization of some unidentified phases. Some additional phases were later identified in ESEM analysis, which are likely to include some of the unidentified ones here. Among these are sphalerite, galena, columbite and monazite (which is non-opaque but has similar reflectance to some opaque minerals). Unless otherwise stated, all the micrographs are taken in reflected light. A bulk Fe and P content is included where available, from analyses made by the Danish drilling company Kryolitselskabet Øresund A/S in the 1950's (Bøgvad, 1951).

**Mineral key**

**Magnetite Fe₃O₄**
- Color: Pale grey with brownish tint
- Crystal system: Cubic
- Reflectance: Medium (21.1)
- Bireflectance: None
- Anisotropy: Isotropic
- Internal reflections: None
- Hardness: Hard (6), < pyrite, hematite; ~ ilmenite.
- Form: Sometimes euhedral. Often pitted surface. Replacement by hematite common.

**Hematite Fe₂O₃**
- Color: Greyish white with bluish tint
- Crystal system: Hexagonal
- Reflectance: Medium (27.2), > magnetite
- Bireflectance: Weak
- Anisotropy: None to weak in these samples, but often reported as strong, blue to red.
- Internal reflections: Common - red
- Hardness: very hard; > magnetite, ilmenite; ~ pyrite.
- Form: Often as lamellae and overgrowths in, and replacing magnetite.

**Pyrite FeS₂**
- Color: cream to pale yellow
- Crystal system: Cubic
- Reflectance: High (54.5)
- Bireflectance: None
- Anisotropy: Isotropic
- Internal reflections: None
- Hardness: Very hard; >> chalcopyrite, > pyrrhotite, arsenopyrite; < cassiterite
- Form: Often in euhedral rectangles.
- Notes: Occurs sometimes as euhedral rectangles, as often as anhedral subrounded crystals that are pitted with a non-opaque mineral. Sometimes overgrown by magnetite. Occurs in proximity of all types of magnetite, but also in veins.

**Chalcopyrite CuFeS₂**
- Color: Brassy yellow
- Reflectance: Medium; < pyrite
- Bireflectance: none
- Anisotropy: Possibly weak greyish anisotropy.
- Internal reflections: possibly (small)
- Hardness: difficult to evaluate
- Form: Roundish subhedral, crystals; often as small inclusions on the margins of magnetite or on the rim of a subhedral to euhedral pyrite.
GO1 (unidentified grey opaque mineral 1)
Color: Medium grey (less red/brown than a neighbouring magnetite)
Reflectance: Medium low; < magnetite
Bireflectance: none
Anisotropy: Weak; translucent in CPL
Internal reflections: slight brown/red
Hardness: -
Form: subhedral; pre-dates the overgrowing euhedral pyrite.

Type locality of GO1: R11 at point A. Right: GO1 is represented by the medium grey, subhedral crystals. The GO1 crystal in the centre is overgrown and surrounded by euhedral pyrite crystals. 400x PPL. Centre and left: At CPL, the entire matrix shows brown-yellow internal reflections and greyish blue to yellowish brown anisotropy and the GO1 crystals are virtually indiscernible. Pyrite is isotropic. 400x CPL.

GO2 (unidentified grey opaque mineral 2)
Color: Brown/grey
Crystal system:
Reflectance: low, < magnetite
Bireflectance: Low.
Anisotropy: isotropic
Internal reflections: none
Hardness: -

GO3 (unidentified grey opaque mineral 3, similar to GO2)
Color: Brown/medium grey
Reflectance: low, < magnetite
Bireflectance: None.
Anisotropy: from yellow-green to dark grey
Internal reflections:
Hardness: -

Conversion table from magnification to field of view, which is equal to the width of the micrograph:

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R1

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<tr>
<td>Sample size:</td>
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Opaque minerals:

- Magnetite
- Hematite

The sample is brittle due to weathering and was broken during polishing. It was glued together with epoxy before a second polishing. The bad condition of the sample has made the polishing uneven. There is both yellow and red-brown rust but a better characterization was not made. Magnetite and hematite are abundant in Type 2 clusters.
Depth (m): 10.18-10.46  % Fe  -
Rock Type: Carbonatite % P  -
Sample size: 70 x 37 mm

Opaque minerals:
Magnetite
Hematite

Abundant intermediate Type 1-Type 2 clusters of magnetite and hematite in a carbonate mineral matrix. Hematite breaks out in needles. In the magnetite masses hematite is forms lamellae in the magnetite, often forming small hexagonal crystals with a slightly reddish tint.

Virtually an absence of pyrite.
Ubiquitous veinlets with an opaque, isotropic mineral. Often in close association with the red mineral.
The red mineral is concentrated in areas visible in hand sample, but is visible throughout the sample in sporadic patches and specifically rimming the magnetite clusters.

Intermediate Type 2 magnetite-hematite cluster. 200x, PPL and CPL.

Iron oxides and red internal reflections in a crystal form. 400x, PPL and CPL.
R3: thin section

| Depth (m): | 10.83-11.58 | % Fe | - |
| Rock Type: | Carbonatite | % P | - |

Opaque minerals:

- Magnetite
- Hematite
- Pyrite (trace)
- Galena (trace)
- Sphalerite (trace)

Type 2 magnetite-hematite clusters. Magnetite and hematite form rims around ankerite in a siderite matrix. Galena and sphalerite are found intergrown with pyrite in ESEM analysis.

*Type 2 clusters of hematite-magnetite and in the centre, pyrite with intergrown galena and sphalerite identified in ESEM. Loc.5, 100x, PPL and CPL.*

Ankerite with iron oxide rims. Loc.1, 25x, PPL reflected and CPL transmitted light.

*A close up of previous, with magnetite and hematite. Loc.1, 100x, PPL and CPL.*
The sample is weathered and somewhat rusty. Abundant Type 2 clusters where magnetite and hematite sometimes concentrate independently in adjacent areas, and sometimes mix together. Hematite forms replaces and forms exsolution lamellae in magnetite.

Abundant hematite veins and patches with concentrated red mineral.
R5

Depth (m): 16.36-16.73
Rock Type: Carbonatite
Sample size: 100 x 20 mm

% Fe 37.1
% P 0.50

Opaque minerals:
Magnetite
Hematite
Pyrite, trace

Magnetite and hematite occurs in Type 2 clusters. As in R7, the two oxides split as exsolution lamellae, with hematite often preferring a needle form and in this sample is often the dominating mineral within the clusters.

Pyrite is very scarce, sometimes as small an- to subhedral crystals in the red areas. The red mineral is abundant throughout the sample, concentrating in areas visible in hand sample and around the magnetite masses.

Type 2 magnetite-hematite cluster. 200x, PPL and CPL.

Hematite in the process of crystallizing? Loc.1, 100x, PPL and CPL.

Magnetite and hematite. 400x, PPL.
### R6: thin section

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#### Opaque minerals:
- Magnetite
- Hematite

Type 2 hematite-magnetite clusters and a large red area in lower right-centre, with abundant microveins of opaque grey mineral.

Type 2 magnetite-hematite cluster with large hematite needles in the interior. 100x, PPL in reflected (left) and transmitted (right) light.

Close-up of the same cluster. 400x, PPL and CPL.

Close-up of the red area. 400x, PPL and CPL.
R7

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</table>

Opaque minerals:
- Magnetite
- Hematite
- Pyrite, trace

In the sample Type 2 clusters are found mostly in 0.5-2cm angular forms as with small magnetite crystals with lamellae of hematite. At 1, two different Type 2 clusters are seen: one with dominantly magnetite, that breaks out in the hematite needles that eventually form a distinct mass.

A single small crystal of pyrite was found in the sample. The red mineral is ubiquitous, sometimes concentrating in veins.

Hematite microveins are found scarcely in small areas outside the edges of the Type 2 clusters.

*Type 2 cluster with predominantly hematite. Loc. 1, 100x, PPL and CPL.*

A gap between the hematite and magnetite clusters. Loc. 1, 200x, CPL and PPL.
R8

Depth (m): 25.63-25.78 % Fe 32.8
Rock Type: Carbonatite % P -
Sample size: 40 x 35 mm

Opaque minerals:
Magnetite
Pyrite, trace
GO1
Chalcopyrite

Type 2 magnetite is cut by a 0.5-1cm thick vein of a red mineral and a thinner vein of milky white carbonate: calcite?.
Euhedral to subhedral pyrite scattered around the sample.
GO1 is sometimes seen close to pyrite, with small inclusions of chalcopyrite.
A microvein filled with hematite is seen confined in a zone between the red mineral and Type 1 magnetite. The microveins are also seen at other locations in slightly different forms, in association with the red mineral.
There are microveins of the red mineral that at points crystallize in grey, opaque, isotropic minerals, presumably hematite.

Type 2 cluster, predominantly magnetite. 200x, PPL and CPL.

Euhedral pyrite close to Type 2 cluster. 100x, PPL and CPL.
R9

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>25.63-25.78</th>
<th>% Fe</th>
<th>32.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock Type:</td>
<td>Carbonatite</td>
<td>% P</td>
<td>-</td>
</tr>
<tr>
<td>Sample size:</td>
<td>45 x 30 mm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Opaque minerals:

- Magnetite
- Pyrite
- Chalcopyrite

Type 2 magnetite occurs in a large mass that constitutes about 50% of the sample. A microvein structure of presumably hematite is seen outside the borders of the magnetite masses, with associated red mineral. Pyrite is found around the sample mostly as small (<10 microns) sub to euhedral crystals in microveins, pods or rarely around a carbonate crystal. When in veins, it’s associated with small magnetite crystals without the two intergrowing. Chalcopyrite is seen close to pyrite being replaced by magnetite.

*Type 2 magnetite, 200x, PPL and CPL.*

*Pyrite being replaced by magnetite, small spots of brassy yellow chalcopyrite around and hematite with red internal reflection. 400x, PPL and CPL.*

*Euhedral pyrite in a cluster close to Type 2 magnetite and along grain boundaries. 100x, PPL and CPL.*
R10

<table>
<thead>
<tr>
<th>Depth (m):</th>
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<th>32.9</th>
</tr>
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<tbody>
<tr>
<td>Rock Type:</td>
<td>Carbonatite</td>
<td>% P</td>
<td>-</td>
</tr>
<tr>
<td>Sample size:</td>
<td>60 x 28 mm</td>
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<td></td>
</tr>
</tbody>
</table>

Opaque minerals:

- Magnetite
- Pyrite, minor

Type 2 magnetite-hematite filling 5-10 mm large angular clusters. Concentrations of a red mineral visible in hand sample.

*Type 2 cluster, 100x, PPL and CPL.*

*Magnetite forming euahedral crystals along a grain boundary, associated with a red mineral. 200x, PPL and CPL.*
R11

<table>
<thead>
<tr>
<th>Depth (m):</th>
<th>32.86-32.97</th>
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<th>27.3</th>
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<tbody>
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<td>Rock Type:</td>
<td>Carbonatite</td>
<td>% P</td>
<td>-</td>
</tr>
<tr>
<td>Sample size:</td>
<td>60 x 28 mm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Opaque minerals:

- Magnetite
- Pyrite, minor
- GO1 (trace)
- Hematite (trace, 500x required)

The sample comprises of roughly 60-70% Type 1a magnetite in 0.3-3cm blocks of irregular shape. The rest of the rock is green mineral and red mineral that are intergrown with milky white carbonate mineral.

Magnetite forms Type 1 clusters. There are inclusions (exsolution?) of hematite within some magnetite crystals, seen as small splashes or subparallel lamellae at 500x magnification.

The magnetite sometimes forms cubic crystals at or outside the margins. Possibly pseudomorphic after pyrite?

The red crystal is sometimes seen seemingly replacing magnetite peripherally, where in contact with the white carbonate mineral.

Pyrite is inclusion-free and appears in euhedral groups, in all sizes up to 2mm, especially concentrated in dark areas where sometimes intergrown with magnetite or GO1. Couple of larger pyrite crystals are found separately in the ground mass.

*Type 1 magnetite, 200x, PPL and CPL.*

*Euhedral pyrite with an unknown low reflectant phase. Loc.1, 400x, PPL and CPL.*
### R12

<table>
<thead>
<tr>
<th>Depth (m):</th>
<th>38.89-39.15</th>
<th>% Fe</th>
<th>27.3</th>
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<tbody>
<tr>
<td>Rock Type:</td>
<td>Carbonatite</td>
<td>% P</td>
<td>-</td>
</tr>
<tr>
<td>Sample size:</td>
<td>65 x 15 mm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Opaque minerals:

- Magnetite
- Pyrite

Apart from the upper left corner where there’s a part of a > 1.5 cm Type 1 magnetite mass, the magnetite appears in 1-6 mm Type 1, virtually inclusion-free masses that are separated by a mush of the white-to-grey zoned calcite with ubiquitous red mineral inclusions that are slightly concentrated at the margins of the magnetite (compare with R13 and R14).

A 1 mm thick vein cuts through the middle of the sample, displacing both the magnetite masses and the interstitial calcite, with high concentration of the red mineral and abundant small an- to subhedral pyrite.

The pyrite appears flanking the Type 1 magnetite (the typical association) and also in sub to euhedral crystals in dark areas. An interesting pyrite formation is found at (1), where an oval crystal of a carbonate mineral grows inside the large magnetite mass. The crystal shows the following zoning: dark rims in CPL, with a sharp contact to the central calcite mass that is white close to the rim and has more red inclusions towards the centre. An- to subhedral, medium sized pyrite crystals grow within the crystal. Outside its rim there’s a dense concentration of intergrown magnetite and pyrite, with the pyrite forming larger crystals and an outer rim some distance from the crystal edge.

*Type 1 magnetite cluster, 100x, PPL and CPL.*

*Same spot, 400x magnification. PPL and CPL.*
R13

Depth (m): 38.89-39.15 % Fe 27.3
Rock Type: Carbonatite % P -
Sample size: 70 x 25 mm

Opaque minerals:
Magnetite
Pyrite
GO1
Chalcopyrite

Magnetite is evenly distributed over the sample in Type 1 (~70% grade) elongate clusters of ~1-10 mm in diameter. The clusters have the same preferred orientation as the dark non-opaque mineral bands (within the yellow dashed lines) and the vein at (3). Magnetite also grows as single larger, subhedral crystal (as in A, see micrograph below).

The matrix is similar to R12 and R14 - milky white to dark grey zoned, surrounding magnetite and a dark non-opaque mineral, with concentrations of the red mineral.

Pyrite appears as up to 700 microns sub- to anhedral crystals, with GO1 in close proximity. At (4), euhedral pyrite of varied sizes grows around the rims of the red mineral, with a larger anhedral crystal of GO1 that carries inclusions of euhedral pyrite. Similar association at other places.

GO1 partly fills the vein at (3) that cuts through the sample, with abundant inclusions of small sub- to anhedral pyrite (up to 10 microns) and tiny (<3 microns) spots of chalcopyrite. The vein is also concentrated in the red mineral compared to its surroundings.

GO1 and Type 1 magnetite with associated red mineral that inhabits small crystals of an opaque mineral. Loc. A, 200x., PPL and CPL.

Type 1 magnetite clusters and a large pyrite crystal in carbonate matrix with smaller pyrite in its vicinity. 25x, PPL and CPL.
R14

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>45.03-45.49</th>
<th>% Fe</th>
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<tbody>
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<td>Carbonatite</td>
<td>% P</td>
<td>-</td>
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<tr>
<td>Sample size</td>
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</tr>
</tbody>
</table>

Opae minerals:

- Magnetite
- Pyrite (< 1%, concentrated at specific locations)
- GO1 (< 1 %, concentrated at specific locations)

Magnetite forms large Type 1a masses that are disturbed by irregular zones of carbonate that are bilaterally zoned from grey to creamy white. The red mineral grows in these veins, and occurs often with pyrite and magnetite that are intergrown.

Magnetite is of Type 1 with pyrite growing along the margins of the clusters in small sub- to euhedral crystals.

At point 4, within the Type 1 magnetite cluster, a wizard-shaped form that is filled with larger magnetite crystals and pyrite. The pyrite concentrates around the rims of the form, with gradually larger crystals inwards. The magnetite also breaks seamlessly into the patchy matrix.

At places, pyrite occurs intergrown with anhedral (possibly GO1), outside of the Type 1 magnetite from which it's distinguished by being more coherent, and transparent and with slight anisotropy in CPL. At point 3 the unidentified mineral reveals cocentric zoning in CPL: white rims encapsules a less defined zone with red-brown to yellow internal reflections and a dark center area.

The red mineral is abundant. At point 2, the red mineral has a peripheral overgrowth of intergrown pyrite (larger, sub- to euhedral) and magnetite (smaller, anhedral).

Type 1 magnetite with crossing carbonate showing a flow-like pattern. 400x, PPL and CPL.
The sample comprises carbonate minerals that appear 'dirty' in CPL, flecked by red mineral inclusions. A purer milky white (carbonate?) vein with dark rims cuts across the sample.

Magnetite appears in Type 1 masses, the main one a large form that almost looks like a xenolith (above (1)).

Pyrite mostly appears occasionally flanking the Type 1 magnetite in sub- to euhedral, rectangular crystals in various sizes, that seem to be overprinted by the magnetite.

Both pyrite and magnetite occur independently and together scattered in small an- to subhedral crystals in the carbonate matrix. Possibly around concentrations of the red mineral. Occasionally pyrite carries small inclusions of a grey, opaque mineral (magnetite?) and vice versa.

Both pyrite and magnetite are virtually inclusion-free at 500x magnification.
R15: thin section

<table>
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<tr>
<th>Depth (m)</th>
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<tbody>
<tr>
<td>Rock Type</td>
<td>Carbonatite</td>
<td>% P</td>
<td>-</td>
</tr>
</tbody>
</table>

Opaque minerals:

- Magnetite
- Pyrite (accessory)
- Sphalerite
- Chalcopyrite

Type 1 magnetite cut by veinlets of pyrite. Pyrite subhedral to euhedral. The pyrite crystals are partly replaced by magnetite, peripherally and with intergrowths.

Sphalerite found in proximity of magnetite (location 1) being partly replaced by a carbonate mineral. It has ingrowths of small (<2 microns) opaque crystals. A subhedral crystal with red internal reflections is found between sphalerite and magnetite, which is shown to be a REE carbonate in ESEM.

At location 2, magnetite is seen replaced by a mineral with red tint.

*Reflect sphalerite and an REE-mineral with bright red internal reflections. Loc 1.*

*Pyrite seen replaced by magnetite in a Type 1 magnetite cluster. 200x PPL.*
R16b

<table>
<thead>
<tr>
<th>Depth (m):</th>
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</tbody>
</table>

Opaque minerals:

- Magnetite
- Pyrite
- Chalcopyrite
- Hematite

The sample is part of the olivine dolerite dyke, with a calcite vein at 1 and in the bottom. The bottom vein has a concentration of the red mineral close to the contact with the dolerite. The calcite also occurs as white, 2-8 mm wide flecks around the sample.

Anhedral magnetite is scattered evenly around the sample. The crystals are relic-like, with irregular and broken margins, pitted, concentrated around dark (badly polished?) areas in the sample. There are inclusions of Hematite in the magnetite and also a darker GO2 that might not be opaque, that sometimes (e.g. at 2 forms crystals with magnetite).

Distinguishing features in the sample are the magnetite lamellae in GO2. Around 1, a relic-like, anhedral crystal of chalcopyrite is found intergrown with GO1. In this location there are also pyrite and magnetite within the silicate mineral of the ground mass.

At 1 the single large (1mm) euhedral pyrite crystal in the sample is found. Otherwise, the pyrite is occurring in an- to subhedral crystals associated with magnetite.

There are some occurrences of the red mineral, seemingly close to and partly growing with the magnetite.

*Lamellae of magnetite in GO2, Loc A, 200x, PPL and CPL.*

*Magnetite replacing pyrite with yellow internal reflections, Loc 1, 400x, PPL and CPL.*
R17

<table>
<thead>
<tr>
<th>Depth (m)</th>
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<tr>
<td>% Fe</td>
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<tr>
<td>Rock Type</td>
<td>Essexite</td>
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<tr>
<td>% P</td>
<td>-</td>
</tr>
<tr>
<td>Sample size</td>
<td>120 x 31 mm</td>
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</tbody>
</table>

Opaque minerals:

Magnetite
GO1

Abundant large (~1mm) anhedral magnetite crystals. The crystal edges are somewhat jagged, but still define sharp crystal faces.

At 1 pyrite grows within an unidentified grey opaque anisotropic mineral. Other unidentified anisotropic opaques found scattered around the sample.

*Typical texture of the sample. Loc 1, 25x, PPL and CPL.*

*Unknown opaque showing white-translucent internal reflections. Loc 2, 25x, PPL and CPL.*

*Typical texture of magnetite. Loc 2, 25x, PPL and CPL.*
R18

<table>
<thead>
<tr>
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<td>Essexite</td>
<td>% P</td>
<td>-</td>
</tr>
<tr>
<td>Sample size:</td>
<td>62 x 30 mm</td>
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</tbody>
</table>

Opaque minerals:
- Magnetite
- Pyrite
- Hematite
- Chalcopyrite

The sample exhibits the "essexite texture" with tabular crystals of plagioclase in of dark non-opaque minerals.

Two different exsolution lamellae are found at (2): A trellis-type and parallel. The lamellae are isotropic, possibly magnetite. The lamellae cover the entire underlying lower reflectant (but possibly opaque) mineral. The larger crystal almost looks like starting to form massive magnetite at places, in areas confined within the trellis lamellae. Those areas also exhibit thinner magnetite lamellae.

Pyrite occurs in several forms: from anhedral, skeletal 1mm crystal and small euhedral rectangles, to filling microveins C.

At A, there are circular rims formed by elongate opaque crystals with blue- to red anisotropy.

At C, there’s a display of an interplay between pyrite, magnetite, chalcopyrite and possibly a fourth opaque mineral. A dark non-opaque mineral is broken into needles within the structure.

*Left: Trellis type lamellae of magnetite. Loc B, 400x, PPL. Right: Magnetite, pyrite and rims with elongate opaque phase. Loc A, 100x, PPL.*

*The elongate crystals show red to blue anisotropy in partly crossed polars. Loc A, 400x.*
**R19**

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>92.36-93.23</th>
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<tbody>
<tr>
<td>Rock Type:</td>
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<td>-</td>
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<tr>
<td>Sample size:</td>
<td>50 x 12 mm</td>
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</tr>
</tbody>
</table>

Opaque minerals:
- Magnetite, minor
- Pyrite, trace
- GO1, trace

The dark, fine grained matrix in the hand sample is translucent in CPL with dark tabular crystals (~ 20-30% abundance) seemingly showing a preferred general orientation (flow direction?). There are occasional spots of red crystals in CPL (e.g. at 3) that appear as medium reflectant opaque minerals, similar to the abundant magnetite in PPL. Possibly GO1.

Magnetite is evenly scattered around the sample in an- to subhedral isolated crystals, often preferring to reside in the dark, tabular mineral. By visual estimate, abundance is around 1-2%. Sometimes occupies microveins.

Pyrite is found in < 1% abundance around the sample in sub- to euhedral crystals, with no obvious association.

At 2, a hexagonal crystal of magnetite (the largest in the sample) is found with a rim of an unidentified anisotropic grey mineral with a duller reflectance, possibly GO1.

*Large scale view illustrating the scarcity of the opaque phases. Loc: 1, 25x, PPL.*
R19: thin section

<table>
<thead>
<tr>
<th>Depth (m):</th>
<th>92.36-93.23</th>
<th>% Fe</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock Type:</td>
<td>Microsyenite</td>
<td>% P</td>
<td>-</td>
</tr>
</tbody>
</table>

Opaque minerals:
- Magnetite (minor)
- Pyrite (trace)

The tabular crystals in the fine grained matrix show layering and seem to flow around the scarce larger opaque crystals in the sample and show an overall wavy direction. Broader dark and light layers are also visible over the entire thin section. The opaque minerals are magnetite and pyrite (1, 2, 3, 4) that both show former euhedral forms that have been distorted by replacing minerals. In magnetite, exsolution lamellae of a darker mineral are abundant.

*Magnetite with low reflectant lamellae. Small grains in the matrix seem to flow around the magnetite. Loc.1, 400x, PPL and CPL.*

*Magnetite intergrown with a non-opaque phase. Loc.4, 400x, PPL and CPL.*
R20

<table>
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<tr>
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<th>-</th>
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<tbody>
<tr>
<td>Rock Type:</td>
<td>Essexite</td>
<td>% P</td>
<td>-</td>
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<tr>
<td>Sample size:</td>
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<td></td>
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</table>

Opaque minerals:

Magnetite
Pyrite
Chalcopyrite

The sample shows the "essexite texture" with alternating tabular feldspar crystals in a darker matrix, with no apparent preferred orientation. In CPL, the matrix is mostly white-translucent to ambrose-brown in color, sometimes with batches of flake-like white-translucent crystals in the ambrose mineral. The white calcite vein has a distinct dark reaction rim seen in the hand sample. Another non-opaque mineral shows a radiant, flower-like needles constrained in round forms (photo). Magnetite is found in anhedral, relic-like crystals with holes and sometimes in association with pyrite. Seems to partly occupy crystals of a non-opaque mineral.

Pyrite is less abundant than magnetite but similar in appearance and shows yellow internal reflections in CPL.

Chalcopyrite appears associated with both pyrite and magnetite and also as an inclusion in the unidentified crystal at 1 that also has peripheral replacement by an isotropic, grey mineral.

There’s a few examples of magnetite (?) lamellae within a rectangular crystal at 2, occurring together with small spots of either chalcopyrite or pyrite.

R22

<table>
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<tr>
<th>Depth (m):</th>
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<tbody>
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<td>Carbonatite</td>
<td>% P</td>
<td>-</td>
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<tr>
<td>Sample size:</td>
<td>40 x 30 mm</td>
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</tr>
</tbody>
</table>

Opaque minerals:

Magnetite
Hematite
Chalcopyrite

Type 2 magnetite occurs at small clusters in the vicinity with the lamellae of hematite. <5 micron chalcopyrite occurs in association with the clusters.

Magnetite, hematite and a small grain of chalcopyrite in centre. 400x, PPL and CPL.
R22b

<table>
<thead>
<tr>
<th>Depth (m):</th>
<th>131.90-132.03</th>
<th>% Fe</th>
<th>11.5</th>
</tr>
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<tbody>
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<td>% P</td>
<td>-</td>
</tr>
<tr>
<td>Sample size:</td>
<td>45 x 15 mm</td>
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</table>

Opaque minerals:

- Magnetite
- Pyrite
- Chalcopyrite
- Hematite?

The sample is split between two distinct parts by the white calcite part in the middle of the sample. Above the calcite, the green mineral is present with a dark non-opaque mineral and magnetite which is a mix between low concentrated Type 1 and 2. Hematite is possibly present in the Type 2 clusters. Below the calcite, the patches of magnetite seem to be overgrowing a darker mineral. The patches are separated by a calcite matrix and flecks of the green mineral. The sample is characterized by dense concentrations of a red mineral, at 2 filling a crystal form with magnetite. This dark red mineral (visible to the left of 2 in the picture) could be a different one than the otherwise common red mineral that has a slightly lighter color, which here is concentrated in small veins and around crystal margins.

Type 1 magnetite, 200x, PPL and CPL.

Magnetite and dark red mineral filling crystal forms Loc.2, 25x, PPL and CPL.

Pyrite overgrowing magnetite. Flecks of brassy yellow chalcopyrite. Loc.2, 400x, PPL and CPL.
R23

<table>
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<tr>
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<tr>
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<td>% P</td>
<td>1.10 (above)</td>
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<tr>
<td>Sample size:</td>
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</tbody>
</table>

Opaque minerals:
- Magnetite (trace)
- Pyrite (trace)
- GO1 (trace)
- GO2 (trace)
- Chalcopyrite (possible)

The hand sample is composed of a dark mineral matrix that is white-grey in CPL. It is cut by veins of a white mineral (calcite?) close to 1 and a pink/red mineral in the bottom half. There’s also a darker and more fine grained mineral in a thick band above 1. Note also the white, roundish xenolith that just about escapes the polished surface in top centre. The opaque phases are scarce and small (<200 microns), mostly relict and intergrown.

Typical of the sample: Magnetite is found close to 1 together with GO1 (possibly; here with particularly strong red/brown/amber internal reflections) that forms a rim around the relict magnetite. Within the magnetite, there’s an inclusion of a subhedral pyrite crystal split in half with by GO2. Pyrite also appears as tiny (<30 microns) sub to euhedral crystals in small clusters in the veins.

Within the dark, fine grained fragment above 1, there’s a single large magnetite crystal.

*Typical view of the matrix. Loc. 1, 25x, PPL and CPL.*

*Small euhedral pyrite in the white matrix. Loc. 1, 400x, PPL and CPL.*
R24

| Depth (m): | 160.69-161.20 | % Fe | 23.3 |
| Rock Type: | Carbonatite | % P | - |
| Sample size: | 130 x 31 mm |

Opaque minerals:

Magnetite
Hematite
Pyrite
GO1
GO2

The dark non-opaque minerals are surrounded by a rim of magnetite intergrown with hematite. The intergrowths are seamless, mostly with rounded boundaries between the two minerals, occasionally lamellar. The mineral form is irregular, loosely connected and skeletal, with broken margins and many holes. At CPL, there are inclusions of a bright red anisotropic mineral. The underlying matrix is often red-stained. This could be hematite.

Inclusions of magnetite and GO1 occur around the sample with no obvious association.

Abundant Type 2 microveins are found throughout the sample, often associated with and forming networks within concentrations of the red mineral.

Pyrite is found as scarce, subhedral crystals (~0.5-1mm) with overgrowths of GO2 at 1, and as small, scarcely scattered anhedral flecks (~5 microns). At 2, euhedral pyrite occurs within a dark mineral (in CPL).
The yellow-green non-opaque minerals in the sample are surrounded by a rim of two (or possibly three) opaque minerals. Magnetite is intergrown with hematite, that typically forms needles.

A swarm of hematite needles is emanating from the two lone large (~2 mm) anhedral pyrite crystals in the sample at 1. The hematite needles infiltrate the pyrite, concentrating on the inside of the pyrite margin. Magnetite also grows within the pyrite, often overgrown by the hematite needles.

Elsewhere, pyrite is only found in tiny euhedral crystals at 500x magnification.

Two large pyrite crystals with swarm of hematite needles. Loc. 1, 25x, PPL and partly crossed polars.

Magnetite and hematite in the rims in vicinity of loc. 1. 400x, PPL and CPL.
R25: thin section

<table>
<thead>
<tr>
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<th>163.84-164.80</th>
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<tbody>
<tr>
<td>Rock Type</td>
<td>Carbonatite</td>
<td>% P</td>
<td>-</td>
</tr>
</tbody>
</table>

Opaque minerals:
- Magnetite
- Hematite
- Pyrite

Carbonate textures, with peripheral overgrowths of magnetite and hematite. Blue crystal in CPL is barite. Loc.4, 25x, transmitted light, PPL and CPL.

Magnetite-hematite rims around siderite and ankerite. Loc.3, transmitted light, 25x, PPL and CPL.

Hematite needle flowers in siderite. Loc.1, transmitted light, 100x, PPL and CPL.
R27

Depth (m): 187.69-187.71
Rock Type: Nepheline syenite?
Sample size: 45 x 30 mm

Opaque minerals:
- Magnetite (trace)
- Pyrite (trace)
- GO1 (trace)

Trace amounts of magnetite, GO1 and pyrite, scattered around the sample. Magnetite somewhat concentrated at the pointy end of the sample. Occasional concentrations of the red mineral in the pink matrix.

R29

Depth (m): 199.40-199.72
Rock Type: Carbonatite
Sample size: 90 x 30 mm

Opaque minerals:
- Magnetite
- Pyrite
- Chalcopyrite
- GO1
- GO3

The minerals in the sample include the green mineral, dark red specks and abundant green mineral, mingled with a darker non-opaque mineral to the right of A. The largest crystals and concentrations of opaque minerals occur around the "mixed zone" to the right of A and between 2 and (3.

Pyrite occurs as large 500-1500 microns an- to subhedral skeletal crystals that are broken and fractured in various degrees, even within the same crystal. Sometimes a more coherent, sub- to euhedral rectangular opaque phase is overgrown on the pyrite. Sub- to euhedral pyrite crystals (2-50 microns) are clustered in some veins with high red mineral concentration, and sometimes around margins of non-opaque minerals. Sometimes in veins together with GO1. Large crystals (500-1500 microns) of magnetite is characteristic of this sample, with tiny inclusions of chalcopyrite and euhedral inclusions of pyrite, both inside and on the margins of the magnetite. Microveins of a medium grey opaque, isotropic mineral, possibly hematite, occur sporadically over the sample, often associated with concentrations of the red mineral.

Inclusion of GO3 is found in type 1b magnetite at 3: grey/brown, low reflectance, anisotropy from yellow green to dark grey. At this location, the red mineral is apparently replacing magnetite with clear convex ingrowth and possibly forming an opaque phase at the contact.
Appendix B

Raman spectra of ankerite, siderite, magnetite and hematite.
Sample R3. Raman spectra of carbonates. Ankerite (A in photo) with typical bands at 166, 279, 721, 1092, 1437 and 1740 cm$^{-1}$ and siderite (S in photo) with typical bands at 186, 287, 730, 1087 and 1730 cm$^{-1}$. The carbonates have been identified after comparisons with reference spectra; ankerite RRUFF ID X050018 and siderite RRUFF ID R050262 in Downs (2006). The black border of minerals that surrounds ankerite consists of Fe-oxides.
Sample R25. Raman spectra of Fe-oxides. Two phases of Fe-oxide are shown in the photo; the bluish-grey phase is hematite with typical bands at 226, 245, 292, 410, 497, 612, 660 and 1320 cm$^{-1}$; the brownish-grey is a mixture of magnetite with typical bands at 300, 560 and 670 cm$^{-1}$ and hematite (marked with “hem”). The Fe-oxides are identified after comparisons with reference spectra; magnetite RRUFF ID R060656 and hematite RRUFF ID R050300 (Downs 2006).
Appendix C

EDS data for chalcopyrite and galena.

EDS point data was used sparingly because of a technical problem caused by the software AZtec. In each spot, O was added by the software for calculation in oxides, causing the data for minerals with no oxygen such as sulfides and fluorite to falsely show a high oxygen percentage. Because of this, the EDS data presented here for chalcopyrite and galena was used for identification only together with petrographic observations and their association with other sulfides— as well as the plausibility of galena and chalcopyrite being mineral hosts for lead and copper respectively. The author holds about 200 additional EDS point data from samples R3, R6 and R25 that can be sent to the interested reader upon request.
1. Galena. R3, loc. 5.

**BSE image.** A small crystal of galena (zoomed) is seen intergrown with sphalerite (light grey), pyrite (medium grey) and barite (white) in a matrix of ankerite (black) and siderite (dark grey).

**EDS data.** The EDS picks up some C, Fe, Zn, Ca, S and O from the surroundings. However, 35.8 wt.% oxygen is unrealistically high, caused by the software error. The Pb:S ratio (4.9:1) is slightly lower than for galena (6.46:1), probably explained by the surrounding sulfides affecting the analysis.

**BSE image.** An anhedral chalcopyrite crystal is identified outside a Type 1 magnetite cluster, associated with anhedral sphalerite and chlorite. At this location, a vein of euhedral pyrite (rectangular crystals in lower left) predates the magnetite cluster that it is apparently cutting, shown by overgrowing magnetite (octahedral crystals).

**EDS data.** The EDS picks up some Ca, Mn, O and extra Fe from the surrounding matrix. However, 44.8 wt.% oxygen is unrealistically high, caused by the software error. Cu and S are unlikely to be present in the matrix and accordingly, the analyzed Cu:S ratio is roughly 1:1, which is the case for chalcopyrite.