# Basaltic Glass With High-Temperature Equilibrated Immiscible Sulphide Bodies With Native Iron From Disko, Central West Greenland

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**Abstract.** Immiscible sulphide bodies show eutectic quench textures in a basaltic glass rock (mg = 66) from a native iron-bearing dyke chilled at $T = 1,200°$ C and $P = 250$ bars. The sulphide bodies are composed of troilite (90–91%), iron (9–10%) and very scarce vanadium-rich chromite and approach a ternary cotectic in the Ni-poor part of the system $Fe-Ni-S$. Transition element partition between olivine (mg = 83), silicate glass (mg = 59) and sulphide blebs indicate that the phases were equilibrated at 1,200° C. $D_{vanadium\,(olivine/glass)}$ is close to unity and reflect the reducing nature of the rock, for which estimates of $f_{O_2} \sim 10^{-12\,to-13}$ and $f_{S_2} \sim 10^{-5}$ have been made. $D_{nickel,\,cobalt,\,copper\,(sulphide/glass)} = 4,300$, 230 and 380 respectively, are much higher than reported experimentally determined $D$'s on$_{monosulphide/basalt\,glass}$ at the same temperature and show increasing positive deviation ($\Delta Ni > \Delta Co > \Delta Cu$) with the increasingly siderophile character of the elements. $K_{D\,nickel-iron\,(sulphide/olivine)} = 63$ is much higher than an experimentally reported value (33) and comparison with published thermodynamic data on Ni-partition between olivine and iron metal suggests that the positive deviation is roughly proportional to the excess metal component in the sulphide melt. The occurrence of strongly Ni-depleted reduced basalts on Disko shows that fractionation of metal and sulphides was a common and geologically important process.

## Introduction

A number of rapidly cooled basaltic rocks with tiny sulphide bodies interpreted as quenched immiscible sulphide liquids have been reported from Earth, either from lava lakes (e.g. Desborough et al., 1968; Skinner and Peck, 1969) or from glassy pillow margins (e.g. Moore and Calk, 1971; Mathez, 1976; Czamanske

and Moore, 1977). These sulphide bodies are composed of $Fe-Ni-Cu$-sulphides plus varying amounts of magnetite. Tiny sulphide blebs are also well documented from extratelluric rocks, such as lunar basalts and breccias (e.g. Skinner, 1970; Blau and Goldstein, 1975; Misra and Taylor, 1975) or in chondrites (e.g. Heymann, 1967). These blebs are devoid of a magnetite component and are composed of $Fe-Ni-Cu$-sulphides plus one or more of the phases nickel-iron, cohenite and schreibersite. Recently a number of strongly reduced natural glasses have been recovered from Tertiary native iron-bearing volcanic rock units in Disko and Nûgssuaq, Central West Greenland. Sulphide blebs with native iron are preserved in several of these glasses, notably in tuffs (Pedersen, 1978a) and in dyke chills.

Segregation of immiscible sulphide melts from ultramafic and mafic magmas are known to be of major economic importance for certain elements. However, igneous rocks, in which high-temperature equilibration between basic silicate melt and immiscible sulphide melt have been preserved, seems to be conspicuously lacking and the same seems to be the case with igneous rocks showing the effects of sulphide melt fractionation (Fleet et al., 1977) with the possibly predominantly metal-fractionated eucritic meteorites as an exception (Nichiporuk et al., 1967). The glassy dyke rock from Disko to be described below provides an example of basalt magma equilibrated with a sulphide melt at high temperature and low pressure and low oxygen fugacity.

## Geological Setting

Fundal (1975) found and described in detail (under the name the Kitdlît dyke) a native iron-bearing basaltic dyke in South Disko (Fig. 1), and Pedersen (1977) made additional observations and some reinterpretations on the same dyke-body which was called the Kitdlît-Nângissat dyke. Further observations are given by Ulff-
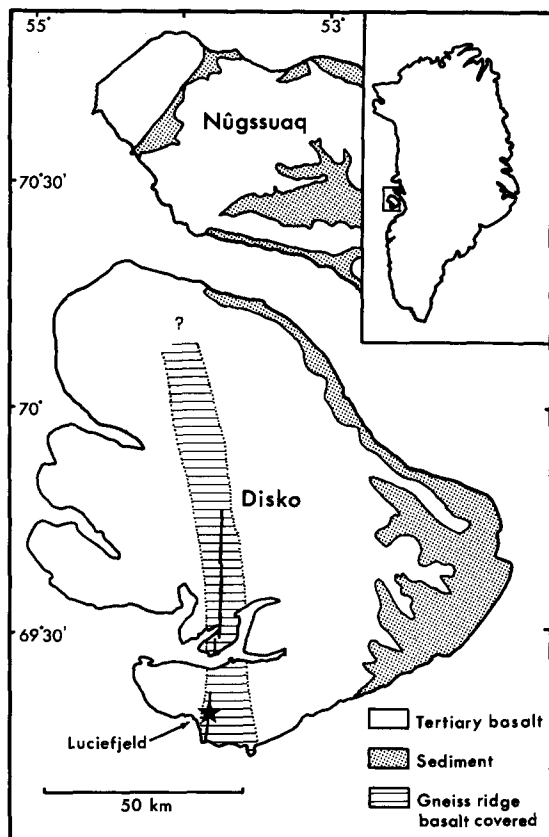
**Fig. 1.** Locality map showing the Kitdlît dyke cutting basalt covered gneiss. The position of the investigated samples at Luciefjeld is marked with arrow and star

Møller (1978 in press). The dyke cuts through Precambrian gneiss and early Tertiary tholeiitic plateau-basalts (for a review of the Tertiary volcanism see Clarke and Pedersen, 1976) and is now known to be more than 55 km in N-S extension. In the south it is 6 to 8 m thick and entirely basaltic. Towards the north the thickness increases and the dyke becomes composite with a core of intermediate strongly contaminated rock and a basaltic margin (Ulff-Møller, 1978 in press). This is a clear indication that the magma has been injected from a magma chamber in central Disko and of extensive horizontal movement of magma towards the south. A similar magma flow pattern has recently been demonstrated on Iceland (Sigurdsson and Sparks, 1978).

The observation that the Kitdlît dyke is cutting Precambrian gneisses has been used as the main argument for the derivation of native iron on Disko from the earth's lower crust or mantle (Fundal, 1975) or deep interior (Bird and Weathers, 1977). This argument is perceptibly weakened by the new field observations.

Where the dyke intrudes the basaltic lavas a number of up to 4–5 cm thick glassy apophyses and breccias occur; the quenching was probably enhanced by the presence of circulating water in the buried lava pile. Where the dyke forms an even contact against the lavas a glassy chill has also formed but is rarely more than 0.5 to 1 cm thick.

The dyke rock resembles olivine microporphyritic lavas (now removed by erosion from that part of Disko) from the upper part of the Maligât Formation (Pedersen, 1977, Table 9 nos 4–6) and from the stratigraphy it can be estimated that the samples to be described here were quenched about 0,7 to 0.9 km below the palaeosurface at a confining pressure of roughly 250 bars (F.

Ulff-Møller, personal communication 1978). Native iron and sulphide (pictured by Fundal, 1975, Figs. 7–10) occur as up to centimetre-sized aggregates in zones here and there in the inner parts of the dyke. A decimetre-sized, complex body of intergrown native iron, cohenite and sulphide with several accessory phases has been found inside the dyke and demonstrated to have been a sulphide melt with an excess metal component displaying a complex crystallization history (Ulff-Møller, personal communication 1977). Partly digested glassy gneiss xenoliths and fragments of tholeiitic basalts are common, even more so are xenoliths composed of one or several of the minerals graphite, basic plagioclase ($An_{76}$ to $An_{93}$ measured in a few xenoliths), mullite, corundum, spinel, and cordierite. It has been proposed (Fundal, 1975; Bird and Weathers, 1977) that the graphite-bearing xenolith types should represent evidence for an unusual lower crust or mantle from which the native iron should originate. However the graphitic xenolith types have now been proven elsewhere on Disko to be modified carbonaceous shales (see Pedersen, 1979) as suggested by many earlier workers.

## Petrography

The glassy samples were collected from a few centimetres thick brecciated apophysis at the dyke contact at Luciefjeld (69°19′ 17″N, 53°46′41″W), southern Disko. Basaltic glass makes up about 90% (Table 1) of the rock. It is colourless to light greenish or yellow in thin section; along cracks and towards sphaerulitic and microcrystalline parts of the dyke the glass becomes dark brown in colour, and a dark brown coloration is also observed around many microphenocrysts.

Olivine microphenocrysts are next in abundance (8–9 vol%). The olivines vary in size from 0.4 mm and down to a few microns. They are euhedral, of short stumpy habit (Fig. 2a) and usually contain glass inclusions (up to a few microns in size) in the cores.

Plagioclase microphenocrysts are missing in the analysed samples, in others a few lath-shaped crystals ($An_{73}$ to $_{69}$) are found.

Sulphide-rich blebs occur scattered throughout the glass, forming sphaeroidal or lensoidal bodies, mostly with very smooth outlines against the enclosing glass (Fig. 2b–d). They are mostly well below 50 µm in size, but a few reach 150 µm. Occasionally larger sulphide bodies are found, especially in the partly devitrified inner parts of the glass zone; These have a more irregular outline (Fig. 2e).

The smoothly shaped sulphide blebs are composed of troilite and numerous sphaeroidal grains of nickel-iron, mostly less than 1–2 µm in size, and their textures (Fig. 2b–d) are very similar to eutec-

**Table 1.** Modal analyses of glass rocks

|  | GGU 176669 | GGU 176671 |
|---|---|---|
| In vol % | | |
| Olivine | 9 | 9 |
| Basaltic glass | 91 | 90 |
| Xenoliths + xenocrysts | tr | 0.8 |
| Points counted | 1,605 | 2,055 |
| Graphite[a] | 0.01 | 0.02 |
| Sulphide blebs[a] | 0.07 | 0.23[b] |

[a]  Points counted with grid ocular  72,000     115,000
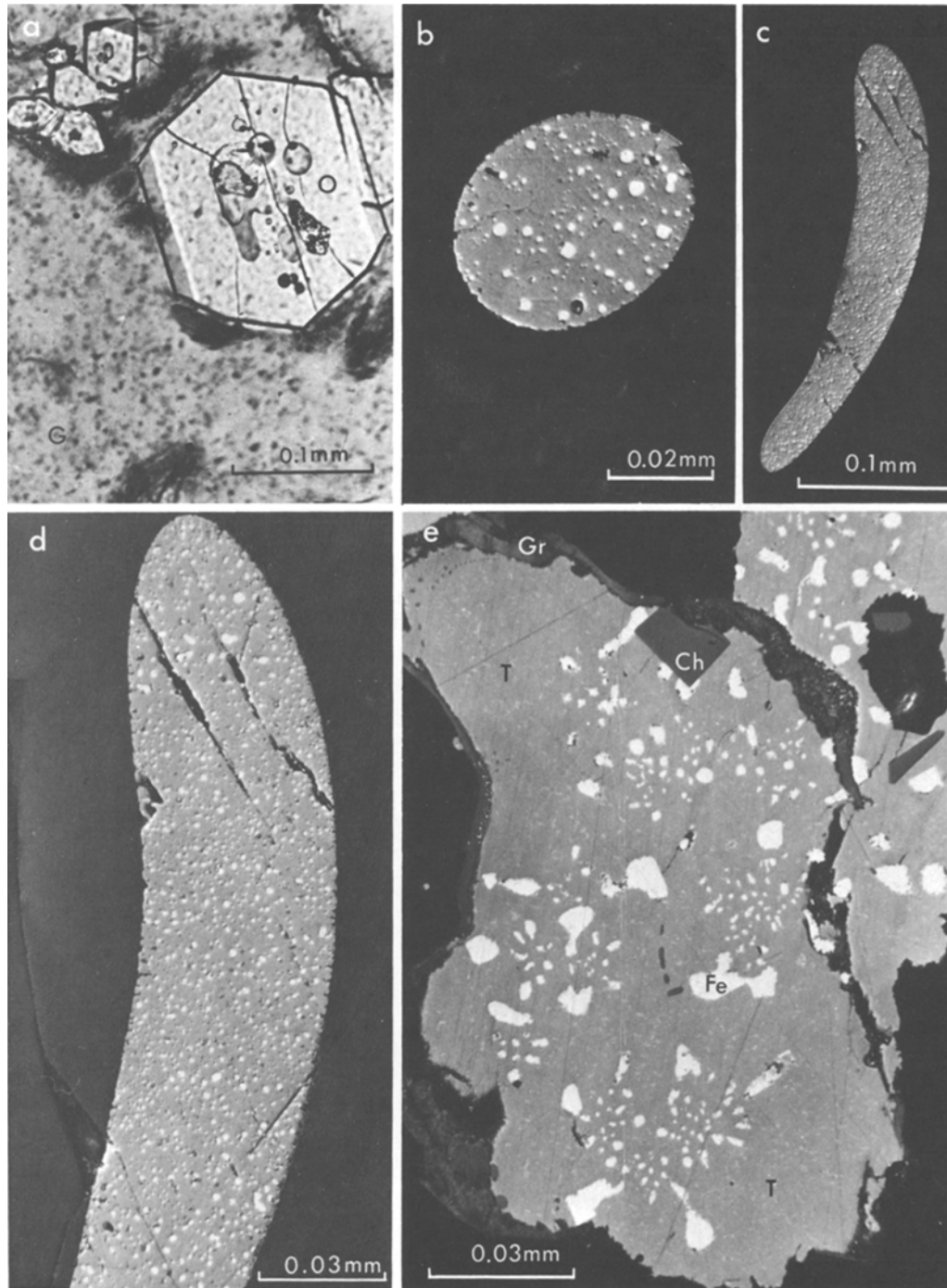[b]  Very inhomogenous size population

Fig. 2a–d. GGU 176669. e GGU 176671. a Euhedral olivine phenocrysts with numerous glass inclusions in slightly green to colourless basaltic glass. Dark brown patches of glass in a state of incipient quench crystallization is seen around the olivines. O: olivine; G: glass. b Ellipsoidal immiscible sulphide bleb in glass. Tiny nickel-iron up to 2–3 μm are set in a mass of troilite. c Large sausage shaped immiscible sulphide body in glass. Note the smooth outlines against the glass. The sulphide bleb is estimated to have been quenched from more than 200° C above its liquidus. d Magnification of the bleb shown in c. The bleb is composed of troilite and iron, while oxides are extremely scarce of missing. The texture indicates very fast quenching. e Large sulphide body from a slightly less fast cooled part of the dyke chill. Similar textures have been produced experimentally from eutectic Fe-FeS melts. T: troilite with numerous thin platelets of exsolved Cu- and Ni-rich sulphides; Fe: nickel-iron; Gr: graphite found along the margins; Ch: early crystallized vanadium-rich chromite. A few tiny unidentified oxides in the centre may be wüstites

tic quench textures illustrated by Albright and Kraft (1966, Fig. 2) and Usselman (1975, Plate 1). The sulphide textures become gradually coarser when moving from the glassy into the sphaerulitic to the microcrystalline parts of the rock. One of these coarser sulphide bodies is shown in Fig. 2e. They consist of *troilite* grains with numerous thin platelets of *copper-* and *nickel-rich phases* and up to 10 μm sized grains of *native iron*. Euhedral crystals of *chromite*, which apparently crystallized early, can be observed very rarely within the sulphide blebs (Fig. 2e).

Modal analyses (Table 1) of the quench-textured sulphide blebs made on high-magnification microphotographs show a close approach to the composition iron monosulphide *90–91 vol%*, iron *9–10 vol%*. Modal analyses of sections through the more coarse-textured blebs are less likely to be representative and show in accordance with this a considerable scatter in iron from 6–12 vol %.

*Graphite* occurs as single flakes or as small clusters of flakes, rarely exceeding a few tens of microns in size. It also occurs intergrown with troilite.

## Chemistry

### Bulk Rock and Glass

Chemical analyses of two glass chill samples are presented in Table 2. It is slightly olivine- or quartz-normative tholeiitic basalt with very high *hy* (32–35%), a high *hy/di*-ratio (2.1–2.7) and with basic *plag* (An 62–63%). Ferric iron was not detected by wet chemical methods in analysed separated glass, indicating both the unusually reduced nature of the rocks and also that it is unaltered. The mg-number is 0.66.

The $H_2O^+$ contents are very low for Tertiary basalt glasses, and similar to those found in MORB-glasses with a corresponding $K_2O$ level (Moore, 1970). The low $H_2O^+$ may partly reflect the strongly reduced state of the magma (high $H_2/H_2O$-ratio). Total sulphur as sulphide is around 850 ppm in the separated basalt glasses, which is similar to the sulphur saturation level as determined experimentally for basaltic melt at the same FeO-level and temperatures (Haughton et al., 1974) and in natural MORB-glasses (Moore and Fabbi, 1971). The sulphur contents of the bulk chill samples vary substantially, even from chip to chip within the same sample, the range found being from 1,000–1,600 ppm, which means that 15–43% of the sulphur in the rocks is bound in the immiscible sulphide blebs. For comparison, Czamanske and Moore (1977) found only 12 ppm S bound in immiscible sulphides in MORB-glasses, that is only about 1.5% of the total sulphur in these glasses.

*Trace Elements.* Table 2 shows some trace elements in the bulk chill rocks and in separated glass. The chill rocks are low in Ni, Cu and less so in Co for high magnesium basalts, and the separated glasses are exceedingly low in these elements. Cr is remarkably high in the glasses, compared to normal basaltic glass from Earth (e.g. Leeman and Scheidegger, 1977; Hill and Roeder, 1974). It clearly reflects the low oxygen fugacity in the magma. The extremely low Ni/Cr ratios of about 0.01–0.02 are probably unique for any basalt glass from Earth.

The chill rocks are enriched in the large lithophile elements Cs, Ba, Th, and U and in the light RE elements (normalized La/Sm ~ 1.4) compared to MORB-glasses.

The chill rocks, which compositionally approach the boninites (e.g. Dallwitz et al., 1966; Kuroda and Shiraki, 1975) but are more Ca-rich, closely resemble in major and trace element chemistry magnesium-rich silicic basalts from the Vaigat and Maligât Formations from Disko and tuffs from Nûgssuaq. These basalts has been shown by Pedersen (1975; 1978a) to have been formed by sediment-contamination of high-Mg tholeiitic basalts (picrites) from which they differ by higher concentrations in some incompatible elements and light REE, by enrichment in radiogenic Sr ($Sr^{87}/Sr^{86}$ ~ 0.710, S. Pedersen, personal communication) and by the widespread occurrence of sedimentary xenoliths and xenocrysts. A similar origin caused by magma reaction with carbonaceous sediments with compositions as given by Pedersen (1979) is therefore inferred. From Fig. 3 the parental magma (crystals-+melt) is estimated to have contained at least 12–14 wt% MgO and hence at least 300–500 ppm Ni.

### Olivines

*Olivine* microphenocrysts show very little compositional variation, being slightly normally zoned from mg=84.5 to 83.3 in cores, to 82.5 in the margin of crystals. The trace element analyses (Table 1 no. 5 to 6) show that the olivines are remarkably low in Ni (110–160 ppm) compared to magnesian olivines in ultramafic nodules and mafic igneous rocks as compiled by Fleet et al. (1977, Fig. 1). However, they are Ni-rich compared to olivine equilibrated with nickel-iron in pallasitic meteorites (Buseck and Goldstein, 1969). The Cr content is not significantly different from that of many terrestrial basaltic olivines (Leeman and Scheidegger, 1977), but much lower than in many lunar basaltic olivines (e.g. Hewins and Goldstein, 1974).

### Sulphide Bleb Chemistry

Microprobe analyses have been made of the bulk composition of a number of the smoothly shaped

**Table 2.** Chemical analyses of rocks, glasses and olivines

| Analyses | 1 | 2 | 3[f] | 4[f] | 5[g] | 6[f] |
|---|---|---|---|---|---|---|
| **Major elements in wt %** | | | | | | |
| $SiO_2$ | 52.09 | 51.87 | 53.11 | 53.24 | 39.8 | 39.40 |
| $TiO_2$ | 1.35 | 1.35 | 1.50[e] | 1.50[e] | | 0.06 |
| $Al_2O_3$ | 13.81 | 13.86 | 15.46 | 15.57 | 0.1 | 0.07 |
| $FeO$[h] | 9.44 | 9.64 | 8.84 | 8.73 | 15.7 | 15.69 |
| $MnO$ | 0.16 | 0.17 | 0.14[d] | 0.15[d] | 0.2 | 0.20 |
| $MgO$ | 10.48 | 10.50 | 7.16 | 7.00 | 44.0 | 44.22 |
| $CaO$ | 9.06 | 9.64 | 9.90 | 9.96 | 0.3 | 0.25 |
| $Na_2O$ | 1.82 | 1.88 | 2.14 | 2.16 | | |
| $K_2O$ | 0.66 | 0.67 | 0.68 | 0.72 | | |
| $P_2O_5$ | 0.16 | 0.15 | 0.16[e] | 0.15[e] | | |
| $H_2O^+$ | 0.42 | 0.33 | 0.22 | 0.16 | | |
| C | 0.09[a] | 0.12[a] | | | | |
| S | 0.10[b] | 0.15[b] | 0.09[b] | 0.09[b] | | |
| Less O | 0.05 | 0.08 | 0.05 | 0.05 | | |
| Total | 99.59 | 100.25 | 99.19 | 99.38 | 100.1 | 99.89 |
| mg | 66.4 | 66.0 | 59.1 | 58.8 | 83.3 | 83.4 |
| **Trace elements, in ppm** | | | | | | |
| S | 1,000[b] | 1,500[b] | 890[b] | 850[b] | | |
| Sc | 30[c] | 27[d] | 33[c] | 30[d] | < 10[d] | < 10[d] |
| V | 240[d] | 240[d] | 230[d] | 235[d] | 240[d] | 280[d] |
| Cr | 810[e] | 810[e] | 810[e] | 830[e] | 700[d] 980[f] | 1000[d] |
| Co | 76[d] | 78[d] | 20[c] | 21[d] | 88[d] | 100[d] |
| Ni | 135[d] | 160[d] | 9[d] | 15[d] | 110[d] | 160[d] |
| Cu | 67[d] | 78[d] | 27[d] | 36[d] | 14[d] | 16[d] |
| Ga | 12[d] | 15[d] | 16[d] | 17[d] | < 10[d] | < 10[d] |
| Sr | 142[d] | 155[d] | 200[d] | 220[d] | 16[d] | n.d. |
| Zr | 123[d] | 128[d] | 135[d] | 150[d] | 35[d] | 42[d] |
| Sb | 0.03[c] | | 0.08[c] | | | |
| Cs | 0.43[c] | | 0.48[c] | | | |
| Ba | 131[e] | 131[e] | 182[d] | 210[d] | 25[d] | 20[d] |
| La | 9.1[c] | | 13.3[c] | | | |
| Sm | 3.66[c] | | 4.12[c] | | | |
| Yb | 1.98[c] | | 2.66[c] | | | |
| Hf | 3.24[c] | | 3.61[c] | | | |
| Ta | | | 0.46[c] | | | |
| Th | 2.18[c] | | 2.36[c] | | | |
| U | 0.99[c] | | 0.84[c] | | | |

Major elements by GGU's chemical laboratories after the procedure by Sørensen (1975)

[a]  Total carbon as C, by LECO carbon analyser

[b]  Sulphur by LECO iodometric titration. E. Kiss

[c]  Instrumental neutron activation. Procedure after Brunfelt and Steinnes (1969) and Gordon et al. (1968)

[d]  Optical emmission spectrography. H. Bollingberg

[e]  X-ray fluorescence

[f]  Electron microprobe, wavelength dispersive analysis

[g]  Electron microprobe, energy dispersive analysis. $mg = 100 \times Mg/Mg + Fe^{2+}$, total Fe as $Fe^{2+}$

[h]  Total iron as $Fe^{2+}$

1: GGU 176669, glassy basalt with native iron-bearing sulphide blebs from chilled apophyses where dyke intrudes tholeiitic plateau basalts. Luciefjeld, Disko; 2: GGU 176671, glassy basalt from brecciated dyke apophyses. Locality as GGU 176669; 3: Separated glass from GGU 176669; 4: Separated glass from GGU 176671; 5: Separated olivine from GGU 176669; 6: Separated olivine from GGU 176671
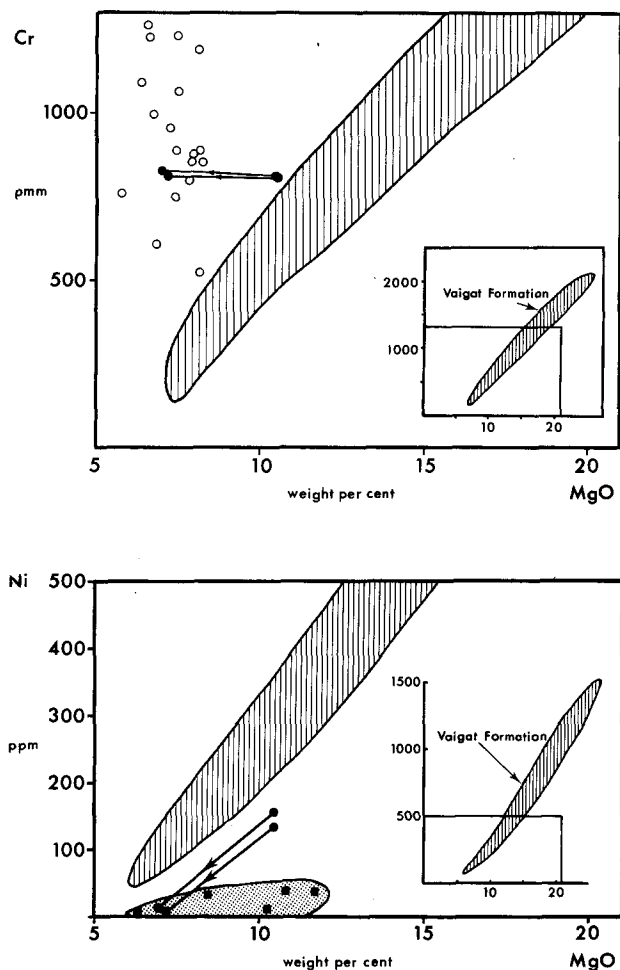
**Fig. 3. a** Cr-MgO diagram. *Solid circles* show the Luciefjeld rocks, *arrows point* from bulk compositions to the separated basalt glasses. *Vertical ruling* shows magnesian tholeiites from the Vaigat Formation of Disko, which define an olivine control line. By comparison with these tholeiites it can be estimated that the Luciefjeld rocks originated from a parent with at least 12–14 wt% MgO. For comparison are also shown microprobe analyses of reduced tuff glasses from Nûgssuaq (Pedersen, 1978a) **b** Ni-MgO diagram. *Solid circles* and vertical ruling as above. *Solid squares,* outlined by a fine-dotted field, indicate nickel-poor basalts from Disko which must have been affected by iron and sulphide fractionation. If the parental magma for the Luciefjeld rocks is assumed to conform to the Vaigat Formation trend and contained at least 12–14 wt% MgO it contained at least 300–500 ppm Ni



**Fig. 4.** The Luciefjeld sulphide blebs (*solid circles*) and their minerals (*open circles*, see also Table 3) plotted in the Ni-poor part of system Fe-Ni-S. Phase fields at 1,000° C and 900° C after Kullerud (1963). Field of α-iron is omitted. Cobalt is included with nickel for the natural phases

quench-textured sulphide blebs and of minerals in a single coarse-textured sulphide body (Table 3). The blebs consist essentially of the elements Fe, Ni, and S and the composition plots close to a ternary cotectic (Fig. 4). A liquidus temperature not higher than 990° C is indicated from the works of Jensen (1942), Kullerud (1963), and Usselman (1975). Next in abundance is Cu followed by Co. Cr is detected while Zn (<0.03%) and P (<0.01%) are not. The analyses total close to 100% suggesting at most a very small oxide component. This is in accordance with the mic-
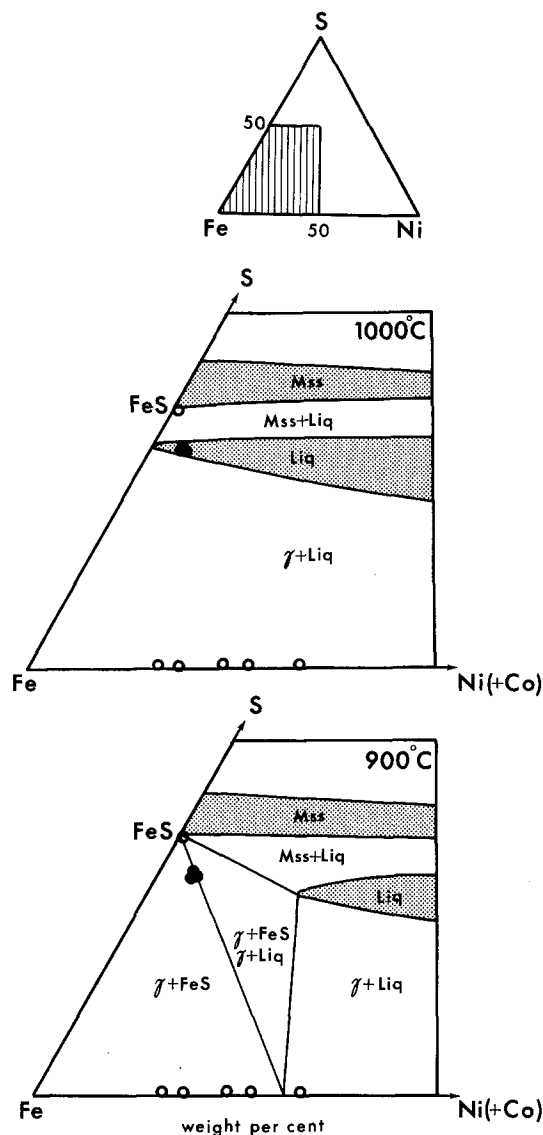
roscopic observations. Trace element analyses made on separated sulphide blebs (Table 3) show the presence of Mn, V, and Ti. These separates may possibly have included a few chromites of the type described below.

*Monosulphide* originally formed the bulk of the sulphide blebs. The grains now consist of troilite (Table 3 no. 4) with numberous extremely tiny platelets of exsolved copper and nickel-rich sulphides.

*Metallic iron* in a coarse sulphide bleb (Fig. 2e) show a considerable range in the $100 \times Ni/Ni + Fe$

**Table 3.** Microprobe analyses of sulphides and iron from sulphide blebs

| Analyses | 1[a] | 2[a] | 3[a] | 4[b] | 5[b] | 6[b] | 7[b] | 8[a] | 9[b] |
|---|---|---|---|---|---|---|---|---|---|
| Major elements, in wt % | | | | | | | | | |
| P | < 0.03 | < 0.03 | < 0.03 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.03 | < 0.05 |
| S | 30.64 | 30.76 | 30.86 | 36.9 | 0.80 | 0.35 | 0.70 | 0.41 | 0.40 |
| Cr | 0.08 | 0.06 | 0.05 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Fe | 64.06 | 63.49 | 63.47 | 62.2 | 82.4 | 80.7 | 74.9 | 72.63 | 66.2 |
| Co | 0.43 | 0.41 | 0.53 | n.d. | 2.1 | 1.9 | 2.2 | 2.15 | 1.9 |
| Ni | 3.92 | 4.11 | 3.55 | 0.35 | 13.4 | 16.4 | 21.6 | 24.50 | 30.9 |
| Cu | 1.10 | 1.06 | 0.91 | 0.38 | 0.50 | 0.63 | 0.68 | 0.69 | 1.5 |
| Total | 100.23 | 99.89 | 99.37 | 98.83 | 99.20 | 99.98 | 100.08 | 100.38 | 100.9 |
| Major elements, in atomic % | | | | | | | | | |
| S | 43.53 | 43.79 | 44.08 | 49.86 | 1.40 | 0.61 | 1.23 | 0.72 | 0.70 |
| Cr | 0.07 | 0.05 | 0.04 | | | | | | |
| Fe | 52.24 | 1.89 | 52.04 | 49.60 | 83.26 | 81.30 | 75.38 | 73.14 | 66.58 |
| Co | 0.33 | 0.32 | 0.41 | | 2.01 | 1.81 | 2.10 | 2.05 | 1.81 |
| Ni | 3.04 | 3.20 | 2.77 | 0.27 | 12.88 | 15.72 | 20.69 | 23.48 | 29.58 |
| Cu | 0.79 | 0.76 | 0.65 | 0.27 | 0.45 | 0.56 | 0.60 | 0.61 | 1.33 |
| $100 \times$ Cu/Cu+Ni | 20.6 | 19.1 | 22.0 | 50.9 | 3.3 | 3.4 | 2.8 | 2.5 | 4.2 |
| $100 \times$ Ni/Fe+Ni | 5.5 | 5.80 | 4.9 | 0.5 | 13.4 | 16.2 | 21.5 | 24.3 | 30.6 |

| Modal composition in volume % | | | |
|---|---|---|---|
| Sulphide | 91 | 90 | 90 |
| Metallic iron | 9 | 10 | 10 |

Separated sulphide blebs from GGU 176669.
Trace elements, in ppm

| | |
|---|---|
| Sc | < 10 |
| Ti | 430 |
| V | 135 |
| Cr | 730 |
| Mn | 340 |

Analysis by optical emission spectrography. H. Bollingberg

[a] Wavelength dispersive microprobe analysis
[b] Energy dispersive microprobe analysis

1: Immiscible sulphide bleb with native iron, Fig. 2c–d
2: Immiscible sulphide bleb
3: Immiscible sulphide bleb
4: Troilite from coarse sulphide bleb, Fig. 2e
5–9: Nickel iron bodies from coarse sulphide bleb, Fig. 2e
1–3: GGU 176669
4–9: GGU 176671

Wavelength dispersive microprobe analyses reported in this paper were made on a Hitachi XMA-5B scanning electron Microanalyser at the Institute of Mineralogy, University of Copenhagen.
Energy dispersive microprobe analyses were made on a TPD-microprobe at Research School of Earth Sciences, Canberra, using a procedure modified after Reed and Ware (1975)

ratio from 13.4 to 30.6 (Table 3 no. 5 to 9). This is by far the most nickeliferous iron yet analysed from Disko. Next in abundance is Co followed by Cu while neither Cr nor P are detected. Because of the small size of the iron grains ($< 12\,\mu m$) the sulphur content reported may partly originate from the enclosing troilite matrix. The high totals indicate a very low carbide component in the iron.

The *chromites* (Table 4) are very low in Mg, Al, and Mn, low in Ti but unusually high in $V$. When cations are calculated on the basis of 32 oxygens on the assumptions of divalent Fe and trivalent Cr and $V$, they total around 24.15. Assuming stoichiometry this indicates that parts of one or more of Fe, Cr, and $V$ are present in a higher oxidation state. Recent work on strongly reduced magnesian spinels from Disko (Pedersen, 1978b) indicates a strong preferred acceptance of Cr as $Cr^{3+}$ in the spinels, and this is probably also valid for the present ones. Stoichiometry would require a $\dfrac{Fe^{3+}}{Fe^{2+} + Fe^{3+}}$ ratio of 0.04–0.05, or a $\dfrac{V^{4+}}{V^{3+} + V^{4+}}$ ratio of 0.20–0.25 or a combination

**Table 4.** Vanadium rich chromites crystallized from sulphide melt (Fig. 2e) in sample GGU 176671

| Analysis | 1[a] | 2[a] | 3[b] | 4[a] | 5[b] |
|---|---|---|---|---|---|
| $SiO_2$ | 0.27 | 0.28 | n.a. | 0.49 | n.a. |
| $TiO_2$ | 0.69 | 0.70 | 0.7 | 1.91 | 1.1 |
| $Al_2O_3$ | 0.25 | 0.20 | 0.2 | 0.52 | 0.2 |
| $V_2O_3$ | 6.60 | 7.85 | 8.2 | 8.73 | 9.5 |
| $Cr_2O_3$ | 57.01 | 56.63 | 56.6 | 52.64 | 52.6 |
| $FeO^c$ | 33.77 | 34.00 | 33.6 | 33.87 | 34.3 |
| MnO | 0.39 | 0.35 | 0.5 | 0.36 | n.d. |
| NiO | 0.10 | 0.08 | n.d. | 0.09 | n.d. |
| MgO | 0.32 | 0.24 | 0.3 | 1.45 | 0.4 |
| ZnO | 0.23 | 0.12 | 0.2 | 0.12 | 0.2 |
| Total | 99.63 | 100.45 | 100.3 | 100.18 | 100.3 |
| mg | 1.7 | 1.2 | 1.8 | 7.1 | 2.2 |
| $100 \times V/$ Al+V+Cr | 10.4 | 12.3 | 12.8 | 14.2 | 14.9 |

Cations on the basis of 32 oxygens

| | | | | | |
|---|---|---|---|---|---|
| Si | 0.081 | 0.083 | | 0.144 | |
| $Ti^{4+}$ | 0.155 | 0.156 | 0.157 | 0.423 | 0.246 |
| Al | 0.088 | 0.070 | 0.070 | 0.181 | 0.070 |
| $V^{3+}$ | 1.585 | 1.868 | 1.957 | 2.062 | 2.264 |
| $Cr^{3+}$ | 13.496 | 13.290 | 13.319 | 12.257 | 12.835 |
| $Fe^{2+}$ | 8.457 | 8.441 | 8.365 | 8.343 | 8.530 |
| Mn | 0.099 | 0.087 | 0.125 | 0.089 | |
| Ni | 0.024 | 0.019 | | 0.021 | |
| Mg | 0.143 | 0.106 | 0.133 | 0.636 | 0.177 |
| Zn | 0.051 | 0.026 | 0.044 | 0.026 | 0.045 |
| Total cations | 24.179 | 24.147 | 24.170 | 24.182 | 24.167 |

[a]    Wavelength dispersive microprobe analysis
[b]    Energy dispersive microprobe analysis
[c]    total iron as FeO
n.a.: not analysed for; n.d.: not detected
$mg = 100 \times Mg/Mg + Fe^{2+}$

of both. The work by Schreiber (1977) on simulated lunar magmas indicates that $V$ may have been present in a combination of the states $V^{3+}$, $V^{4+}$, and $V^{5+}$ in the chill rocks. The oxidation state of Fe or $V$ in the chromite has therefore not been conclusively determined.

The chromites resemble spinels crystallized in sulphide melts from La Perouse gabbro (Czamanske et al., 1976) and from nickel ores in Western Australia (Ewers et al., 1976; Groves et al., 1977) but differ in having a much smaller magnetite component, if any.

## Transition Element Partition in the Chilled Rocks

The chilled rocks consisted prior to quenching essentially of three phases each of which showed only very limited compositional variation, namely forsteritic olivine, basaltic melt and an iron-nickel-sulphide melt (neglecting the rare early chromites in sulphide melts, the graphite flakes and the scarce xenoliths and xeno-

crysts). Table 5 shows empirical element partition coefficients for the three phases.

To test for evidence of any sulphide contamination in the olivine and glass separates, an olivine – glass pair was analysed in each of the two chill rocks where the two glasses showed significantly different but very low contents of Ni (9 and 15 ppm). The resulting two pairs of very similar partition coefficients (Table 5) indicate clean separates and probably also small-scale effects of fractionation and re-equilibration between sulphide melt and silicate melt + olivine.

The transition element partition of the rock was strongly affected by the composition of the sulphide melt, which was governed by the intensive parameters $f_{O_2}$ and $f_{S_2}$. The oxygen fugacity prior to quenching is not well determined, some constraint being that $f_{O_2}$ was high enough to stabilize chromite and low enough to exsolve nickel-iron upon cooling. Ulff-Møller (personal communication 1977) observed coexisting wüstite, chromite and iron during the cooling of related sulphide melts from the same dyke. The unidentified tiny grey phase on Fig. 2e is probably wüstite. As a crude approximation an $f_{O_2}$ of $10^{-12}$ to $10^{-13}$ at 1,200° C can be estimated by extrapolating the iron-wüstite $f_{O_2}$ buffer (Sato et al., 1973) allowing for the activity of iron being well below 1 in the sulphide melt prior to quenching. An estimate of $f_{S_2}$ of $10^{-5}$ at 1,200° C is obtained from the experimental work on iron-sulphur melts by Štofko et al. (1974).

### Equilibria Between Olivine and Basalt Melt

Work on Mg − Fe partition (Roeder and Emslie, 1970; Roeder, 1974; Leeman, 1978; Longhi et al., 1978) has shown that $K_D = \dfrac{X^{ol}_{FeO}}{X^{ol}_{MgO}} \cdot \dfrac{X^{liq}_{MgO}}{X^{liq}_{FeO}}$ is largely temperature independent at low pressures and close to 0.30 within wide magma compositional limits (spanning the presently studied glass rocks). By this criterion olivine and melt were in equilibrium in the Luciefjeld chilled rocks ($K_D = 0.28$ and 0.29), and application of olivine/melt thermometry (Table 5) indicates that quenching occurred around 1,200° C.

The $Ni$-partition is known to show a strong dependence on the Mg-content of the melt (see review by Hart and Davis, 1978). The present rocks have $D_{Ni}$ ($Ni_{olivine}/Ni_{glass}$ wt%) values of 10.7–12.2 slightly outside the range of most experimental determinations at comparative MgO. $D_{Ni}$ is, however, likely to be dependent of $f_{O_2}$ (Mysen and Kushiro, 1976) and this effect is presently not well established.

The $\underline{Mg - Co}$ $K_D = \dfrac{X^{ol}_{CoO}}{X^{ol}_{MgO}} \cdot \dfrac{X^{liq}_{MgO}}{X^{liq}_{CoO}}$ for the two Luciefjeld rocks is 0.72 and 0.75. This is slightly higher than the $K_D = 0.61$ found in a cobalt-analogue basalt

**Table 5.** Element partition in the glass rock GGU 176669 and 176671

| Elements | Sc | Ti | V | Cr | Mn | Co | Ni | Cu |
|---|---|---|---|---|---|---|---|---|
| $D$, wt% ratio | | | | | | | | |
| Olivine/glass | <0.04 | 0.08 | 1.0 | 1.0 | 1.2 | 4.4 | 12.2 | 0.5 |
| | (<0.04) | (0.04) | (1.2) | (1.2) | (1.3) | (4.8) | (10.7) | (0.4) |
| Sulphide bleb/glass | | 0.05 | 0.6 | 0.9 | 0.3 | 230 | 4,300 | 380 |
| Sulphide bleb/olivine | | | | | | 52 | 351 | 730 |
| Sulphide/glass, Rajamani and Naldrett (1978) | | | | | | 80 | 274 | 243 |

| | | |
|---|---|---|
| $K_D$, mole fraction ratio. | | $T°C_{Mg} = 1188$ (1181), Roeder and Emslie [1970, Eq. (11)] |
| Olivine/glass, Mg−Fe | 0.29 | |
| | (0.28) | $T°C_{Fe} = 1203$ (1200), Roeder and Emslie [1970 Eq. (12)] |
| Olivine/glass, Mg−Co | 0.72 | |
| | (0.75) | Sulphide bleb composition is taken as the mean of anal. 1–3 in Table 3 |
| Sulphide bleb/olivine, Fe−Ni | 64 | without brackets: GGU 176669 |
| same, estimate from litera- | | Bracketed: GGU 176671. |
| ture, see text | 53 | |

at temperatures above 1,200° C by Coons et al. (1976). The Co-partition between olivine and glass indicates equilibrium compared to experimental results (see review by Irving, 1978).

Cr partition has been established by many workers (e.g. Ringwood and Essene, 1970; Schreiber and Haskin, 1976; and Leeman and Scheidegger, 1977). The present $D_{Cr}$-values are close to unity, which is in accordance with experiments simulating lunar basalts and imply proximity to equilibrium.

The $V$-partition is strongly $f_{O_2}$ dependent, $D_V$ of about 0.05 being found at values of $f_{O_2}$ characteristic for terrestrial basalt magmas (Duke, 1976) while much higher $D_V$ (1.3) has been determined in experiments simulating lunar basalts (Ringwood, 1970). The Luciefjield chilled rocks show $D_V \sim 1.0$ and 1.2 in accordance with the reduced nature of the chill rocks.

In conclusion, element partition imply equilibration at 1,200° C between olivine and melt (glass), which constitutes more than 99 vol % of the rock, and reflects a low $f_{O_2}$.

*Equilibria Between Sulphide and Silicates*

Table 5 gives sulphide melt-silicate melt partition coefficients. $D_{Ni}$ (Ni sulphide/Ni glass wt%) is extremely high ($4.3 \times 10^3$) while $D_{Co}$ (230) and $D_{Cu}$ (378) are much smaller, though still reflecting the strong siderophile and chalcophile character of these elements. Rajamani and Naldrett (1978) determined $D_{Ni, Co}$ and $_{Cu}$ in coexisting slightly magnetite bearing monosulphide melt and basalt melt and found $D$ values (Table 5) much lower than in the Luciefjield chill rocks. The discrepancy decreases from $D_{Ni}$ (×15.7) through $D_{Co}$ (×2.9) to $D_{Cu}$ (×1.6), that is with decreasing siderophile character. This suggests that the $D$'s found in the Luciefjield rocks are func-

tions of excess metal components in the sulphide melts.

Sulphide melt-olivine equilibria shall next be compared. These are more easily compared with experiments since transition element values of $D$ show a considerable dependance on the silicate melt composition (e.g., Irving, 1978) Table 5 gives sulphide melt – olivine partition coefficients. Clark and Naldrett (1972) studied the reaction

$FeS + NiSi_{0.5}O_2 \leftrightarrows NiS + FeSi_{0.5}O_2$ and found
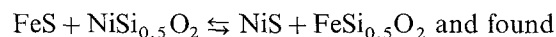
$$K_D = \frac{X_{NiS}}{X_{FeS}} \cdot \frac{X_{FeSi_{0.5}O_2}}{X_{NiSi_{0.5}O_2}} = 33.2 \pm 3.4 \text{ at } 900° C$$

and Fleet et al. (1977) equilibrated slightly oxide bearing sulphide melt with forsterite-rich olivine + basaltic melt, both not much different from the Luciefjield chill phases and found $K_{D_{Ni}} \sim 33$ and possibly insensitive to olivine composition and temperature. The Luciefjield

$$K_D = \frac{X_{\text{"NiS"}}}{X_{\text{"FeS"}}} \cdot \frac{X_{FeSi_{0.5}O_2}}{X_{NiSi_{0.5}O_2}}, \quad \begin{array}{l} \text{"NiS"} = NiS + \text{excess Ni} \\ \text{"FeS"} = FeS + \text{excess Fe} \end{array}$$

is distinctly higher (64) and this deviation is probably due to the excess metal component of the sulphide melt.

A simplistic approach is to consider the sulphide melt as being composed of stoichiometric monosulphide and excess metal. Buseck and Goldstein (1969) investigated nickel-iron-olivine equilibria in pallasites and calculated the equilibrium constant for the exchange reaction

$Fe_{metal} + NiSi_{0.5}O_{2 \text{ olivine}} \leftrightarrows Ni_{metal} + FeSi_{0.5}O_{2 \text{ olivine}}$
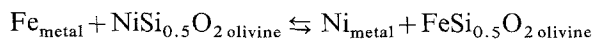
as a function of temperature, assuming ideality, and calculated a $K_D$ around 190 at 1,200° C for olivines similar to the Luciefjield olivines. By simply combining the $K_D$'s for monosulphide (Fleet et al., 1977) and

metal parts (Buseck and Goldstein, 1969) of the sulphide melt in proportion to their atomic % mode in the Luciefjeld sulphide blebs (87.6% Monosulphide, 12.4% Metal), a $K_D$ of about 53 is found, which is not far from the measured value (64). This may be a further indication that the sulphide melt was equilibrated with melt+olivine. In the absence of successful experiments on Ni partition between olivine and metal, no better estimate has presently been obtained.

## Evidence of Sulphide Fractionation

The Luciefjeld chill rocks display evidence of sulphide fractionation (see Fig. 3). The estimated parent magma possibly contained about 300–500 ppm Ni and the silicate (olivine+glass) part of the chill rocks has only about 20–30 ppm. Neglecting the important effect of a few per cent of olivine fractionation, the total variation in Ni from 400–20 ppm could be accounted for by only 0.5 wt% sulphide melt fractionation (equilibrium fractionation, Shaw [1970 p. 239 Eq. (11)].

More detailed modelling is unrealistic because studies of other iron-bearing volcanic rocks and their xenoliths on Disko indicate that the early stages of magma/sediment interactions was characterized by a rapid exchange of elements, in particular sulphur and C-H-O-components. The rapidly varying $f_{O_2}$ would affect the content of excess metal components in immiscible sulphide melts and hence affect the transition metal element partition dramatically.

The presence among the reduced volcanic rocks on Disko of (a) segregated sulphide and metal bodies (igneous cumulates) and (b) basaltic intrusives and lavas with strongly depleted patterns of chalco- and siderophile transition metal elements (e.g. Fig. 3) strongly suggests that magmatic metal and sulphide fractionation was a common and important process.

## Conclusion

The Luciefjeld glass rocks provide an example of fresh quenched strongly reduced basalt. At a quenching temperature close to 1,200° C, 250 bars pressure, $f_{O_2}$ ~ $10^{-12}$ to $10^{-13}$, $f_{S_2}$ ~ $10^{-5}$, the magma was undersaturated in $H_2O$ and consisted of olivine, basalt melt and minor immiscible sulphide melt. Sulphide blebs showing quench textures are of nearly cotectic composition in the Ni-poor part of the system Fe-Ni-S and quenching of the chilled rocks started more than 200° C above the liquidus temperature of the sulphide melt. Despite the small amounts of immiscible sulphide blebs the three phases were apparently high-temperature equilibrated. Comparison with experi-

mental determination of Ni, Co, and Cu partition between basalt and monosulphide and olivine and monosulphide shows that these elements in the Luciefjeld case are unusually strongly partitioned into the sulphide phase. The deviation from the literature values increases with the increasingly siderophile character of the elements (Ni > Co > Cu) suggesting that the partition is strongly dependent on the excess metal component in the sulphide melt. Comparison with experimental and thermodynamic data on Ni-partition in olivine-sulphide and olivine-metal pairs suggests that the increase in partition coefficients is roughly proportional to the excess metal component. Examples from the native iron bearing volcanic rocks on Disko show that the magmatic sulphide and metal fractionation was both common and geologically important.

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