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# PLAGIOCLASE-SPINEL-GRAPHITE XENOLITHS IN METALLIC IRON-BEARING BASALTS, DISKO ISLAND, GREENLAND

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## Abstract

Tertiary basalt flows from west Greenland commonly contain metallic iron and graphite. They are thus some of the most reduced of terrestrial basalts, and are of interest in connection with basalt studies in general, and in connection with the origin of certain meteorites (Lovering, 1964).

Xenoliths composed mainly of plagioclase ($An_{70-75}$), graphite, rose-colored spinel and rarely corundum are included in these basalts on Disko Island. The xenoliths are remarkably similar to reconstituted shale xenoliths in basaltic rocks from other localities except for the presence of graphite and in the composition of the spinel. The spinel has $n = 1.747 \pm 0.001$, $a = 8.119 \pm 0.002$ and $D = 3.81 \pm 0.01$, and electron microprobe analysis gave Mg $= 13$ and Fe $= 8.9\%$. These data indicate a spinel with composition about $Sp_{78}He_{22}$. This unusually low Fe content compared to spinels from other aluminous xenoliths in basaltic rocks is evidently related to the low oxygen fugacities in basaltic magmas in contact with graphite, particularly in an environment such as Disko, where active reduction of ferrous iron to iron evidently occurred.

The close similarities in the mineralogy of the xenoliths from specimen to specimen indicate complete equilibration of magma and xenoliths. This equilibration involved mainly loss of K and Si, and gain of Ca, Mg, Al and Na by the xenoliths.

The xenoliths in their similarities to known reconstituted shale xenoliths, their graphite content, and low-iron spinel substantiate the idea of derivation of the metallic iron by near surface reduction of basaltic magma by carbonaceous sedimentary rocks (Törnebohm, 1878; Steenstrup, 1882), rather than derivation of the metallic iron from the mantle (Lindgren, 1933; Urey, 1952).

## Introduction

The origin of metallic nickel-iron in terrestrial basalts has been the subject of much speculation. Outstanding in this regard are the nickel-iron alloys which occur in some basalts from Disko Island, West Greenland. These basalts, in view of the abundance of graphite in addition to metallic nickel-iron, are some of the most reduced of terrestrial rocks. They are thus of interest in connection with basalt studies in general, and in connection with the origin of certain meteorites (Lovering, 1964b).

The petrologic collections of the U. S. National Museum contain a large and heretofore unstudied suite of basalts from Uivfaq, Disko Island. Most of these were collected by Captain Robert Bartlett during an expedition to Greenland around 1930. This collection is the subject of the present study.

The principal objective of this paper is to point out the bearing of abundant plagioclase-spinel-graphite xenoliths in these basalts on the general mechanism of derivation of the iron. The physical chemical interpretation of the pre-eruption and cooling history of these unusual basalts will be presented later.

An ARL electron beam microprobe was the principal analytical tool used to determine the compositions of the minerals of the xenoliths. Spinel compositions were substantiated by their index of refraction, unit cell dimension and density. Chemically analyzed minerals of compositions similar to the plagioclase and spinel in the xenoliths were used as microprobe standards, and no corrections were made for matrix effects.

## Previous Work

At least four different origins have been postulated for the Disko iron:

(1) Meteoritic (Nordenskiöld, 1870)

(2) Near surface reduction of basaltic magma by coal beds (Steenstrup, 1882).

(3) "Desulphurization" of basaltic pyrrhotite by graphite (Lofquist and Benedicks, 1941).

(4) Direct derivation of some of the metallic iron from the upper mantle (Lindgren, 1933, and Urey, 1952).

Most recent papers which mention the Disko iron, such as Lovering 1964a), favor origin 2.

The reduction of basaltic magma by carbonaceous material has been demonstrated unequivocally in at least one locality. Searle (1958) noted small grains of metallic iron about a carbonized log in a New Zealand basalt flow. On the other hand, basalt flows on Disko Island have been noted which contain abundant graphite but only rare grains of metallic iron (Münther, 1951).

As in the present study, Vaasjoki (1964) places considerable emphasis on the occurrence of aggregates of graphite, spinel and plagioclase in the Disko basalts where they contain metallic iron. However, he interprets these aggregates as the product of crystallization of "anorthositic" magma. Evidence is presented here which indicates these are reconstituted shale xenoliths, as first suggested by Törnebohm (1878), and that they support the idea of derivation of the metallic iron by reduction of basalt by carbonaceous sedimentary rocks.

The earlier views concerning the metallic nickel-iron in the Disko basalts and a description of their field relations are summarized by Steenstrup (1882, English translation, 1884). This paper and the accompanying one by Lorenzen (1882, 1884) are, to the writers' knowledge, the most informative of the many early papers on the Disko basalts.

## Geologic Setting

The basalts of western Greenland are mainly of Tertiary age and unconformably overlie Pre-Cambrian metamorphic rocks and a series of

Cretaceous and Tertiary sedimentary rocks (Noe-Nygaard, 1947). The sedimentary sequence contains carbonaceous rocks which were thought to have caused reduction of the Disko basalts (Steenstrup, 1882).

Analyses, such as those by Nauckhoff (1874), and modes by the writer indicate that the Disko metallic iron-bearing basalts are olivine tholeiites. The basaltic specimens examined in the present study consist of over 90

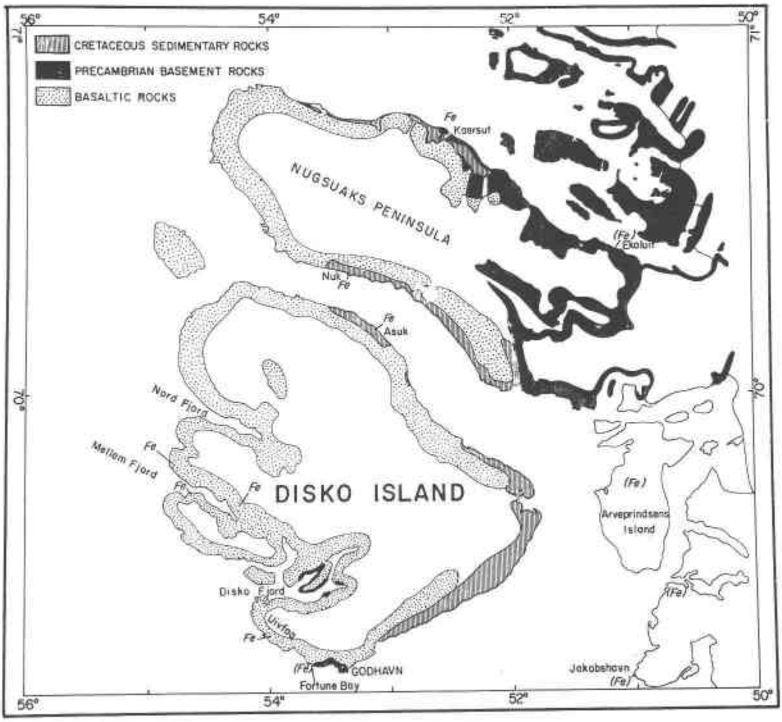


FIG. 1. Metallic nickel-iron bearing basalt occurrences, West Greenland. Modified from Steenstrup (1882). Iron basalt in loose blocks noted by Fe in parentheses. Remaining localities have iron basalts in situ.

per cent plagioclase and clinopyroxene. Olivine occurs rarely as phenocrysts and matrix granules.

Figure 1 shows the localities where metallic iron was noted by Steenstrup (1882) on Disko Island and vicinity. An additional locality, Kaersut, Nugsuaks Peninsula, was noted by Schuchert and White (1898). This locality is also shown on Fig. 1.

Figure 2 shows the locality at Uivfaq where most of the specimens of the present study were collected. The specimens are from the base of an approximately 500 foot cliff composed of horizontal basalt flows. Single specimens from Asuk, Disko Island, and Kaersut, Nugsuaks Peninsula, are the only other localities represented in the U. S. National Museum collections.

## Xenoliths

A remarkable feature of the basalts from Uivfaq is the occurrence of angular coarsely crystalline xenoliths composed of about 90 per cent plagioclase and lesser amounts of rose-colored spinel and graphite (Figs.

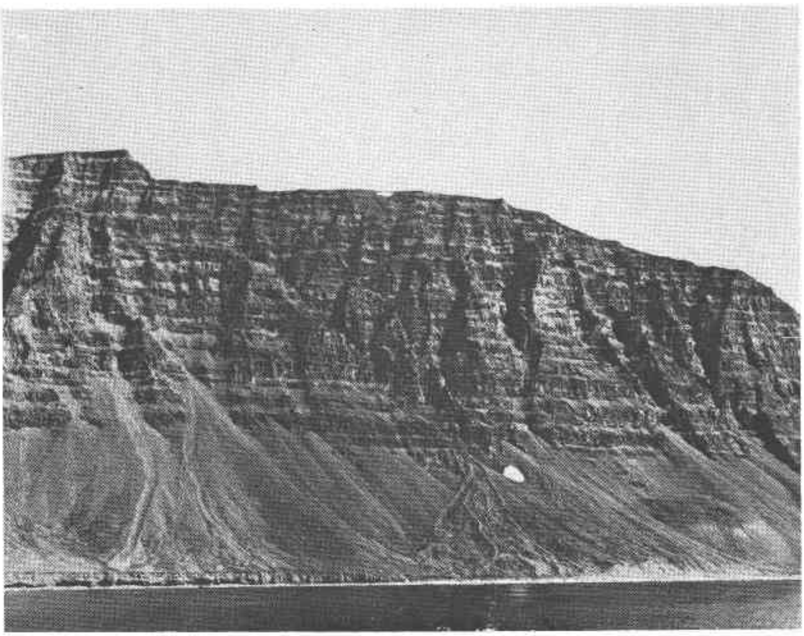

Fig. 2. Basalt cliffs of Uivfaq, Disko Island, Greenland. The picture was taken from the deck of the Morissey. Metallic nickel-iron rich basalts were collected at base of cliffs by Captain Bartlett.

3, 4). The xenoliths were noted in most specimens which contain metallic nickel-iron. This association indicates that the origins of the xenoliths and nickel-iron are related, as suggested previously by Törnebohm (1878), Steenstrup (1882), Lorenzen (1882), and Vaasjoki (1965).

*Texture.* Large granoblastic crystals of plagioclase which are up to 1.5 centimeter in diameter are the main constituents of the xenoliths. Graphite occurs as small flakes up to a millimeter in diameter dispersed throughout the plagioclase and composes between 5 and 30 per cent by volume of the xenoliths. Rose-colored spinel occurs in most of the xenoliths. The spinel typically contains inclusions of graphite (Fig. 4). Small grains of colorless corundum occur rarely.

The xenoliths are characteristically angular. Some are intricately veined by basalt and in a few specimens individual crystals of spinel and graphitic plagioclase occur as isolated single crystals in basalt.

*Plagioclase.* Early work on plagioclase of the xenoliths indicated that it was anorthite (Lorenzen, 1882). However, a composition of about $An_{70}$ is indicated by microprobe analyses and by the optical-crystallographic curves of Slemmons (1962).

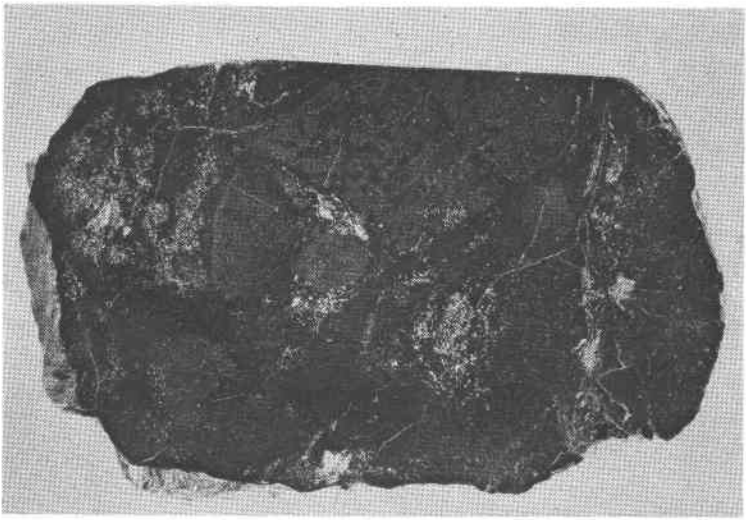

FIG. 3. Basalt with angular plagioclase-spinel-graphite xenoliths (light-gray) and interstitial grains of metallic nickel-iron. Uivfaq. 10×15 cm. U.S.N.M. 108308-15.

The plagioclase in the interior of the xenoliths is characteristically unzoned. However, the plagioclase has a thin rim of graphite-free zoned plagioclase where in contact with the basalt (Fig. 5). The composition of the rims is of the same range as that of the plagioclase microlites in the basalt ($An_{65}$-$An_{50}$). These rims are thus evidently the result of post-extrusion crystallization of plagioclase overgrowths on the more calcic plagioclase of the xenoliths.

The cores of the rare graphite-free plagioclase phenocrysts (Fig. 6) are of about the same composition as the plagioclase of the xenoliths.

*Spinel.* Small anhedral crystals of rose-colored spinel compose up to 10 per cent of some xenoliths. They are unzoned and within a given speci-

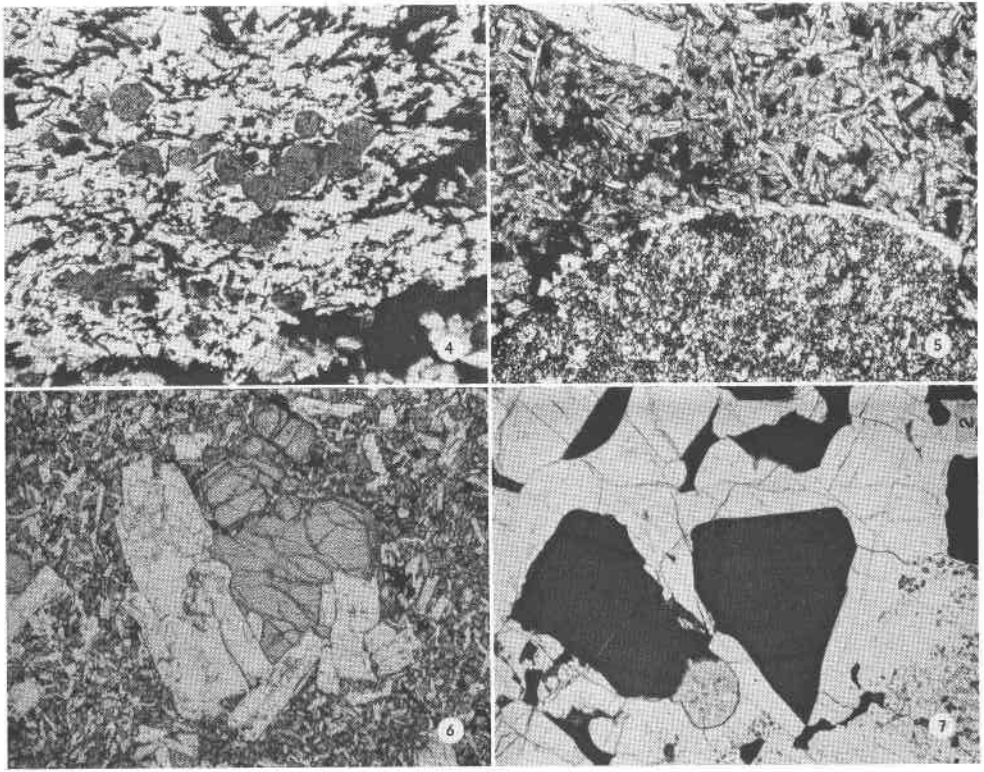

FIG. 4. Graphite (opaque) and spinel in plagioclase ($An_{70}$). Spinel crystals are a maximum of 0.2 mm. in diameter. Uivfaq. U.S.N.M. 108308-10.

FIG. 5. Plagioclase-spinel-graphite xenolith in basalt. Xenolith has clear zoned plagioclase overgrowth ($An_{70}$-$An_{50}$). Note graphite-free plagioclase phenocryst in upper left. Width of field about 5 mm. U.S.N.M. 108308-22.

FIG. 6. Clot of clinopyroxene, olivine (upper part of clot) and plagioclase ($An_{70}$) phenocrysts in matrix composed mainly of plagioclase and clinopyroxene. Width of field about 4 mm. U.S.N.M. 108308-22.

FIG. 7. Hercynitic spinel-plagioclase in reconstituted shale xenolith, Loch Scridain, Mull. Mullite "needles" in lower right hand corner. Width of field about 4 mm. U.S.N.M. 109515.

men are of constant composition. Microprobe analyses indicate a composition of about 22 per cent hercynite molecule (Mg = 13%, Fe = 8.9%). The amount of Mg and Fe present recalculated as MgO and FeO suggests that there is little ferric iron present. The spinel is thus entirely within the spinel-hercynite series.

The composition of the spinel as indicated by microprobe analysis is in accord with its density (3.81 ± .01), index of refraction (1.747 ± .001) and unit cell dimension (8.119 ± .002 Å) (Deer *et al.*, 1962).

Table 1 gives the results of a spectrographic analysis of spinel from specimen 108308-10 from Uivfaq. A notable feature is the high chromium content.

TABLE 1. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS OF SPINEL (U.S.N.M. 108308-10).

| | | | | | |
|---|---|---|---|---|---|
| Al | Major | Si | .15 | Mo | .0007 |
| Fe | Major | Mn | .1 | Zr | .0007 |
| Mg | Major | Ca | .02 | Cu | .0005 |
| Cr | .7 | B | .003 | Ba | .0003 |
| V | .7 | Ga | .007 | Sc | .0003 |
| Ti | .3 | Ni | .007 | Be | .0002 |
| Zn | .2 | Co | .007 | Ag | .00002 |

The following elements are below the limit of detectability: Na, K, P, As, Au, Bi, Cd, Ge, Hf, Hg, In, La, Li, Nb, Pb, Pd, Pt, Re, Sb, Sn, Sr, Ta, Te, Th, Tl, U, W, Y, Yb. Results are reported in per cent to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1 et cetera; which represent approximate midpoints of group data on a geometric scale. The assigned group for semiquantitative results will include the quantitative value about 30% of the time.

Analyst: Helen W. Worthing, U. S. Geological Survey.

Microprobe analyses indicate no compositional differences between spinels which occur within graphitic plagioclase and those isolated in the basaltic matrix. The spinels are also of similar compositions in each of seven xenoliths examined in detail.

In some xenoliths the spinel is deeply embayed, suggesting that it was partly resorbed. This was also noted by Vaasjoki (1965).

The spinel from the xenoliths was previously analyzed by Lorenzen (1882), and his method of separation of spinel from plagioclase was used in the present study. In Lorenzen's analysis, all iron was first converted to the ferric state and thus the original amount of FeO present is unknown. However, by using his MgO value, and assuming a stoichiometric spinel composition, a spinel of about $He_{30}$ is indicated.

Bøggild (1953) also gives an early analysis of the spinel. Contrary to the analyses obtained in the present study, this analysis departs widely from spinel stoichiometry ($N_{FeO}+N_{MgO}=0.50$; $N_{Al_2O_3}+N_{Fe_2O_3}=0.74$). The $Al_2O_3$ is particularly high (74.93%) compared to the values obtained by microprobe analyses (average $Al_2O_3$ about 65%).

*Corundum.* Corundum occurs rarely as colorless anhedral grains in the spinel-bearing xenoliths. Microprobe analyses indicate Fe equals .2 per cent in corundum in xenoliths from Asuk (U.S.N.M. 100215). Smith (1879) was the first to report corundum in association with the iron-bearing basalts. Lorenzen (1884) doubted this identification and the validity of Smith's (1879) analysis and implies corundum was not present. However, the specimens examined in the present study show that spinel and corundum coexist in some xenoliths.

TABLE 2. COMPOSITION OF XENOLITHS COMPARED WITH AVERAGE SHALE COMPOSITION

| | 1 | 2 | 3 |
|---|---|---|---|
| $SiO_2$ | 42.04 | 44 | 64.05 |
| $TiO_2$ | — | — | 0.72 |
| $Al_2O_3$ | 35.87 | 36 | 16.98 |
| $Fe_2O_3$ | — | — | 4.43 |
| FeO | 4.46 | 1 | 2.70 |
| MgO | 3.17 | 3 | 2.69 |
| CaO | 12.83 | 13 | 3.43 |
| $Na_2O$ | 1.64 | 3 | 1.43 |
| $K_2O$ | — | — | 3.57 |

1. Light-gray foliated rock. Groundmass of plagioclase and graphite with red spinel, Uivfaq. Nauckhoff, analyst (1874, p. 128–129) Recalculated on a carbon and sulfur free-basis.
2. Spinel-plagioclase-graphite xenolith, Uivfaq. U.S.N.M. 12118. Recalculated from mode (1500 counts), mineral densities, composition of plagioclase ($An_{70}$) and spinel ($SP_{78}$) on graphite-free basis.
3. Average shale composition (Pettijohn, 1957, p. 344). Recalculated on an $H_2O$, $P_2O_5$, $CO_2$, $SO_3$, and organic-free basis.

## ORIGIN OF XENOLITHS

The xenoliths are probably reconstituted carbonaceous shale inclusions. Some of the evidence for this origin are:

1. Plagioclase-spinel xenoliths are commonly the product of reconstitution of shale inclusions by basaltic magma (Thomas, 1922),
2. Angular, platy shape of the xenoliths,
3. Occurrence of carbonaceous sedimentary rocks in the sedimentary sequence underlying the basalts.

Törnebohm (1878) suggested that the xenoliths were derived from shales rich in alumina and lime. However, the departure of these xenoliths from the composition of most shales is striking (Table 2), and, as was shown by Thomas (1922) for some aluminous xenoliths from Mull, Scotland, is most likely a result of metasomatic exchange during equilibration of magma and shale.

The attainment of equilibrium between xenoliths and magma is indicated by the essentially constant composition of plagioclase and spinel from one xenolith to another. The actual change in the bulk composition of the shale during this equilibration is suggested by Table 2. Although the exact change in composition of the xenoliths was in large part a function of the initial composition of the shale, major loss of $SiO_2$ and $K_2O$ and gain of CaO, $Al_2O_3$ and $Na_2O$ probably occurred. As indicated by the spectrographic analysis (Table 1), chromium from the magma was significantly partitioned into the spinel of the xenoliths.

The few published analyses of the metallic iron-bearing basalts indicate that the composition of the basalts was not greatly altered by this equilibration. This suggests the ratio of magma to xenoliths was very large. However, a recently analyzed basalt from Asuk (Vaasjoki, 1964) is unusually high in silica and potash (contains 17.60 normative quartz, and 7.90 normative orthoclase). This composition is perhaps a result of contamination of the magma by xenoliths.

Steenstrup (1882) suggested that the xenoliths were direct precipitates from the magma. The main evidence against this origin is the angular shape of the xenoliths.

Vaasjoki (1964) suggested that the aggregates of plagioclase, spinel, ang graphite were the products of crystallization of "anorthositic" magma. The evidence that these inclusions are reconstituted shale xenoliths argues against Vaasjoki's (1964) suggested origin. The xenoliths are characteristically platy and small hand specimens commonly contain some which were originally larger than the hand specimen. The xenoliths then have a dike-like appearance. This feature may have led to the interpretation of the plagioclase-spinel-graphite as resulting from separate intrusions.

## Comparison with Aluminous Xenoliths from Other Localities

The restricted suite of samples from Disko in the Museum's collection does not show any intermeditae stages which may have been involved in the development of the xenoliths. On the other hand, the stages in the development of spinel-plagioclase xenoliths from shale inclusions in basalt have been recorded by Thomas (1922) for xenoliths from Mull, Scotland. The sequence of assemblages in some of the xenoliths noted by Thomas are as follows:

1. Center: buchite (sillimanite (mullite ?) and glass, essentially isochemical fusion of xenolith by basalt)
2. Glass and scattered crystals of plagioclase, often skeletal, and needles of sillimanite
3. Completely crystalline plagioclase zone
4. Plagioclase and corundum with minor spinel
5. At contact with basalt: Plagioclase and spinel with minor corundum.

Corundum was noted in one of the seven xenoliths from Uivfaq studied in detail. It occurred as a single grain in a xenolith otherwise rich in

TABLE 3. COMPOSITION OF SPINELS IN RECONSTITUTED SHALE XENOLITHS FROM MULL, SCOTLAND

| | 1 | 2 |
|---|---|---|
| $Al_2O_3$ | 60.84 | 61.95 |
| FeO | 24.00 | 15.04 |
| $Fe_2O_3$ | 4.26 | 5.05 |
| MgO | 9.37 | 16.22 |
| $SiO_2$ | 0.77 | 1.07 |
| $TiO_2$ | 0.50 | 0.10 |
| MnO | 0.15 | — |
| CaO | 0.36 | 0.20 |
| $H_2O$ | 0.14 | 0.18 |
| | 100.39 | 99.81 |

1. Bailey (1924).
2. Buist (1961).

rose-colered spinel. Corundum was also noted in a spinel-plagioclase-graphite xenolith in basalt from Asuk (U.S.N.M. 100205).

Thomas (1922) records cordierite in many of the xenoliths from Mull. Although searched for petrographically and by microprobe traverses, cordierite was not noted in the xenoliths examined in detail.

The xenoliths from Uivfaq and Asuk differ from reconstituted shale xenoliths from other localities in two significant and undoubtedly related ways: in their high graphite content, and in the low FeO content of the spinel. Table 3 gives the composition of the hercynitic spinels from Mull (Bailey, 1924; Buist, 1961). Figure 7 shows such an FeO-rich spinel in a xenolith from a locality on Mull. Although analyses of spinels from similar xenoliths from other localities are needed, it appears that the Disko spinel is significantly lower in FeO and essentially free of $Fe_2O_3$

compared to that in aluminous xenoliths from basalt which do not contain graphite and metallic iron.

These relations suggest that, although shale xenoliths in general react with basaltic magmas so as to give spinel and plagioclase, the composition of the spinel may be related to the oxygen fugacity during reconstitution of the xenoliths. Where FeO was apparently being reduced to metallic iron during reaction of basaltic magma and graphite, the activity of FeO may have been reduced considerably. Spinel forming during such reduction may be unusually low in FeO.

## Spinel-Plagioclase Stability Fields in Experimental Basalt Systems

Spinel and plagioclase crystallize in the anorthite-rich portions of the simplified basalt systems forsterite-anorthite-enstatite (Andersen, 1915) and forsterite-anorthite-diopside (Osborn and Tait, 1951). It is thus not surprising that the reconstitution of aluminous xenoliths leads to these assemblages. Moreover, the recurrence of these xenoliths in many localities indicates that many tholeiitic magmas are nearly saturated with regard to these phases and that but slight modifications in the composition leads to their precipitation.

## Summary and Conclusions

1. The plagioclase-spinel-graphite xenoliths in the metallic nickel-iron bearing basalts from Disko Island, Greenland are reconstituted carbonaceous shales as first suggested by Törnebohm (1878). However, their composition has been greatly modified by equilibration of the shale and basaltic magma. This equilibration involved mainly loss of $K_2O$ and $SiO_2$, and gain of $Al_2O_3$, CaO, $Na_2O$, $Cr_2O_3$ by the xenoliths.
2. Aluminous sedimentary rocks commonly give rise on reaction with basaltic magmas to plagioclase-spinel xenoliths.
3. Other things being equal, the composition of spinel in such xenoliths is evidently a reflection of the oxygen fugacity of the magma.
4. The xenoliths in the Disko basalt specimens from Uivfaq and Asuk support the ideas of Steenstrup (1882) and Törnebohm (1878) that the metallic nickel-iron of these basalts formed by reduction of basaltic magma by carbonaceous sedimentary rocks, and lend no support to the idea of derivation of the metallic phase fromthe upper mantle (Lindgren, 1933; Urey, 1952).

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