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# SPINEL INCLUSIONS IN PLAGIOCLASE OF METAGABBROS FROM THE ADIRONDACK HIGHLANDS[1]

PHILIP R. WHITNEY, *Geological Survey, New York State Museum & Science Service, Albany, New York 12224*

### ABSTRACT

Clouding of plagioclase by dustlike spinel inclusions is found in metagabbros of the Adirondack Highlands. Spinel compositions are close to the magnesium aluminate–hercynite join, with small amounts of magnetite or magnesioferrite in solid solution. Chromium content is negligible. Cell edges of the spinels range from 8.116 to 8.136 Å; refractive indices from 1.761 to 1.792. Occurrence of spinel clouding is limited to olivine bearing rocks. The spinels are formed by diffusion of iron and magnesium into plagioclase at high temperatures and pressures during solid–state reactions which have produced prominent coronas between olivine and plagioclase.

## INTRODUCTION

The clouding of intermediate plagioclase by minute inclusions of other minerals is frequently observed in basic rocks from high-grade metamorphic terranes, and is especially common in rocks which show reaction coronas between olivine and plagioclase. The most abundant inclusions in clouded feldspars are usually one or more of the following: opaque ores, spinel, garnet, biotite, hornblende, and rutile (Poldervaart and Gilkey, 1954). In the olivine–bearing coronitic metagabbros of the Adirondack Highlands, clouded plagioclase is universal, and the inclusions have been identified as primarily green spinel, with lesser amounts of pyroxenes and amphiboles (Shand, 1945; Levin, 1950; Poldervaart and Gilkey, 1954). Similar spinel–clouded plagioclases have been reported from various localities in Norway (Frodesen, 1968; Starmer, 1969), Quebec (Osborne, 1949), and Ontario (Friedman, 1957). While the phenomenon of spinel clouding in plagioclase has been frequently mentioned in the literature, the writer is not aware of any published analyses of these spinels. The present work was undertaken in connection with a more general field and laboratory study of the Adirondack metagabbros to determine the composition of the spinels and if possible to clarify the question of their origin.

Samples have been taken from the layered, sill–like gabbro bodies near Tahawus Club (Newcomb Quadrangle), Texas Ridge (Schroon Lake Quadrangle), and the larger layered basic intrusion near Jay

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Mountain, Ausable Quadrangle (Whitney, 1972), Adirondack Highlands, New York. The dominant rocks in these bodies are troctolites and olivine gabbros with well–developed reaction coronas between olivine and plagioclase. The coronas normally consist of an olivine core surrounded in turn by an inner shell of fine grained clino– and ortho–pyroxenes, a thin moat of clear plagioclase, and an outer shell of garnet with inclusions of clinopyroxene. Plagioclase outside the garnet shell occurs in lath–shaped grains exhibiting original igneous cumulate textures. This primary plagioclase is, in most cases, heavily clouded with minute grains of green spinel. They range from rodlike to nearly equant, and commonly have sharp outlines although larger grains near the edges of the plagioclase tend to be rounded. Distribution of the inclusions within a single plagioclase grain may be either uniform or patchy, with the inclusions showing distinct tendency to form concentrations parallel to the albite and, less commonly, the pericline composition planes. Clear border zones, free of inclusions or with a few larger spinel grains, are observed along grain boundaries between adjacent plagioclase laths or between plagioclase and pyroxene

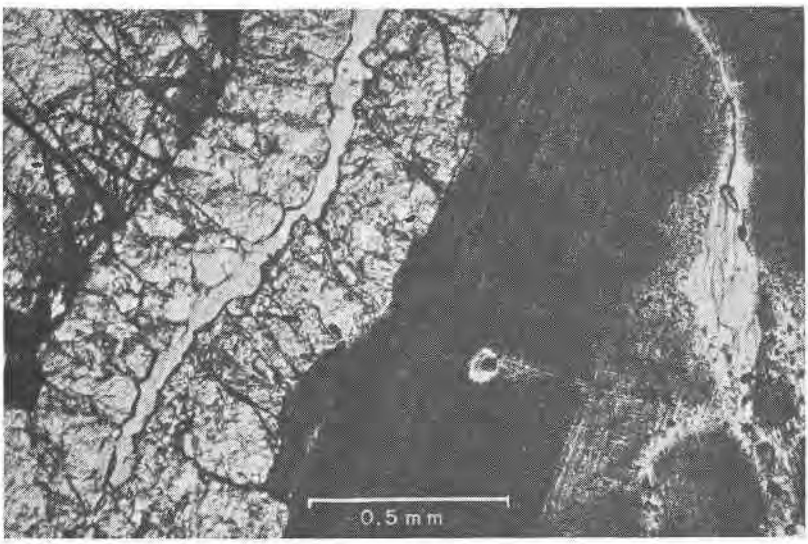


FIG. 1. Photomicrograph of typical corona. Olivine in upper left, bordered by inner shell of fine grained pyroxene, moat of clear plagioclase, and outer shell of garnet with clinopyroxene inclusions. Garnet is in contact with spinel–clouded plagioclase. Concentrations of spinel inclusions parallel albite twin lamellae. Plane light.

or garnet, and along healed cracks within plagioclase grains. A typical corona is illustrated in Figure 1. Spinel clouding in plagioclase is lacking in noncoronitic (*i.e.*, olivine–free) layers of the same intrusions. In parts of the Jay Mountain body, olivine bearing coronite layers a few centimeters thick containing green, clouded plagioclase alternate with olivine free layers containing clear plagioclase. Within the coronites, intensity of clouding tends to increase with increasing modal abundance of olivine.

The clear border zones of the plagioclase laths and the clear plagioclase in the moats range from $An_{30}$ to $An_{45}$. While quantitative compositions for the heavily clouded zones are unobtainable, electron–probe traverses from clear into clouded areas indicate no substantial difference in An content. By contrast, clear primary plagioclase in olivine–free gabbros of the same intrusions commonly has compositions in the $An_{50}$–$An_{60}$ range. Normative plagioclase varies from about $An_{55}$ to $An_{70}$. Olivine compositions fall in the range $Fo_{60}$–$Fo_{75}$.

## Methods

Whole rock samples were crushed and sieved to 100–200 mesh. Plagioclase was separated by flotation with tetrabromoethane. For each sample, roughly 50 grams of plagioclase was treated several times with cold 5 percent hydrofluoric acid to release the spinel inclusions. This resulted in a spinel concentrate of at least 90 percent purity, the major impurities being garnet and insoluble fluorides. The latter were removed by boiling in 2*M* ammonium citrate. Three samples, numbers 74B, 109, and 111, yielded concentrates of better than 99 percent purity, visually estimated. The spinel grains in the concentrates are light green by transmitted light. Shapes range from prismatic to slightly rounded; most grains are in the 1- to 5-$\mu$m size range with occasional rodlike forms up to 20 $\mu$m long and 1- to 2-$\mu$m in diameter. In some of the samples, a second, smaller, population of larger spinel grains, commonly rounded and 10- to 30 $\mu$m in diameter, is also observed.

Cell-edge measurements were obtained using a 2:1 mixture of spinel and powdered silicon metal (5 nines purity), sieved through 400 mesh and sprinkled in a thin layer on a vaseline–coated petrographic slide. Diffractometer tracings of the (311) and (220) peaks of spinel were obtained at a scan speed of 1/8° $2\theta$/min using Si(111) as an internal standard. Reproducibility of $a$ measurements using duplicate slides is within $\pm$.002Å.

Refractive index measurements were made using a sodium light source and Cargille index liquids at intervals of 0.005. Liquids were mixed to obtain intermediate values. The grains within a sample vary in refractive index over a range of almost 0.01 units; the indices reported represent an approximate median value. No consistent relationship could be found between size or shape of the grains and refractive index.

The three purest concentrates were analyzed for $Al_2O_3$, total iron, MgO, MnO, CaO, and $Cr_2O_3$ by atomic absorption following lithium metaborate fusion. $SiO_2$ and $TiO_2$ were determined by X–ray fluorescence. Only MgO and total iron were determined on the remaining four concentrates.

## Results

Table 1 presents the X-ray and optical data, compared with the Mg/(Mg + Fe) atomic ratios of the spinels and of the rocks from which they were obtained. Table 2 gives the chemical analyses of three spinels and MgO plus total Fe as FeO for the remaining four. Relative amounts of FeO and $Fe_2O_3$ in the three complete analyses have been calculated from total iron data assuming $R^{2+}:R^{3+} = 1:2$.

All the spinels examined are pleonastes, with compositions intermediate between magnesium aluminate and hercynite and with a small amount of magnetite or magnesioferrite in solid solution. If all $Fe_2O_3$ is calculated as magnetite, the compositions of the three fully analyzed samples is as follows: 74B, $Sp_{46}Hc_{51}Mt_3$; 109, $Sp_{56}Hc_{42}Mt_2$; and 111, $Sp_{53}Hc_{46}Mt_1$. The (Mg/Mg + Fe) ratios for the spinels and the corresponding whole rocks are clearly correlated, probably reflecting variations in the initial composition of olivine. There are no consistent differences between the spinels from olivine gabbros (samples 74B, 102, and 116) and from troctolites (29, 73B, 109, 111). Within a given rock, the order of increasing Mg/( Mg + Fe) ratios in the ferromagnesian minerals is:

Garnet < Spinel < Olivine < Orthopyroxene < Clinopyroxene

## Origin of the Spinel Inclusions

The heavy concentration of spinel in the plagioclase appears to rule

TABLE I

COMPARISON OF CELL EDGES, REFRACTIVE INDICES AND Mg/(Mg + Fe) RATIOS FOR SPINEL INCLUSIONS FROM PLAGIOCLASE

| Sample | Location | $a_o$ (A) | $n_o$ | Spinel $\frac{Mg}{Mg + Fe}$ | Whole rock $\frac{Mg}{Mg + Fe}$ |
|---|---|---|---|---|---|
| 29 | Tahawus Club | 8.116 | 1.762 | 0.56 | 0.63 |
| 73B | Texas Ridge | 8.134 | 1.786 | 0.42 | N.D. |
| 74B | Texas Ridge | 8.136 | 1.782 | 0.43 | 0.54 |
| 102 | Jay Mountain | 8.125 | 1.765 | 0.50 | 0.63 |
| 109 | Jay Mountain | 8.122 | 1.765 | 0.54 | 0.67 |
| 111 | Jay Mountain | 8.126 | 1.769 | 0.52 | 0.66 |
| 116 | Jay Mountain | 8.136 | 1.792 | 0.40 | 0.54 |

TABLE II
CHEMICAL ANALYSIS OF SPINEL INCLUSIONS

| Sample # | 74B | 109 | 111 |
|---|---|---|---|
| $SiO_2$ | 0.57 | 0.88 | 0.42 |
| $TiO_2$ | 0.06 | 0.01 | 0.07 |
| $Al_2O_3$ | 60.82 | 62.50 | 63.55 |
| $Fe_2O_3$ | 2.62 | 1.53 | 0.56 |
| FeO | 24.08 | 19.84 | 21.39 |
| MgO | 11.31 | 14.18 | 13.39 |
| CaO | 0.08 | 0.06 | 0.00 |
| MnO | 0.07 | 0.07 | 0.06 |
| $Cr_2O_3$ | < 0.01 | < 0.01 | < 0.01 |
| TOTALS | 99.61 | 99.05 | 99.44 |

NUMBER OF IONS ON THE BASIS OF 32 (O)

| | 74B | | 109 | | 111 | |
|---|---|---|---|---|---|---|
| Si | .122 | 15.966 | .185 | 15.953 | .088 | 15.974 |
| Ti | .010 | | .002 | | .011 | |
| Al | 15.410 | | 15.524 | | 15.787 | |
| $Fe^{3+}$ | .424 | | .242 | | .088 | |
| $Fe^{2+}$ | 4.329 | 7.983 | 3.498 | 7.976 | 3.771 | 7.988 |
| Mg | 3.623 | | 4.453 | | 4.206 | |
| Ca | .018 | | .013 | | .000 | |
| Mn | .013 | | .012 | | .011 | |

Partial Analyses

| | 29 | 73B | 102 | 116 |
|---|---|---|---|---|
| Fe as FeO | 18.94 | 25.54 | 21.63 | 25.75 |
| MgO | 13.53 | 10.43 | 11.99 | 9.71 |

out an exsolution origin. Two possible modes of origin for the spinel inclusion may be postulated as follows:

(a) Trapping of spinel microlites suspended in magma by growing plagioclase crystals;
(b) Growth of inclusions in plagioclase grains by solid–state reactions with olivine.

The first hypothesis would imply that spinel was the liquidus phase in the magma, nucleating as abundant, very small crystals which were then trapped in growing plagioclase crystals. Spinel has been shown experimentally to appear at the liquidus in the plagioclase–forsterite system at pressures over 5 kbar by Emslie and Lindsley (1969). However, several observations make this interpretation doubtful for these rocks.

(1) The previously mentioned absence of spinel clouding in plagioclase in olivine–free rocks of rhythmically layered sequences is not readily explained by the magmatic hypothesis, but is predicted by the solid-state reaction model.
(2) In certain plagioclase–rich layers where close packing of the feldspar laths indicates that considerable adcumulus growth must have taken place, spinel clouding extends without change or interruption into those portions of individual grains which are almost certainly of adcumulus origin. This clearly favors a post–solidification origin for the spinels.
(3) The very low chromium content of these spinels is also unfavorable to the primary magmatic hypothesis. By contrast, very low Cr content would be expected in spinels formed by an olivine–plagioclase reaction, as neither mineral has structural sites capable of accommodating more than a trace of Cr.

Hypothesis "b" therefore appears to be the more probable of the two. It is clear that olivine and plagioclase have reacted, and the nature of the reactions may be inferred from the coronas. Detailed petrographic and electron probe studies of the coronas, to be published elsewhere, indicate that while the corona–forming process cannot be treated as a strictly closed system, it may be approximated by the reactions:

(1) Olivine + plagioclase = aluminous pyroxenes + spinel
(2) Aluminous pyroxenes + spinel + plagioclase = garnet + clinopyroxene

These reactions have been studied experimentally by Kushiro and Yoder (1966), Green and Ringwood (1967), Irving and Green (1969), and Green and Hibberson (1970). On the basis of the experimental data, Griffin and Heier (1969) and Griffin (1971) have concluded that similar coronas in some Norwegian anorthosites have formed by intrusion and crystallization at depth followed by slow cooling under pressures of 9–12 kbar. During this process, reaction (1) would occur at temperatures in the range 850–1100°C with reaction (2) following at somewhat lower temperatures. A similar process for the origin of the Adirondack coronas is supported by independent geological evidence (Whitney 1972).

The spinel clouding in the plagioclase is most probably related to reaction (1). The following hypothetical process is compatible with the observed data: Reaction (1) takes place in a zone between olivine and plagioclase where these phases are in contact. This produces an inner shell of orthopyroxene, adjacent to and replacing olivine, and an outer shell of clinopyroxene crowded with rounded or vermicular grains of green spinel. In the occasional corona where reaction (2) has failed to occur, the clinopyroxene plus spinel shell is preserved and textural evidence shows that it replaces plagioclase. The spinel grains in this shell are considerably larger than the "dust" in the plagioclase but do not differ significantly in composition from the latter. Magnesium and iron derived from the olivine, and sodium from replacement of plagioclase in the outer zone, diffuse into the plagioclase laths and react with the anorthite component of the feldspar to produce spinel and a more sodic plagioclase. Intracrystalline diffusion would be facilitated by the high temperatures at which the reaction occurs. Calcium, released by breakdown of anorthite, diffuses out of the feldspar to form additional clinopyroxene in the corona. The portion of the reaction occurring within the plagioclase laths may be approximated as follows:

$$3\ CaAl_2Si_2O_8 + x\ Mg^{2+} + (2-x)Fe^{2+} + 2\ Na^+ = Mg_xFe_{(2-x)}Al_4O_8 + 2\ NaAlSi_3O_8 + 3\ Ca^{2+} \quad 0 \leq x \leq 2 \qquad (3)$$

The fact that the plagioclase of the coronites commonly has an anorthite content 20 to 30 percent An lower than the normative plagioclase is consistent with this mechanism. Apparently a limit exists beyond which the replacement of plagioclase does not proceed; even in rocks with relatively little plagioclase and a large excess of olivine, no plagioclase more sodic than about $An_{30}$ has been observed.

Subsequently, upon increasing pressure and /or falling temperature, reaction (2) is initiated, with garnet nucleating at the inside and outside edges of the clinopyroxene plus spinel shell and growing to replace the entire shell. Some of the spinel inclusions in the plagioclase may be consumed in this reaction, leading to the clear zones commonly observed along plagioclase grain boundaries.


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## References


Emslie, R. F., and D. H. Lindsley (1969) Experiments bearing on the origin of anorthositic intrusions. *Carnegie Inst. Washington Year Book,* **67**, 108–112.

Friedman, G. M. (1957) Structure and petrology of the Caribou Lake intrusive body, Ontario. *Geol. Soc. Amer. Bull.* 68, 1531–1564.

Frodesen, S. (1968) Coronas around olivine in a small gabbro intrusion, Bamble Area, Norway. *Norsk. Geol. Tidsskr.* 48, 201–206.

Green, D. H., and W. Hibberson (1970) The instability of plagioclase in periodotite at high pressures. *Lithos*, 3, 209–221.

———, and A. E. Ringwood (1967) An experimental investigation of the gabbro to eclogite transformation and its petrologic applications. *Geochim. Cosmochim. Acta*, 31, 767–834.

Griffin, W. L. (1971) Genesis of coronas in anorthosites of the upper Jotun Nappe, Indre Sogn, Norway. *J. Petrology*, 12, 219–243.

———, and K. S. Heier (1969) Parageneses of garnet in granulite facies rocks, Lofoten-Vesteraalen, Norway. *Contrib. Mineral. Petrology*, 23, 89–116.

Irving, A. J., and D. H. Green (1969) Experimental duplication of mineral assemblages in basic inclusions of the Delegate Breccia Pipes. *Phys. Earth Planet. Interiors*, 3, 385–389.

Kushiro, I., and H. S. Yoder Jr. (1966) Anorthite–forsterite and anorthite-enstatite reactions and their bearing on the basalt-eclogite transformation. *J. Petrology*, 3, 337–362.

Levin, S. B. (1950) Genesis of some Adirondack garnet deposits. *Geol. Soc. Amer. Bull.* 61, 519–565.

Osborne, E. F. (1949) Coronite, Labradorite anorthosite and dykes of andesine anorthosite, New Glasgow, P.Q. *Trans. Royal Soc. Canada*, 43, 85–112.

Poldervaart, A., and A. K. Gilkey (1954) On clouded plagioclase. *Amer. Mineral.* 39, 75–91.

Shand, S. J., (1945) Coronas and coronites. *Geol. Soc. Amer. Bull.* 56, 247–266.

Starmer, I. C. (1969) Basic plutonic intrusions of the Risor-Sondeled Area, South Norway: The original lithologies and their metamorphism. *Norsk. Geol. Tidsskr.* 49, 403–431.

Whitney, P. R. (1972) A layered intrusion near Jay Mountain, New York (abstr.) *Geol. Soc. Amer., Abstr. Programs*, 4, 51.

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