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An occurrence of the spinel end-member Mg_2TiO_4 and related spinel solid solutions

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ABSTRACT. Black, opaque grains of a spinel whose composition is (Mg_2TiO_4) 85.8, ($MgFe_2O_4$) 0.4 ($FeFe_2O_4$) 13.8 (mole %) coexist with a $MgAl_2O_4$ spinel and geikielite in a periclase-forsterite marble that has been thermally metamorphosed against an alkalic ultramafic intrusion of Caledonian age in the Kangerdlugssuaq region of East Greenland. The spinel appears to be the closest recorded approach to the end-member Mg_2TiO_4 among natural rocks, and to be part of a solid-solution series extending across the join Mg_2TiO_4–$MgFe_2O_4$–$FeFe_2O_4$, the existence of which has not previously been reported. The composition of the series appears to be controlled by the f_{O_2} that prevails during metamorphism.

THE compound Mg_2TiO_4 is a recognized end-member of the group of spinel minerals, but it has not been reported as occurring as a distinct mineral; rather it is restricted in published analyses to perhaps 20 wt. % in a more complex spinel.

A thermally metamorphosed limestone in East Greenland has been found to contain a mineral that is 86 mole % Mg_2TiO_4 and seems to be the purest form of the member yet discovered.

The western-most nunatak on the northern edge of Kangerdlugssuaq Glacier (68° 40′ N, 28° 50′ W) was observed by Wager and Deer in their 1935-6 sledging journeys and named by them Batbjerg. In it is an alkalic ultramafic intrusion of Caledonian age composed dominantly of nepheline pyroxenite and nepheline-leucite pyroxenite with lesser amounts of nepheline syenite (Brooks *et al.*, 1981). Part of the intrusion, possibly as much as a half, is under the ice of Kangerdlugssuaq Glacier, and the remainder has a vertical exposure of about 1500 m. The general shape of the exposed portion of the intrusion is arcuate. Although the country rocks are gneisses of amphibolite facies to possible granulite facies, there is in several places a discontinuous screen of marble and occasional quartzite 3 to 20 m in width at the igneous contact. This appears to be the cauldron-subsided remnant of a cover of Lower Palaeozoic sedimentary rocks not previously known in this part of East Greenland.

The grade of metamorphism in this marble unit ranges from only slightly recrystallized, well-bedded, fragmental limestone showing graded bedding to something approaching the pyroxene hornfels facies (periclase-forsterite-spinel-calcite). Erratically distributed in the marble are areas of skarn composed dominantly of garnet and pyroxene. Less common are muscovite, prehnite, pectolite, epidote, and alkali feldspar that suggest a complex history of fluid involvement in some stages of the metamorphism. A number of zoned nodules in the marble are composed of zones of fassaite-spinel, fassaite-garnet, diopside, wollastonite, pectolite, and a quartz core. Others consist of soda-rich melilite cores surrounded by symplectites of kalsilite-diopside-wollastonite and nepheline-diopside-wollastonite with isolated larger grains of titaniferous fassaite and leucite. These nodules also seem to represent a complex metamorphic history in which alkali-alumina metasomatism has been superimposed on high temperature thermal metamorphism. (Gittins *et al.*, 1977).

The general geological setting is, therefore, a high-temperature alkalic ultramafic intrusion of subvolcanic to shallow plutonic character that has thermally metamorphosed a screen of limestone and subjected it to fluid metasomatism.

The occurrence of Mg_2TiO_4 and related spinels. A particularly interesting facies of the marble consists dominantly of calcite with forsterite, periclase (largely hydrated to brucite), transparent spinel, tiny blood red grains of geikielite, and minute opaque black grains of Mg_2TiO_4. All the rocks are highly magnesian with only a low tenor of iron. Other marbles that do not contain Mg_2TiO_4 have, in addition to the minerals mentioned, a fassaite clinopyroxene with up to 12% of the Si site substituted by Al. Fassaite is commonly $Ca_{50}Mg_{45}Fe_5$ but extends to $Ca_{50}Mg_{35}Fe_{15}$. Forsterite is $Fo_{99.5-98.0}$. Geikielite $(Mg_{0.95}Fe_{0.05})TiO_3$, is very close to the ideal composition. (Examples of the spinel compositions are shown in Table I). The ubiquitous transparent spinel is approximately 90% $MgAl_2O_4$ but has a small range of Fe:Al of $Mg_{34}Al_{66}$ (pale mauve) to $Mg_{33}Fe_8Al_{59}$ (brown) suggesting that $Fe^{3+} \rightleftharpoons Al^{3+}$ substitution has occurred (fig. 1). Calcite is somewhat magnesian with MgO contents corresponding to equilibrium temperatures between 650 and 800 °C. These, however, must be considered minimum temperatures since it is not known whether, during the rapid reaction rates of thermal metamorphism accompanying cauldron subsidence, equilibrium would have been reached.

The purest form of Mg_2TiO_4 discovered in these rocks is about 86 mole %. It appears to be in the spinel join Mg_2TiO_4-$MgFe_2O_4$ (magnesioferrite)-$FeFe_2O_4$ (magnetite). Within this plane the composition can be calculated as Mg_2TiO_4 85.8, $MgFe_2O_4$ 0.4, $FeFe_2O_4$ 13.8 mole % (figs. 2, 3) and the mineral is, thus, essentially a Mg_2TiO_4-magnetite solid solution.

It has not been possible so far to determine any of the physical properties of Mg_2TiO_4 owing to the small size of the grains (< 0.1 mm), their relatively small number and the fact that the mineral has been found in only one specimen. Several other specimens, however, contain grains whose compositions appear to cover a range extending toward the join $MgFe_2O_4$ (magnesioferrite)-$FeFe_2O_4$ (magnetite). The ferric/ferrous ratio of these analyses is not known absolutely since they are by electron microprobe but they have been recalculated making the normal assumptions for spinel stoichiometry. It is clear that the content of Fe^{3+} must increase progressively as the compositions become less titaniferous. It appears, therefore, that a solid solution series of quaternary spinels exists in the plane Mg_2TiO_4-Fe_2TiO_4-$MgFe_2O_4$-$FeFe_2O_4$ and essentially on the ternary plane Mg_2TiO_4-$MgFe_2O_4$-$FeFe_2O_4$ (figs. 2, 3). Geikielite accompanies only those members whose Mg content is within 50 mole % of Mg_2TiO_4.

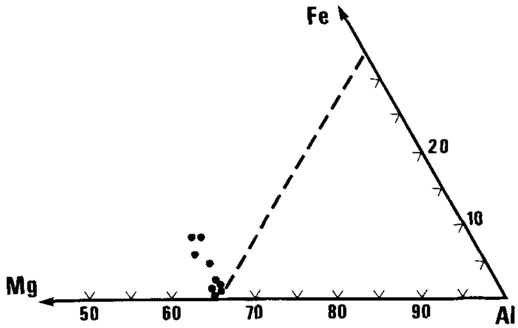


FIG. 1. A portion of ternary spinel plane expressed as atomic Mg-Al-Fe. The dashed line is the join $MgAl_2O_4$ (spinel)-$FeAl_2O_4$ (hercynite). Shown by solid dots are the aluminian spinels found in the marbles.

TABLE I. *Electron probe analyses*

	1	2	3	4	5
SiO_2	—	0.16	0.28	—	—
TiO_2	38.58	18.26	6.96	1.15	65.42
Al_2O_3	2.75	3.56	2.74	64.36	—
FeO	6.26†	16.92†	16.84†	4.62*	2.45*
Fe_2O_3	11.82†	38.50†	53.66†	—	—
MnO	0.41	0.81	0.26	—	0.15
MgO	39.09	20.48	16.58	28.53	30.98
CaO	0.31	0.27	0.09	0.30	0.16
Cr_2O_3	—	—	—	1.04	—
V_2O_5	—	0.34	—	—	—
Total	99.21	99.30	97.41	100.00	99.55
Mg_2TiO_4	85.8	48.5	18.9		
$FeFe_2O_4$	13.8	49.3	50.8		
$MgFe_2O_4$	0.4	2.2	30.3		

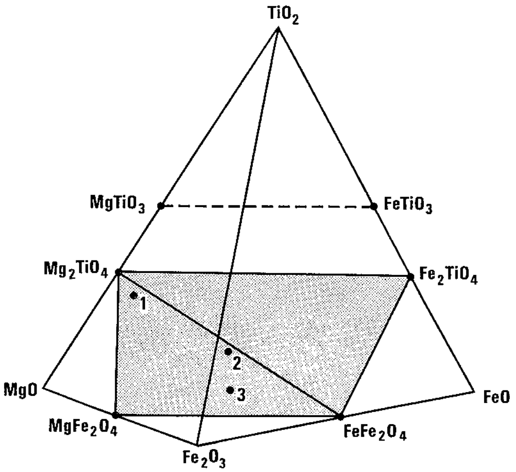
1 and 2. Opaque spinel from calcite-periclase-two spinel-geikielite forsterite marble. 3. Opaque spinel from calcite-periclase-two spinel-forsterite marble (geikielite absent). 4. Pale mauve spinel accompanying opaque spinel, anal. 1 above. 5. Geikielite accompanying opaque spinel, anal. 1 above.

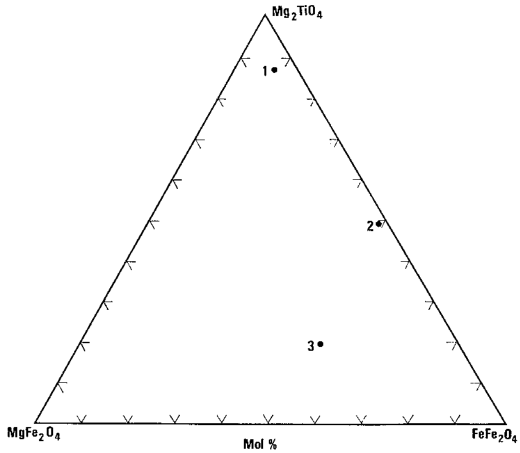
* Total iron expressed as FeO.

† FeO and Fe_2O_3 have been calculated from the requirements of spinel stoichiometry with magnetite the last component in the order of apportioning elements.

In fig. 3 these compositions are plotted in the ternary plane. Analyses 1 and 2 show the essentially binary solid solution between Mg_2TiO_4 and $FeFe_2O_4$ to about 50%. At this composition geikielite is no longer found in the rocks and Mg apparently enters the solid solution series as $MgFe_2O_4$ causing the solid solutions to become essentially ternary (anal. 3).

Since the magnesioferrite-magnetite end of the series obviously requires a higher f_{O_2} than the member which is 86% Mg_2TiO_4, the absence of geikielite in the less titaniferous assemblages is probably attributable to the same cause, which in turn probably reflects wide variations in f_{O_2} associated with fluid transfer along fractures in the marble during metamorphism. It seems likely, then, that f_{O_2} exercises a close control on the composition of the spinel solid solution series in two ways. In the first place geikielite can crystallize along with a Mg_2TiO_4-$FeFe_2O_4$ spinel up to a critical value





FIGS. 2 and 3. FIG. 2 (*left*). The quaternary volume TiO_2-MgO-FeO-Fe_2O_3. Within it are shown the joins $MgTiO_3$ (geikielite)-$FeTiO_3$ (ilmenite) and the quaternary spinel plane Mg_2TiO_4-Fe_2TiO_4-$MgFe_2O_4$ (magnesioferrite)-$FeFe_2O_4$ (magnetite). Numbered points are the representation of analyses presented in Table I. Diagram is in mole %. FIG. 3 (*right*). The ternary spinel plane Mg_2TiO_4-$MgFe_2O_4$-$FeFe_2O_4$ with the three spinels whose compositions are shown in Table I.

of f_{O_2} which is not yet known. Progressive increase of f_{O_2} increases the magnetite component of the spinel at the expense of the Mg_2TiO_4 component and the excess Ti is taken up as geikielite. Secondly, when the critical value of f_{O_2} above which geikielite is no longer stable is exceeded, geikielite ceases to crystallize and the Mg content of the spinel solid solution sharply increases in the form of $MgFe_2O_4$. The exact composition that forms is probably a complex function of f_{O_2} and total available Ti. In the examples described here it seems likely that a progressive increase of f_{O_2} has occurred until a value was reached at which it became buffered.

We know of no records, either of spinels so close to the end-member composition Mg_2TiO_4, or of a solid-solution series of the compositions shown. Although Muan *et al.* (1972) have studied the composition Mg_2TiO_4 the study was at liquidus temperatures for which a solvus exists on the join Mg_2TiO_4-$MgAl_2O_4$ up to about 1370 °C at atmospheric pressure. At least this study explains the coexistence, however, of the titanian and aluminian spinels since the temperature of metamorphism would have been well below this value.

The minerals reported here are present as minute opaque grains and would remain unrecognized except in a detailed grain-by-grain microprobe study. It seems likely that other high-temperature thermal aureoles and marble xenoliths might yield the presence of the same spinels if examined in sufficient detail.

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