

ELECTRON MICROPROBE ANALYSES OF SPINELS AND
THEIR ALTERATION PRODUCT FROM MÅNSARP
AND TABERG, SWEDEN

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ABSTRACT

Spinel lamellae were analysed by electron probe for Al, Fe, Mn, Si, Ti, V and in some cases also for Ca, Cr and Zn. Spinel was identified as pleonaste which has undergone partial alteration. In this process silicon was added and aluminum removed. The alteration product approaches the composition of chlorite. It is concluded that the alteration of pleonaste is combined with the late magmatic alteration of olivine.

INTRODUCTION

Although spinels are widely distributed in nature and are easily synthesized in the laboratory, knowledge of their composition is limited to crystals of not very small size by the present separation techniques. X-ray emission microanalysis, however, allow chemical data to be obtained from extremely thin lamellae of spinel.

The most important earlier descriptions of spinels were cited by Deer *et al.* (1964). Haffner (1960) considered the spinel structure and possible cation distribution and also reviewed recent crystallographic literature. In addition Hjelmqvist (1949) published a detailed description of a single occurrence in Taberg, Southern Sweden. The present author has been working with coexisting magnetite-ilmenite in the titaniferous iron ore in Taberg and has also taken interest in spinel.

ANALYTICAL METHOD

The electron-probe X-ray microanalyzer is now well established as a valuable tool in mineralogical and petrological studies (Ade-Hall, 1964; Keil, 1967). In the present study a Cambridge GEOSCAN instrument was used. The analyses were carried out using an accelerating potential of 15 and 25 keV on the primary electron beam. Analyses were made in several sections in each sample, several lamellae being analyzed in each section and checked in many parts of the same lamella.

The instrument used was equipped with scanning facilities allowing an image to be formed on the screen of a cathode ray tube showing the distribution of a selected element over the surface of the specimen. This image also served as a mean of positioning the electron probe at a particular point on the surface for quantitative analysis.

MINERALOGY OF THE ROCKS

The ore-bearing rocks of Månsarp and Taberg are connected with hyperite which intrudes the surrounding gneiss and gneiss-granite. The northern part of the hyperite body of Taberg is almost exclusively made up of magnetite-olivinite, a fine-grained massive rock consisting almost exclusively of olivine and titaniferous magnetite with small amounts of labradorite and amphibole. The titaniferous magnetite has

lamellae of ilmenite and spinel. Other ore minerals are pyrrhotite, pentlandite, chalcopyrite and pyrite.

In the uneffected rock olivine is fresh and has the composition: SiO₂ 36.20, TiO₂ 0.49, Al₂O₃ 0.91, Fe₂O₃ 1.89, FeO 29.21, MnO 0.28, MgO 29.60, CaO 0.61, H₂O 0.61 percent (Hjelmqvist, 1950). The grains of olivine lie together in dense aggregates with titaniferous magnetite.

Plagioclase occurs in porphyritic crystals partly as anhedral filling between olivine and magnetite. The chemical composition is the same in both cases, having 50–57 percent anorthite (Hjelmqvist, 1950).

The magnetite contains 15.9 percent TiO₂ (Hollander, 1968). Small lamellae of ilmenite with 49.0 percent TiO₂ are as a rule oriented parallel to the octahedral faces of the magnetite. Lamellar intergrowth of spinel is also visible and oriented parallel to the cubic faces of the magnetite.

Granigg (1920) assumed the spinel in this magnetite to be a hercynite. Hjelmqvist (1950) identified it by X-ray diffraction as a common magnesium-spinel. Ramdohr (1953) examined polished sections and suggested the spinel to be "pleonaste". The distribution of elements in magnetite, ilmenite and spinel are shown in Figure 1. The results of the partial analyses of spinel lamellae are given in Table 1.

The analyses show that the major constituents are Al, Fe, and Mg, forming a spinel intermediate in composition between spinel and hercynite. Following the nomenclature of Deer *et al.* (1964) the spinel of the present study with a Mg:Fe ratio between 1 and 3 is called a pleonaste.

ALTERATION OF OLIVINE

The olivine shows alteration to serpentine, carbonate, amphibole, chlorite and secondary magnetite. The olivine in contact with the iron-titanium oxide in Figure 2 has a composition of MgO 39.8, FeO 22.7, Al₂O₃ 0.3 percent¹ (partial microprobe analysis). The grain is traversed by fissures containing serpentine, chlorite and magnetite. The alteration has proceeded so far that the original outline of the olivine grain cannot be clearly seen. The mass between olivine and magnetite consists of a mixture of minerals, mainly serpentine and chlorite. However, in the area in contact with an altered pleonaste two separated zones are found (Fig. 2):

	MgO	FeO	Al ₂ O ₃	SiO ₂ (percent) ¹
Zone in contact with fresh olivine (a)	22.9	70	3	13-20
Zone in contact with magnetite (b)	36.7	26-34	26	<3

¹ The values are uncorrected and therefore only approximate.

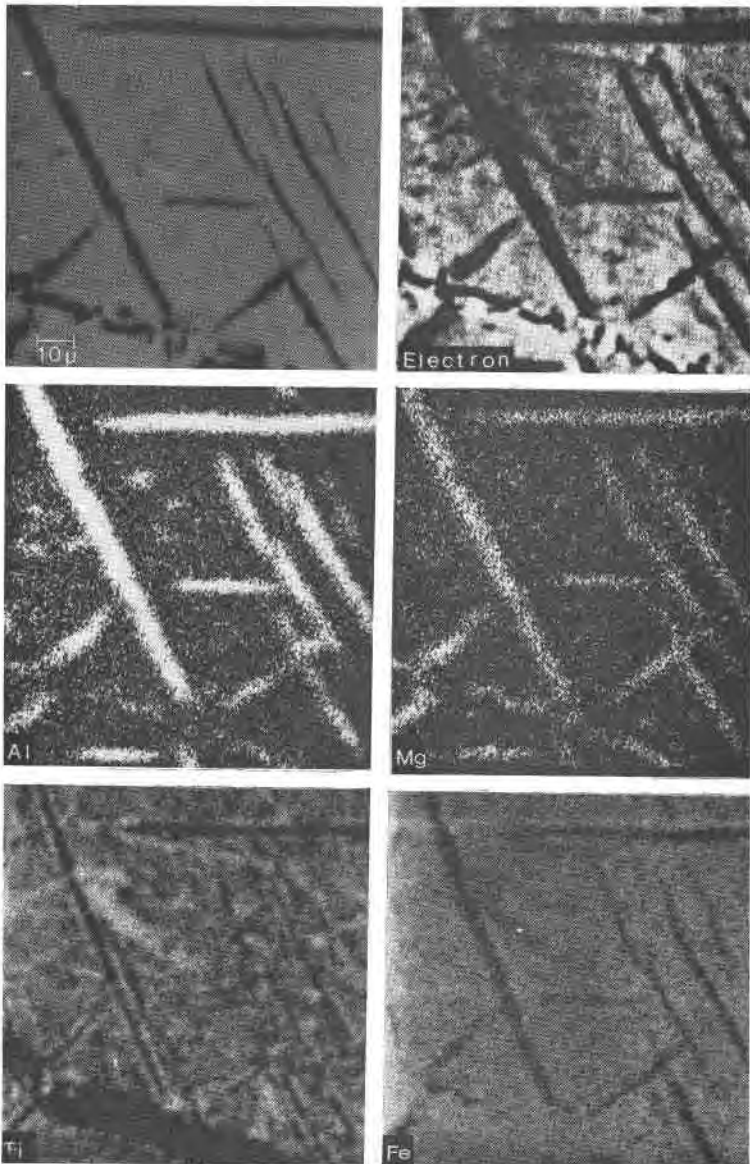


FIG. 1. Micrograph showing spinel lamellae (black) in ilmenomagnetite in sample no. 2. X-ray scan pictures with 15 keV excitation potential.

TABLE 1. ELECTRON MICROPROBE ANALYSES OF SPINELS

No.	1	2	3
SiO ₂	0	0.1	0.1
TiO ₂	0.8	1.6 ^a	1.4±0.3
Al ₂ O ₃	56.5±1.2	61.4±4.2	56.5±0.7
Cr ₂ O ₃	(0.03)	(0.03)	(0.03)
V ₂ O ₃	0.1	0.1	0.1
FeO ^b	23.2±1.2	18.2±2.3	21.8±0.4
MgO	14.0±0.2	11.3±1.4	15.2±1.2
MnO	0.1	0.1	0.1
CaO	0	0	(0.03)
ZnO	0.49	0.4	0.4
Total	95.2	93.2	95.6

^a Mean value.

^b All the iron is calculated as divalent. The second figures (±) refer to the statistical errors in the weight percentage of the oxides. Where no figures are given the statistical error does not influence the oxide values. P, S, Co, Cu, Ni were checked but not found.

Thus the alteration of the olivine in zone *a* has involved a decrease in silicon in these zones as compared with the fresh olivine and a decrease of magnesium in zone *a*. Iron was enriched in zone *a* and aluminum in zone *b*. The changes in the concentration of aluminum and silicon will be considered below.

ALTERATION OF SPINEL

Besides the fresh magnesium-iron spinels there also occur spinels altered in many different modes, especially in specimens showing extensive alteration of olivine to serpentine. These spinels are enclosed in titaniferous magnetite with octahedrally arranged lamellae of ilmenite.

Two types of alteration products are present in the spinels (Fig. 3). The first one suggests a continuous affect on the whole width of the lamellae. In some instances the alteration is "fed" directly by silicates surrounding the oxides, while in others the material exchange was through silicate-containing cracks. In many cases the transporting channels cannot be observed but are then probably outside the volume cut by the thin section. In the second main type of alteration the outer parts of the lamellae were attacked first. This mode of alteration is usually found in close proximity of thin cracks. The altered spinel lamellae often have jagged edges and slightly rough surface. The cracks through the oxides differ from the lamellae by their irregular direction and form.

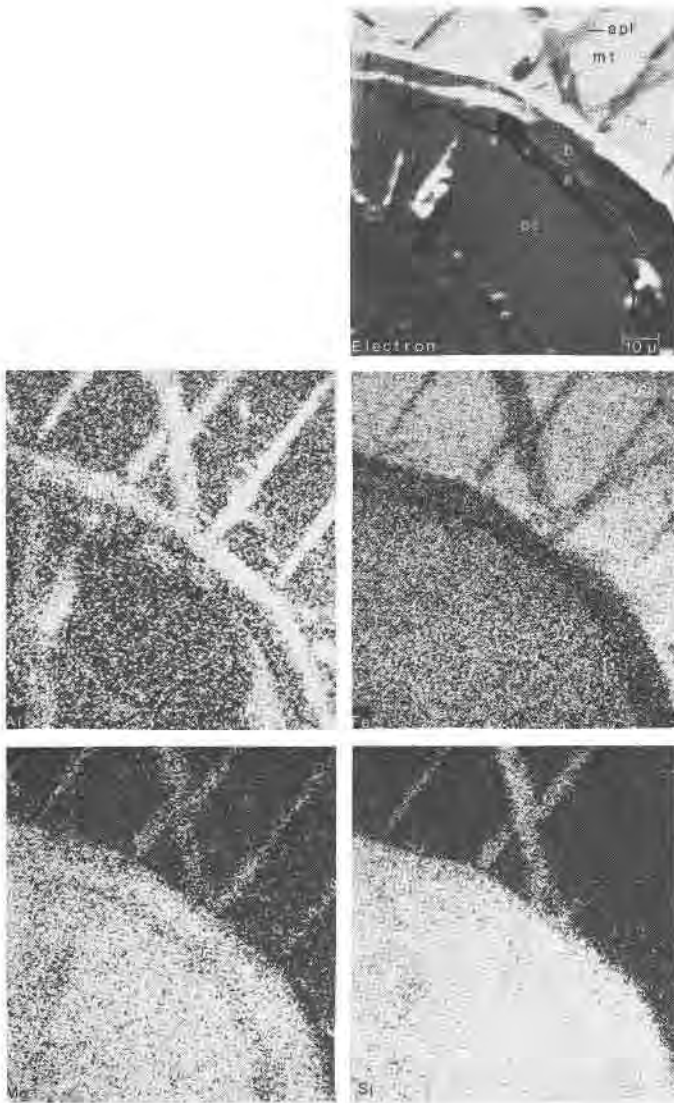


FIG. 2. Contact between magnetite (mt) with altered pleonaste (apl), as shown in Fig. 4, and olivine (ol). For explanation of *a* and *b* see text. Electron and X-ray scan pictures.

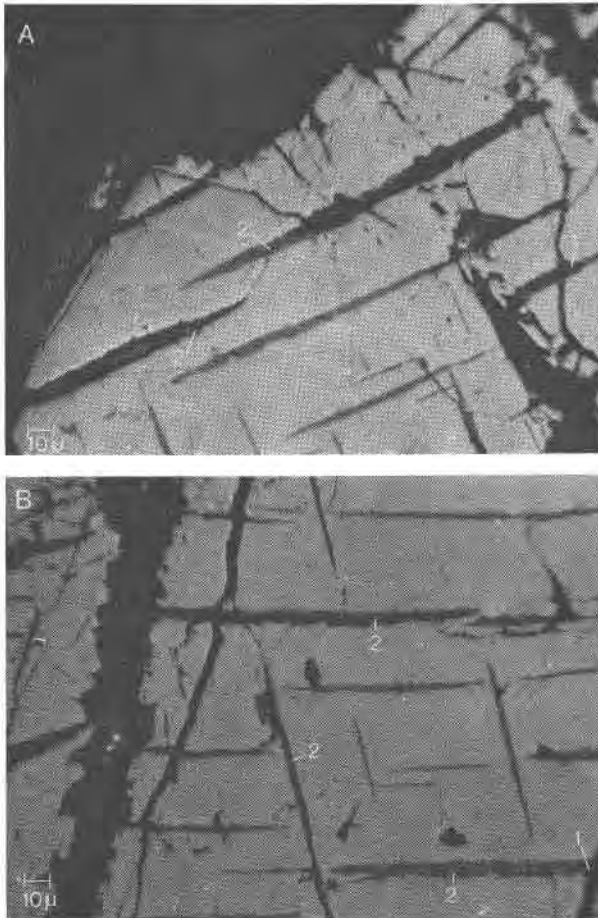


FIG. 3. Cubically arranged lamellae of spinel (gray) and irregular cracks containing silicates (black) in titaniferous magnetite (light gray). The upper left part in upper figure consists of serpentinized olivine. Two types of alteration are evident in the spinels: (1) implies a continuous affect on the whole width of the lamellae; (2) shows that the outer parts of the lamellae are first affected. Reflected light.

X-ray scanning pictures of the distribution of the elements in Taberg ore is shown in Figure 4. The completely altered spinel (Type 1) has the composition:

SiO ₂ 17.1 ± 0.8 ^a	TiO ₂ 1.2 ± 0.3	Al ₂ O ₃ 38.4 ± 2.7	Cr ₂ O ₃ (0.02)
V ₂ O ₅ 0.2	FeO ^b 31.5 ± 2.4	MgO 16.5 ± 0.4	MnO 0.1
CaO 0.1	ZnO (0.01)		

^a The second figures refer to the statistical errors in the weight percentage of the oxides.

^b All the iron is calculated as divalent.

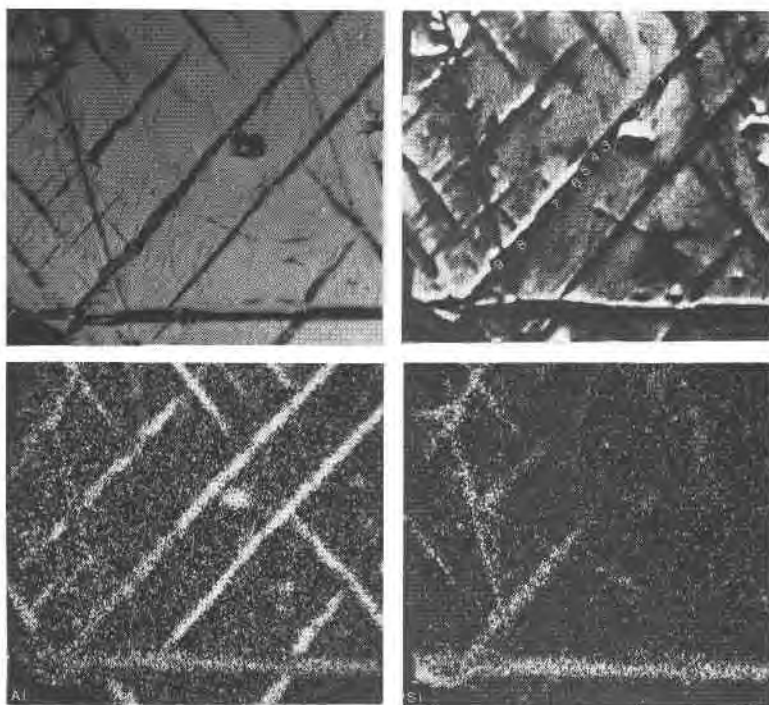


FIG. 4. The photomicrograph (upper left) shows black lamellae of spinel and its (Type 1) alteration product in magnetite; light gray lamellae are ilmenite. Electron (upper right) and X-ray scanning pictures for Al (lower left) and Si (lower right) show the gradual replacement of Al by Si in a spinel lamella. Analysed points are marked with a number also found on the abscissa in Fig. 5.

In Figure 5 the variation of the concentration of the elements as found in the fresh and altered lamella of Figure 4 is plotted against the distance from a reference point in fresh spinel towards the alteration product. The percentages in Figure 5 are not corrected for the atomic number of the element, absorption, fluorescence, background, wavelength and instrument, and are therefore approximate.

DISCUSSION

Figure 4 indicates that the lamella is inhomogeneous consisting of one part low in silicon—unaltered pleonaste, changing abruptly to one rich in silicon—the alteration product. It appears that the alterations represented by the highest silicon values in Figures 4 and 5 are the final stage of the alteration.

The result of the replacement is a strong increase in the amount of Si combined with a strong decrease in Al and increase in Fe.

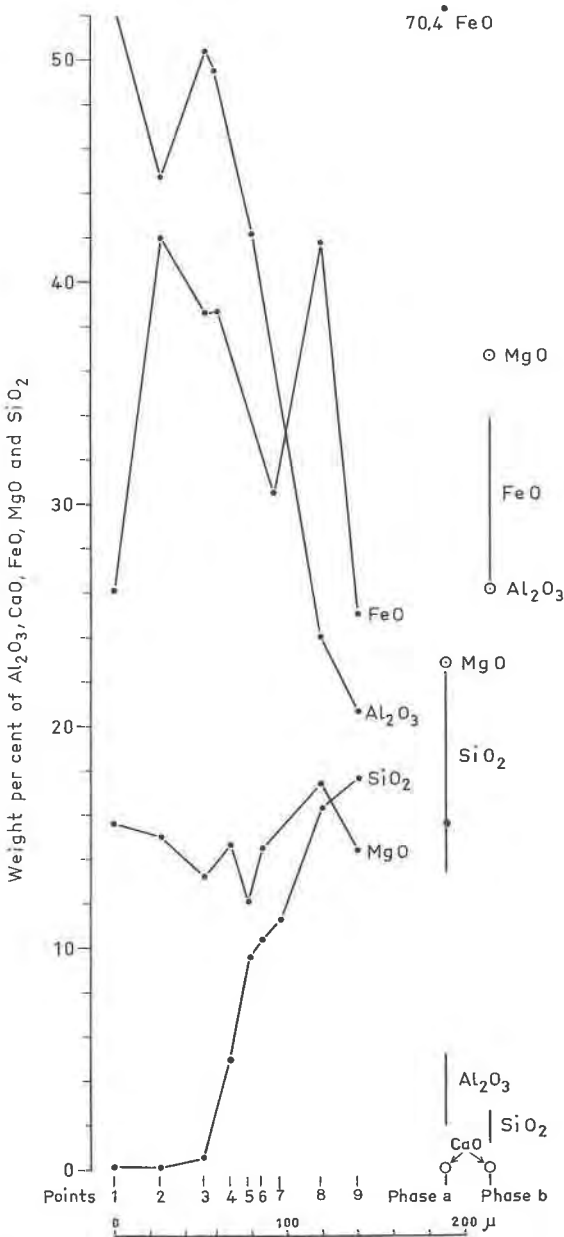


FIG. 5. Al₂O₃, CaO, FeO, MgO and SiO₂ microprobe analyses along the altered spinel lamella shown in Fig. 4. The analyses are point-by-point measurements obtained by moving the section after every analysis, in steps of approximately 10 μm under the fixed electron beam. Phases a and b are located in Figure 2.

Considering the statistical errors as being of the same magnitude as for other analysed spinels and alteration products, and estimating positive corrections, the variation of MgO could be explained by errors in the analyses. The increase in aluminum and corresponding decrease in iron could be explained partly by the analytical errors and partly by the substitution of iron for aluminum. The decrease in aluminum does not appear to be fully compensated by the increase in silicon. This is probably due to the analytical error and substitution of aluminum by iron, as no quartz was found.

The high aluminum content in the contact zone between the olivine and magnetite grains of Figure 2 has probably come from altered pleonaste lamellae. The source of the silicon entering the pleonaste is most likely the altered olivine.

The index of refraction of the spinel is similar to that of its alteration product, both being higher than serpentine. Spinel is one of the few isometric minerals that is invariably isotropic and does not show birefringence, pleochroism or interference figure. In the altered product neither birefringence nor pleochroism could be clearly demonstrated.

Chlorite and sapphirine both have a refractive index close to that of spinel and weak birefringence with parallel extinction, but are difficult to distinguish from one another by microscope. Due to the small size and scarcity of the altered grains, identification by X-ray diffraction was also impossible.

Recalculating the analysis (above, p. 1924) to the number of ions on the basis of 20 oxygens gives good agreement with the formula of chlorite. There is some uncertainty concerning the composition of sapphirine. Frank-Kamenetskii-Kondrateva and Komkov (1962) considered $(\text{Mg}, \text{Fe}^{2+})_7(\text{Al}, \text{Mg})_{17}(\text{Si}, \text{Al})_4\text{O}_{40}$ to be the best approximation, with compositional variance mostly related to the isomorphous substitutions $\text{Mg}^{2+} \rightleftharpoons \text{Fe}^{2+}$, $\text{Al}^{3+} \rightleftharpoons \text{Fe}^{3+}$ and $2\text{Al}^{3+} \rightleftharpoons \text{Si}^{4+} + \text{Mg}^{2+}$. Recalculating the analysis to the number of ions on the basis of 40 oxygen also closely approaches the formula of sapphirine.

As the ore complex of Taberg does not show any signs of regional metamorphism it appears likely that the alteration of the rock is connected with the magmatic period. Bowen and Tuttle (1949) showed that forsterite with small amounts of fayalite could be serpentinized at temperatures around 350°C. This suggests the alteration reactions to be late magmatic.

While chlorite could easily be formed under these conditions sapphirine generally occurs as a high-temperature metamorphic mineral (Yoder, 1952, Deer *et al.*, 1964). Warren (1912) and Foster (1950) describe a sapphirine as of magmatic origin. Vogt (1947) considers

sapphirine a metamorphic as well as a magmatic mineral occurring together with cordierite, spinel and corundum. The occurrence of sapphirine in lower metamorphic facies has not been reported. Considering these observations it does not seem likely that sapphirine could form in connection with Taberg ore.

CONCLUSION

The spinel in the hyperite of Taberg was identified as pleonaste. A study of the chemical composition of partial altered spinel lamellae indicates decreasing aluminum and increasing silicon contents as the alteration proceeds. It was not possible to identify the product of alteration but considering the alteration conditions chlorite is considered probable. The alteration is a result of the interaction of silicon on spinel. The silicon is likely to have been liberated from olivine during hydrothermal alteration of the rock involving the serpentinization and chloritization of olivine.

ACKNOWLEDGMENTS

The author acknowledges the valuable discussions and suggestions made by Prof. H. Ramberg and is also most grateful to Dr. S. Saxena for his advice and encouragement during this investigation. Thanks are due to Drs. B. Collini, R. Gorbatshev and B. Lindqvist for their constructive criticism of the manuscript, to Mrs. Marianne Dahl for chemical analyses of minerals with the Geoscan microprobe, and to the technical staff of the Institute for their help in various ways. The work on Geoscan is supported by grants from the Natural Science Research Council and Malmfonden (Grant no. 87).

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Manuscript received, January 2, 1968; accepted for publication, June 4, 1968.