Chromian spinels from Kuså, Bergslagen, Sweden

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ABSTRACT

Chromian spinels have been observed as disseminated accessories in gabbroic rocks and ores from the abandoned Ni-Cu mine of Kuså, in the Proterozoic metallogenic province of Bergslagen, Sweden. They occur as unzoned grains of “ferritchromit” (Fe$_{0.5}$Mg$_{0.5}$Fe$_{0.5}$Cr$_{0.5}$Al$_{0.5}$O$_{2}$), as two-phase intergrowths composed of an Al-rich phase (Fe$_{0.5}$Mg$_{0.5}$Al$_{0.5}$Cr$_{0.5}$O$_{2}$) and “ferritchromit,” and as zoned grains with chromite cores (Fe$_{0.5}$Mg$_{0.5}$Cr$_{0.5}$Al$_{0.5}$O$_{2}$) rimmed by “ferritchromit.” Between the core and the rim, two intermediate zones were observed: a light zone B (slightly depleted in Cr compared to the core) and a dark zone C enriched in Al (Fe$_{0.5}$Mg$_{0.5}$Cr$_{0.5}$Al$_{0.5}$Fe$_{0.5}$O$_{2}$). “Ferritchromits” of all textural varieties are anomalously anisotropic. Chemical and textural observations on chromian spinels from Kuså suggest a miscibility gap along the magnetite-chromite join between M$_{30}$Chr$_{70}$ and M$_{30}$Chr$_{35}$, and accordingly, a small correction to the previously described solvus is proposed.

INTRODUCTION

Paragenetic investigations of sulfide deposits in the Proterozoic metallogenic province of Bergslagen, central Sweden, revealed the presence of unmixd and zoned chromian spinels in the Ni-Cu sulfide deposit of Kuså. The Kuså mine is located about 13 km west of Falun and was active periodically between 1805 and 1941. A total of 9000 tons of ore containing 1–2 wt% Ni and 1–2 wt% Cu was produced (Grip, 1961). The present investigation was carried out on specimens found on dumps resulting from the latest mining activities of Boliden Mineral AB Company in 1940–1941 and on specimens from their drill cores.

The Ni-Cu sulfide mineralization occurs in the margin of a small differentiated intrusive composed of hornblende, pyroxene-hornblende gabbro-norite, and olivine-pyroxene gabbro (Nilsson, 1984). The ore is a disseminated type, with 10 to 50 vol% of sulfides. The sulfide grains are 1–2 mm in diameter and often occur in clusters up to 10 mm. The main sulfides are pyrrhotite, chalcopyrite, and pentlandite, with accessory sphalerite, mackinawite, bornite, and siegenite. In ores from the dumps, a considerable amount of pentlandite is altered to violarite (Zakrzewski, 1988).

Oxides form less than 1 vol% of the ore. They are represented by disseminated grains of ilmenite, rutile, and chromian spinels. No chromite segregations were observed. This paper presents optical and chemical characteristics of spinels from Kuså and discusses their evolution.

OPTICAL OBSERVATIONS

Chromian spinels from Kuså occur as (1) zoned grains with a chromite core rimmed by “ferritchromit,” (2) two-phase intergrowths of “ferritchromit” and hercynite, and (3) unzoned grains of “ferritchromit.”

Zoned grains are noted in two size classes. The first type includes small, 1–15 μm, euhedral to subhedral grains disseminated in tremolitic- and magnesio-hornblende and in diopsid. The second type consists of subhedral to anhedral grains 100 to 500 μm in diameter. They are interstitial to the silicates, occur on the sulfide-silicate interfaces or, rarely, are found in sulfides. In the disseminated grains, zoning consists only of the darker chromite core (A) rimmed by a lighter “ferritchromit” (D). In the larger grains, two intermediate zones (B and C) may also be observed between the core and rim.

The cores of zoned grains consist of a homogeneous bluish-gray to greenish-gray phase with relatively low reflectivity (estimated 13%). Internal reflections are almost absent. Dark brown internal reflections were rarely observed. The diameters of the cores vary from less than 1 μm in the disseminated type up to several hundred micrometers in the larger grains. Their shapes vary from euhedral, somewhat rounded and lobate crystals to ragged and brecciated grains. Chromite cores may, in rare cases, be in contact with the surrounding silicates, but usually they are rimmed either directly by “ferritchromit” or by two intermediate zones followed by “ferritchromit.” Minute grains of sulfides may be observed between the core and the rim.

The intermediate zones on the edge of the chromite core consist of zone B, which is a few micrometers wide, somewhat lighter than the core, and is followed by an even narrower zone C, which is darker than the core (Fig. 1a). The presence of such intermediate zones has not been noted previously in literature, but may be regarded as typical for Kuså.
The light, intermediate zone B is optically homogeneous. Its estimated reflectance is about 14%. No internal reflections were observed. As a result of the low contrast in reflectivity, it is difficult to observe a transition to the core, but the contrast is sufficient to observe the sharp contact with the dark zone C.

The dark intermediate zone C has an estimated reflectance of 12%, lower than that of zone B and of core A.
The width of zone C is usually up to 5 μm and in exceptional cases up to 15 μm. The widest zone occurs in grains completely surrounded by silicates. Zone C is homogeneous close to the (sharp) contact with the light zone B, but becomes inhomogeneous in the diffuse transition to the rim D (Fig. 1b).

It is estimated that about 90 vol% of the observed spinels from Kuså consist of light pinkish-gray “ferritchromit” of the composition in zone D. It occurs as rims on the chromite cores, as intergrowths with hercynite, and as unzoned grains. In zoned spinels the reflectivity of “ferritchromit” increases continuously from the chromite core toward the edges. The estimated values range from about 13% to about 18% at the edges, which is still distinctly lower than magnetite. Observations at high magnification reveal inhomogeneity and anomalous anisotropy of the “ferritchromit.” The anisotropy effects are distinct even in air with Nicols completely crossed; the anisotropy colors are bluish gray to brownish gray. No bireflectance nor reflection pleochroism was observed. Figure 1b shows a clothlike exsolution pattern at the transition between zones C and D. It consists of a light magnetite-like phase, a dark hercynite-like phase, and a homogeneous-looking gray mass. It seems that at least a part of the variation in the reflectivity discussed above is due to the changing proportions of these three components. Toward the edges of the grains, “ferritchromit” appears to be homogeneous, but anisotropy is still perceptible. The anisotropic, polyphase chromian spinels were also observed in unzoned grains (Fig. 1c) and in association with hercynite. Some of the zoned grains are overgrown by a younger generation of homogeneous-looking isotropic magnetite.

The two-phase chromian spinels from Kuså consist of dark hercynite and inhomogeneous “ferritchromit.” Most of these are composite grains, as in Figure 1d, or have hercynite mantling the “ferritchromit.” Rarely, hercynite forms the center of a grain and is rimmed by “ferritchromit.” The contacts between hercynite and “ferritchromit” are always sharp. The hercynite portions are mostly homogeneous but in places may contain somewhat oriented exsolutions of a magnetite-like phase. “Ferritchromit” often shows clothlike exsolutions of hercynite and may contain oriented ilmenite lamellae. It is distinctly anisotropic in the same way as the “ferritchromit” in the zoned grains described above. Ilmenite lamellae are only a few micrometers wide and are surrounded by even narrower rims of hercynite. These coatings are in optical continuity with both the minute clothlike exsolutions as well as with the large field of hercynite.

**Chemical Investigations**

Electron-microprobe analyses were performed with a Cambridge Instruments Mark-9 device, using corundum, Cr₂O₃, Fe₃O₄ (for Fe), olivine Mg₂[Fe₂SiO₄] (for Mg), rhodonite, ilmenite (for Ti), V₂O₅, NiO, and ZnO as standards. Results were corrected with an on-line ZAF program. In most cases, spot analyses were made; raster mode was used to characterize the bulk composition of inho-
mogogeneous grains. In order to relate the optical zoning with chemical composition, two traverses with steps of 1.4, 3, and 5 μm were performed across the four zones (Fig. 1a). The results are plotted in Figure 2, and selected analyses are given in Table 1. It is obvious that some zones are narrower than the diameter of excitation area of the electron beam, and individual analyses could only be regarded as semiquantitative. Nevertheless, the two profiles in a single grain display good reproducibility and are valuable indicators of the compositional trend in the zoned grains. Selected analyses of other zoned grains and of the two-phase spinels are given in Table 2. The best way to visualize the compositional trends in the spinel group is with the six-component spinel prism. The Kuså spinels, however, have their Mg content coupled to their Al content (Fig. 3), and the system can be reduced to a single plane Fe₃O₄-FeCr₂O₄-MgO-Al₂O₃ (Fig. 4).

The dark cores of zoned spinels are aluminous chromite with a composition plotting around Fe₂₋₃Mgₓ₋₃Crₓ₋₃Al₃₀₋₃Feₓ₋₃O₄ (field A in Fig. 4). Low Mg content could explain the lack of internal reflections. Chromite has low Ti, V, and Ni (up to 0.08 wt% NiO) and moderate Mn contents. Figure 5 shows that the Zn content in spinels from Kuså is related to the Cr content.

The light intermediate zone B that may occur on the edge of the chromite core is characterized by Fe³⁺ substituting for Al and by a constant Cr content somewhat lower than in the core (Fig. 4, points 2 to 8, 31, and 52). The decrease of Al is accompanied by slight decrease of Mg compensated by Fe²⁺ and Mn²⁺. An exceptionally high Mn content of 3 wt% MnO was measured in point 52 (Table 2).

The dark intermediate zone C is characterized by a lowering of the Cr/(Cr + Al) ratio (points 31 to 35, 9, and 10 in Fig. 2). A compositional plot of trivalent cations from zoned grains in Figure 4 indicates that the single analyses are influenced by their surroundings, since the values for Al are too low and these for Fe³⁺ somewhat too high. The instrumental error is minimized for the widest zone C that gave the most representative composition Feₓ₋₃Mgₓ₋₄Crₓ₋₄Alₓ₋₄Feₓ₋₄O₄ (point 71 in Table 2 and in Fig. 4). The transition between zones B and C represents a trend of Al substituting for Cr but with fairly constant Fe³⁺ (between points 52 and 71 in Fig. 4). Mg

Fig. 4. Compositional plot of chromian spinels from Kuså and the approximate position of the solvus according to Loferski and Lipin (1983) (dashed line) and from present study (heavy line). Solid circles indicate analyses of the traverses; open circles are for single analyses. Solid lines connect coexisting pairs of spinels. PES indicate the probable composition of a pre-existing spinel.
and Ti slightly increase, Fe\(^{2+}\) and Mn slightly decrease, and Zn and V are as in the core.

The results of chemical investigations of “ferritchromites” from Kuså are influenced by their inhomogeneity and by the limited resolution of the electron microprobe. Single analyses represent, in most cases, the bulk composition of two or more phases. Chemical traverses (Table 1 and Fig. 2) show that, proceeding outward from the core, both Fe\(^{2+}\) and Fe\(^{3+}\) increase, whereas Cr, Al, and to a lesser degree also Ti, Mn, Zn, and Mg decrease; V and Ni are consistently low. A compositional plot of trivalent cations indicates a continuous transition from Al-rich chromite (zone C in Fig. 4) to magnetite (zone D in Fig. 4). Two subtrends could be recognized in this group,
with the division being around the composition Fe\(_{6+}\)\(_{5-}\)Mg\(_{6}\)\(_{1}\)Fe\(_{1+}\)\(_{2}\)Cr\(_{6}\)\(_{4}\)Al\(_{5}\)\(_{3}\)O\(_{2}\). Limits between the two trends are gradual in both chemical as well as optical characteristics. The first subtrend covers analyses 11 to 15 and 36 to 42 of traverses in Figure 2. Between these points there is a diffuse transition from the dark zone C with a hercynite-like component into a lighter rim. In the second subtrend, the diffuse nature of intergrowths is replaced by a more oriented, clothlike texture. It covers the outside rims of zoned grains (points 16 to 24 and 42 to 45 of the traverses in Fig. 2). The homogeneous-looking outermost zones are Al-poor, but still have considerable Cr content. The end-member is “ferritchromit” (chromian magnetite) with composition Fe\(_{5+}\)\(_{5-}\)Fe\(_{1+}\)\(_{2}\)Cr\(_{6}\)\(_{4}\)O\(_{2}\). The lowest Cr content was observed in magnetites isolated in magnesiohornblende. Their composition is Fe\(_{5+}\)\(_{5-}\)Fe\(_{1+}\)\(_{2}\)Cr\(_{6}\)\(_{4}\)O\(_{2}\).

In the two-phase intergrowths, the light Fe\(_{5+}\)\(_{5-}\)-rich component displays fine, clothlike intergrowths and plots within the second trend of “ferritchromit” (point 101 in Fig. 4 and in Table 2). The dark Al-rich component plots close to a composition Fe\(_{6+}\)\(_{5-}\)Mg\(_{6}\)\(_{1}\)Al\(_{5}\)\(_{3}\)Cr\(_{6}\)\(_{4}\)Fe\(_{1+}\)\(_{2}\)O\(_{2}\) (point 100). There are also significant differences in minor elements: hercynite contains some Zn but is strongly depleted in Ti and V, elements that in turn are strongly enriched in “ferritchromit.” Enrichment in Ti is also manifested by lamellae of ilmenite. The Zn content in magnetite is below the detection limit of the microprobe (about 0.1 wt% ZnO).

**DISCUSSION**

Chromite spinels are common accessory minerals in mafic and ultramafic rocks. Because of their refractory properties they may be useful indicators of the origin and development of the rocks and associated sulfides. In many occurrences, chromites are zoned with, in principle, chromite cores and “ferritchromit” rims. In detail their chemistry is related to the country rocks and to metamorphic influences. In gabbroic rocks, the cores consist of Mg- and Al-rich chromite and the rims of “ferritchromit” with typically low Al but considerable Mg content (Bliss and MacLean, 1975; Wylie et al., 1987). Spinels of metamorphic origin that recrystallized in sulfide melts have low Mg,Al, and (calculated) Fe\(_{5+}\) (Groves et al., 1977) and a high Zn content. Such high Zn contents in chromites are regarded as indicators of Ni-Cu sulfide mineralization (Groves et al., 1983; Wylie et al., 1987).

At Kuså the spinel cores are chromites with high Al and Fe\(_{5+}\), moderate Mg, Mn, and Zn, and low Ti, V, and Ni contents. These characteristics could indicate a magmatic provenance, although the Mg/Fe\(_{5+}\) ratios are lower than in chromites from layered intrusions (e.g., Cameron, 1975). Higher Mg and Al contents are found in the dark intermediate zone C and in the hercynite-rich portions of exsolved spinels.

Exsolved chromian spinels were noted only in a few localities. They provide information about the extent and the shape of the miscibility gap in the natural system FeO-MgO-CrO\(_{2}\)-Fe\(_{2}\)O\(_{3}\)-Al\(_{2}\)O\(_{3}\) (Muir and Naldrett, 1973; Loferski and Lipin, 1983). Exsolved spinels from Kuså appear to be similar, both texturally and compositionally, to those described from other gabbroic intrusions. In the Cr-poor portion of the system, the exsolved pairs were big enough to be analyzed (points 100 and 101 in Table 2 and in Fig. 4). They are comparable to type A intergrowths from the Red Lodge district, Montana (Loferski and Lipin, 1983), and to the “inhomogeneous-looking” chromite from the Giant Nickel mine, British Columbia (Muir and Naldrett, 1973). Exsolutions in the Al-poor portion, along the chromite-magnetite join, are too fine-grained to be analyzed separately. They are similar to the “woven-looking” grains from Giant Nickel mine, with bulk compositions plotting around point 71 in Figure 4, and to type B exsolutions from Red Lodge that plot around points 71 and 72. Papunen and Idman (1982) observed polyphase spinels with bulk compositions of ferritchromite and interpreted them as very fine intergrowths of chromite and magnetite. The fine-grained exsolutions of type C from Red Lodge have still lower Al contents, and finally the very fine intergrowths of the “intermediate phase” from the same locality plot almost on the chromite-magnetite join. These examples indicate that the grain size of exsolution is related to Al content and strongly suggest that only polyphase spinels occur in this part of the system. This implies a miscibility gap between chromite and magnetite, and a minor correction of the solvus proposed by Loferski and Lipin (1983) is given in Figure 4.

Optical observations on the heterogeneous spinels revealed the presence of a light magnetite-like phase intergrown with a dark hercynite-like phase and an intermediate gray spinel. All the individual components are isotropic, and therefore it is somewhat surprising to observe a distinct anisotropy. An anisotropic “ferritchromit” also was observed in zoned chromites from Sykesville, Maryland, by Wylie et al. (1987), who suggested that it is a single phase inverted to lower symmetry from isotropic spinel. This supports the ideas of Seeliger and Mücke (1969), who described donathite, (Fe\(_{5+}\),Mg)-(Cr,Fe\(_{5+}\))\(_{2}\)O\(_{4}\), an anisotropic, tetragonally distorted phase closely related to chromite. The inhomogeneous nature of the anisotropic chromite makes it impossible to prove or disprove the existence of donathite in the Kuså deposit.
A different explanation of the anomalous anisotropy, which does not involve a hypothetical lower-symmetry phase, could be the optical effect of depolarization of the Kalb lines and/or scratches on the polished surface. These lines are abundantly present because of considerable differences of polishing hardness between the exsolved phases. The exsolutions are oriented in certain domains and give oriented Kalb lines and oriented scratches. The depolarization effects could only be observed with crossed Nicols. This explains the fact that both at Sykesville and at Kusá, the strongly anisotropic spinels are not bireflectant. This interpretation of the anomalous anisotropy would further imply that homogeneous-looking anisotropic “ferritchromit” consists, in fact, of submicroscopic polyphase exsolutions. Electron-diffraction studies by Shen et al. (1988) indicate that “ferritchromit” from Heng-Chun, Taiwan, consists of a topotaxial intergrowth of an RO phase (rock-salt structure) and spinel.

Both explanations of the anisotropy—the formation of a tetragonal structure and the submicroscopic exsolutions—indicate that the anisotropic grains from Sykesville define the miscibility gap among the magnetite-chromite join between Mt$_{50}$Chr$_{50}$ and Mt$_{70}$Chr$_{30}$. Studies of synthetic spinels by Cremer (1969) suggested an even larger gap between Mt$_{50}$Chr$_{50}$ and Mt$_{70}$Chr$_{30}$ at 700 °C. An intermediate phase from Red Lodge plots at Mt$_{70}$Chr$_{30}$; its existence has been attributed to an expansion of the miscibility gap by a removal of Al$_{2}O_{3}$ and a drop in temperature (Loferski and Lipin, 1983). This plausible model is probably valid also for other chromian spinels from gabbroic rocks.

Loferski and Lipin (1983) noted that the tie lines of exsolved pairs of spinels are parallel to the Fe-Al join for the Cr-poor compositions and slope toward Fe$^{3+}$ in the Cr-rich portions. This regularity was observed in Kusá spinels on the two-phase spinels (100–101 in Fig. 4) but also, somewhat unexpectedly, on the plot of zoned spinels (tie lines 71–72 and 52–53 in Fig. 4). An extreme case is the tie line 61–62, which is nearly parallel to the Fe$^{3+}$-Cr join and which supports the idea of a miscibility gap between Mt$_{50}$Chr$_{50}$ and Mt$_{70}$Chr$_{30}$.

The presence of the intermediate Al-rich zone C is one of the most intriguing aspects of the zoned chromites from Kusá. The chemical traverses (Fig. 2) show that the enrichment of Al in zone C is accompanied by an impoverishment of Al in a narrow zone B immediately before. This could suggest that the two zones are a genetically related couple, originating by redistribution of Al. On the other hand, Al in the light zone B is compensated for by Fe$^{3+}$ with constant Cr, whereas in the dark zone C, Al takes the place of Cr with almost constant Fe$^{3+}$. This implies that Al could be supplied from the outside rim rather than from the core. This, together with the close analogy between the tie lines of exsolved chromites presented by Loferski and Lipin (1983) and the tie line 71–72 in Figure 4 representing the Al-rich zone C and the rim, may suggest that these are exsolution products of a hypothetical pre-existing spinel (PES). In cases when the PES formed an outer rim on the chromite core, the exsolution products reacted with the core, gaining considerable Cr content. In case of unzoned grains, the PES unmixed into Cr-poor phases 100 and 101. The compositional plot of the PES in Figure 4 is suggested by the surface relations of the exsolved spinels, with approximately 1/5 of the Al-Rich dark phase and 2/5 of the “ferritchromit.” Interreaction of the PES with the chromite core resulted in a fan-shaped collection of tie lines between points 100 and 61 with a common center around Mt$_{50}$Sp$_{50}$Chr$_{50}$ (point 101 in Fig. 4).

Drawing upon the evidence presented above, the following sequence, represented pictorially in Figure 6, is suggested for the evolution of chromian spinels from Kusá:

1. Fe$^{3+}$-poor chromite cores (zone A) were formed magmatically.
2. The Fe$^{3+}$-rich edges (zone B) were then formed, possibly magmatically.
3. The pre-existing spinel (PES) was formed as magmatic overgrowths on chromite cores or as discrete, unzoned grains. (4) Unmixing of these unzoned grains resulted in a hercynite-“ferritchromit” pair (100–101 in Fig. 4), whereas in zoned grains, unmixing and simultaneous interreaction with the core shifted the compositions toward the chromite corner.
(71–72 in Fig. 4). (5) A second unmixing resulting in the formation of woven textures and submicroscopic (anisotropic) intergrowths, possibly of (chromian) magnetite with chromite.

The distribution of Zn indicates its preferential affiliation with chromite. Unzoned grains and the outermost zones of “ferritchromit” have low Zn contents. Extreme differentiation of Zn between the hercynite-rich and magnetite-rich portions is observed in the two-phase grain 100–101 (Table 2). An estimated 0.4 wt% ZnO for the PES is significantly lower than in chromite cores that have ca. 0.8 wt% ZnO. Probably at the time of the formation of PES, sulfides started to form and Zn precipitated as sphalerite. The presence of small sulfide grains between the core and the rim in zoned grains indicates their relative position in the evolution of the spinels.

Conclusions

The principal findings of this study may be summarized as follows: (1) The occurrence of exsolved chromian spinels in Ni-Cu sulfide ores from Kuså confirms their relationships with gabbroic rocks as postulated by Łoferński and Lipin (1983). (2) The compositions of chromian spinels from gabbroic rocks plot close to the FeOo-FeCrOo-MgFeOAlOo plane of the spinel prism. (3) The unusual intermediate Al-rich zone is thought to originate by unmixing of a pre-existing spinel and simultaneous reaction with the chromite core. (4) Anisotropic “ferritchromits” are most probably polyphase, (sub)microscopic, oriented intergrowths. (5) Although in general the present investigations confirm the position of the solvus as proposed by Łoferński and Lipin (1983), there are indications of a miscibility gap along the magnetite-chromite join between Mt40Chr60 and Mt70Chr30.

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