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Alteration of Chromite During Serpentinization in the Pennsylvania-Maryland District[1]

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Abstract

Electron microprobe analysis of samples from the Pennsylvania—Maryland State Line District show that disseminated chromites associated with serpentinites commonly have a ferrit-chromit[2] rind (<1 wt percent Al_2O_3; <3.5 wt percent MgO; >25 wt percent Cr_2O_3). This rind, which completely encloses the chromite core, has an irregular overgrowth of magnetite (>85 wt percent iron oxide) which is embayed by serpentinite silicates. The outline of the original chromite grain may possibly be represented by either (1) the outer or (2) the inner edge of this rind.

The genetic association of chlorite with ferrit-chromit established by Beeson and Jackson (1969) for the Stillwater complex can not be extrapolated to this rock suite. In the State Line deposits, the lack of associated aluminous silicates and the low aluminum content of the ferrit-chromit rule out solid state diffusion for the formation of the ferrit-chromit. Aqueous mobilization of chromium during serpentinization is reviewed as a possible mechanism.

Introduction

The serpentinization of ultramafic deposits in the Pennsylvania—Maryland State Line district has attracted attention ever since 1817 when Isaac Tyson, Jr., a noted Baltimore business man, leased the first chromite mining rights in this area (Pearre and Heyl, 1959). In the ensuing years these serpentinites have been studied by many investigators. Recently, McKague (1964), Lapham and McKague (1964), and Lapham (1967) have detailed the petrology, geochemistry, general geology, and tectonic deformations of the serpentinites and associated chromites in the area along the state line between U.S. Routes 1 and 222. Samples from five localities within this area were used in the present study.

The absence of plagioclase, the presence of relict olivine, and the occasional presence of pyroxene augen in the serpentinites of this area (Fig. 1) leave little doubt as to the ultramafic precursor and petrogenetic sequence of the serpentinization reactions. The schlieren chromites associated with these serpentinites (Fig. 2) suggest a pre-serpentinization cumulus history, while the accessory chromite (Fig. 3) is almost ubiquitous in the serpentine of the area studied. McKague (1964, Table 13) has established that the different chromites of this area show wide variations in major elements. Moreover, he has shown that the schlieren chromite and the accessory chromite both have FeO/Fe_2O_3 ratios that range from 4.73 to 7.35 as opposed to ratios of 2.43-3.81 in the podiform chromite bodies.

As discussed often in the literature (*e.g.,* McKague, 1964; Thayer, 1956), many chromite grains from the State Line area show an overgrowth rimming of magnetite. The accessory chromite often shows a double rimming, schlieren chromite grains show a much thinner single rimming, and the rimming is usually not observable on massive chromite grains. Figure 4 shows in reflected light and at high magnification a typical chromite grain with the double rim. This paper discusses the chemistries and petrofabrics of these double rims.

Experimental Procedure

Qualitative elemental distributions for Mg, Fe, Cr, Al, and Si were studied with a Cambridge electron microprobe utilizing X-ray fluorescence images in diazo-color-enhanced overlays according to the method of Salvage (1969). This qualitative work

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[2] The term ferrit-chromit is used here as defined by Spangenberg (1943).

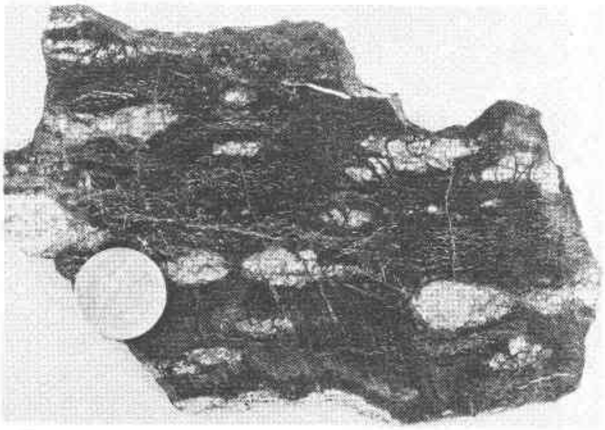

FIG. 1. Chrysotile serpentine (dark) surrounding augen of *clinopyroxene* (originally wehrlite?). From near the intersection of Octoraro Creek and the Pennsylvania-Maryland line. The coin has a diameter of 21 mm.

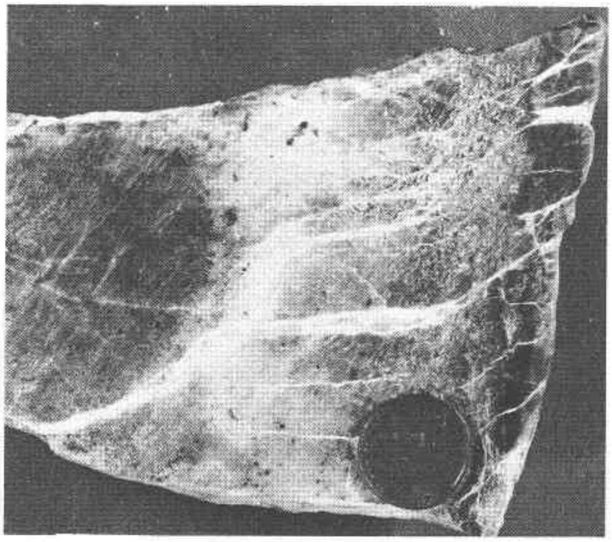

FIG. 3. Disseminated chromite (small dark granules) in massive serpentinite of variegated color. Fractures are filled with later brucite. From a roadcut in the Chester County Boy Scout Camp Grounds, Octoraro Creek, Pa. Coin has a diameter of 19 mm.

was the guide for quantitative analyses of the chromite grains with double rims. Quantitative results for MgO, Cr_2O_3, and SiO_2, and for total iron as FeO, were obtained with a MAC Model 400 electron microprobe with a 15 kV accelerating potential. A 2 μm diameter beam spot was standardized with a gravimetrically analyzed Stillwater chromite, sample 52NL-11, from E. D. Jackson and M. H. Beeson (personal communication). The data were obtained and reduced to weight percentages of oxides by computer, following the procedure of Finger and Hadidiacos (1971).

Determinations of the solubility of chromite in distilled water (pH = 5.6 because of equilibration with atmospheric CO_2) were performed using a Beckman DK-2A spectrometer. Absorption mea-

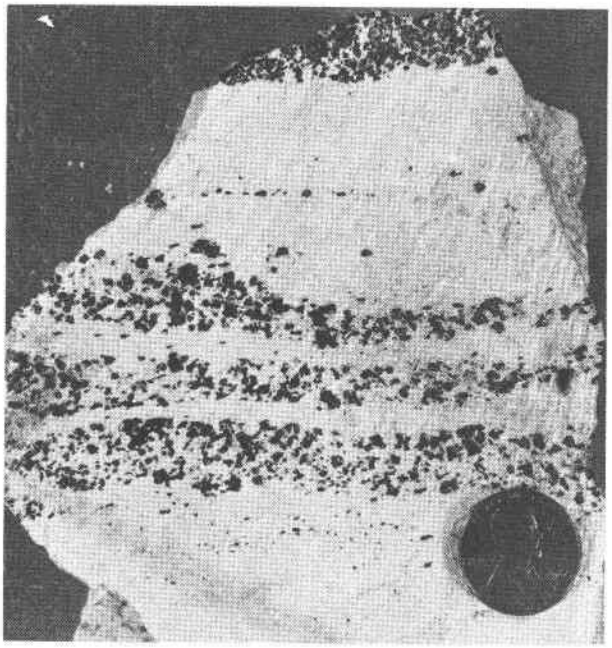

FIG. 2. Layered schlieren chromite (dark) in a serpentine matrix. From a now back-filled prospect pit of the Cedar Hill Quarry on the State Line. Coin has a diameter of 19 mm.

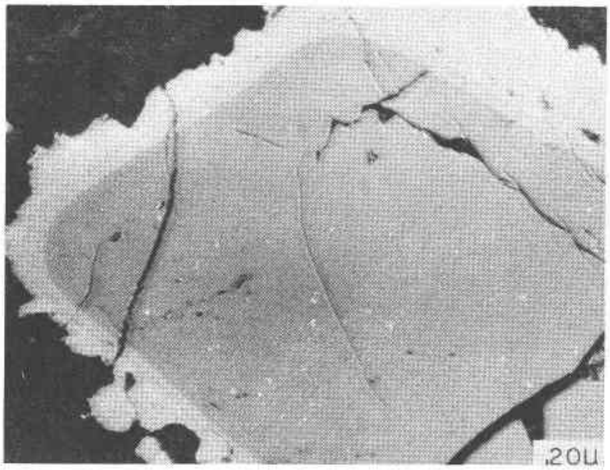

FIG. 4. Reflected light photomicrograph showing a typical disseminated chromite grain. The central gray area is chromite, the lighter gray 8–10 micron thick rind is ferritchromit, the white outer-rim is magnetite, and the surrounding dark areas are chrysotile.

surements were performed at 373 nm, the location of the major absorption band for the Cr^{6+} standard solutions. Volumetric dilution of a stock Na_2CrO_4 solution was employed to obtain calibration points for a Beer's Law unit standardization curve. Ten cc of distilled water (pH = 5.6) were equilibrated at room temperature by agitation with 1 gram of the −80 mesh powdered materials to be tested, and the leaching was decanted into the spectrometer cell. An −80 mesh sample (≤ 177 μm diameter) was chosen because of the similarity in size to disseminated chromite grains in the State Line deposit. Duplicate analyses were performed by adding a fresh 10 cc of the distilled water to the retained powdered residue.

Results

Qualitative electron microprobe analyses of more than four dozen grams of accessory chromite in early chrysotile verified the consistency in composition of the double rims. In Figure 4 the magnetite outer rim is low in Mg, Al, and Cr but the inner rim is an iron-rich, magnesium- and aluminum-poor ferrit-chromit. The matrix of early chrysotile or later antigorite (depending on sample locality) contains very little to no detectable aluminum. The genetic sequence of chrysotile and antigorite and the low aluminum content of associated matrix silicates agrees with McKague's (1964) observations.

The quantitative electron probe results are typified by a single example (of five performed) in Figure 5. Analytical totals of less than 100 percent result from reporting all iron as FeO, omission of the TiO_2 and MnO data, and hydroxide not being reported for the silicate. Significant results of the five quantitative analyses are (in wt percent): (1) the ferrit-chromit rinds have <3.5 MgO and <1.0 Al_2O_3, and (2) the magnetite rims have <1.5 MgO and <0.5 Al_2O_3.

Original Chromite Alteration

The ferrit-chromit rind may be reasonably interpreted as (1) an alteration product of original chromite, or (2) an overgrowth nucleated on top of the original chromite.

Interpretation (1) is contingent upon the feasibility of solid state diffusion in which Mg^{2+} and Al^{3+} diffuse out as iron ions diffuse in.

In 1969 Beeson and Jackson did recognize and discuss the sluggishness of aluminum diffusion rates in considering the blocky inlaid texture of ferrit-chromit in the serpentinized Stillwater chromite grains. However, they showed that the Stillwater ferrit-chromit inlay texture is typically associated with adjacent chlorite. They therefore claimed that during Stillwater serpentinization, Mg^{2+} and Al^{3+} diffused out of the spinel, thereby producing a ferrit-chromit residuum associated with a Mg- and Al-enriched chloritized silicate. Beeson and Jackson were forced to this conclusion by petrographic evidence, and their interpretation of this evidence is—this author believes—unassailable.

However, the petrographic and chemical evidence in the Pennsylvania-Maryland State Line deposits is quite different:

(1) ferrit-chromit does not have an inlay texture, but forms a rind completely enclosing the chromite grains;

(2) ferrit-chromit was found only on disseminated chromite grains, whereas magnetite was found encrusting all types of chromite;

(3) the rounded corners on ferrit-chromit rimmed grains are suggestive of chromite resorption and/or dissolution (Fig. 4) whereas State Line chromite grains are typically angular to euhedral;

(4) ferrit-chromit has been found on disseminated chromite in both chrysotile and antigorite;

(5) no aluminous chlorite or other aluminous silicate has been observed closely associated with ferrit-chromit by this author or by McKague (1964);

(6) the aluminum content of the ferrit-chromit rind is constant in any given sample and is extremely low (<1 wt percent Al_2O_3);

(7) electron microprobe line-scan analysis shows that the decrease in aluminum from the chromite to the ferrit-chromit occurs abruptly and completely at their interface.

Thus secondary inter-diffusion across a magnetite-chromite interface is not a possible explanation for the ferrit-chromit. Furthermore, since the encrusting magnetite is even poorer in Mg and Al than is the ferrit-chromit, it seems attractive to consider at least the possibility that the State Line ferrit-chromit is the result of a precipitated secondary overgrowth on the original chromite.

Overgrowth on Original Chromite

Precipitation of a secondary overgrowth on original chromite requires that chromium be in solution in the serpentinizing fluids.

The acid insolubility of chromite that is high in Cr_2O_3 is well known; flux-fusion-dissolution at elevated temperatures is a typical analytical procedure necessary for chromite analysis (Ingamells, 1960). One is therefore tempted to conclude that solution of Cr^{3+} from chromite is not possible in the pH range of geological environments. Furthermore, while Cr^{6+} oxide compounds are highly water soluble, Cr^{6+} ions would not be a predicted species in serpentinization fluids already high in Fe^{2+}. Equation (1) shows the rapid redox-reaction of Fe^{2+} with Cr^{6+} in the standard analytical procedure for the titrametric determination of iron with dichromate (Diehl and Smith, 1952).

$$Cr^{6+} + 3Fe^{2+} \rightarrow Cr^{3+} + 3Fe^{3+} \qquad \text{Eq. (1)}$$

In Figure 6 the Eh-pH relationships calculated from E° data for chromium species (dashed lines, from Klein, 1962) are super-imposed on the Eh-pH relationships calculated from *E*° data for iron species (dotted line, from Krauskopf, 1967). Just as the reaction in Eq. (1) above predicts, the Eh-pH boundaries indicate that even at 10^{-7}M (Fe^{2+}), Cr^{6+} coexists only with Fe^{3+} and can not coexist with Fe^{2+}, regardless of pH. However, it is instructive to compare actual potentiometric emf values (formal reduction potentials) to the theoretical *E*° values. In Figure 7 formal reduction potentials from Diehl and Smith (1952) have been plotted and show that both half-reactions of Eq. (1) have potentiometric values far from the published theoretical *E*° values. The indicated extrapolation (Fig. 6) indicates that Fe^{2+} and Cr^{6+} species should coexist at pH values greater than 2.8.

Hence, a check of the solubility of chromites in distilled water (pH = 5.6 because of equilibration with atmospheric CO_2) was performed at room temperature (25°C). In Figure 8 the solid line represents actual colorimetric absorptions of standard Cr^{6+} solutions prepared by volumetric dilutions. This standard curve fits Beer's Law very well at these dilutions and therefore can be used to "read" the concentrations of unknown solutions. (The *x* axis of Figure 8 is given in log wt percent so that a "-4 reading" represents 1 ppm concentration.) For example, distilled water equilibrated at 25°C with typical massive low-iron high-aluminum Phillipine chromite and typical high-iron low-aluminum Transvaal chromite (Mikami, Heiligman, and Samuel, 1961) showed a concentration of roughly 5 to 10 ppm Cr^{6+}. Many other chromites from around the world, including both accessory and massive chromite from the State Line district, also seem to give values in the 5 to 10 ppm range at this pH and temperature. For comparison, as-received (untreated, reagent-grade) Cr_2O_3, heat-treated Cr_2O_3, and $MgCr_2O_4$ synthesized in air from the Cr_2O_3 were also determined. The measured concentration value for Cr^{6+} solubility from heat-treated Cr_2O_3 did drop with a second distilled water treatment back to the value for "as-

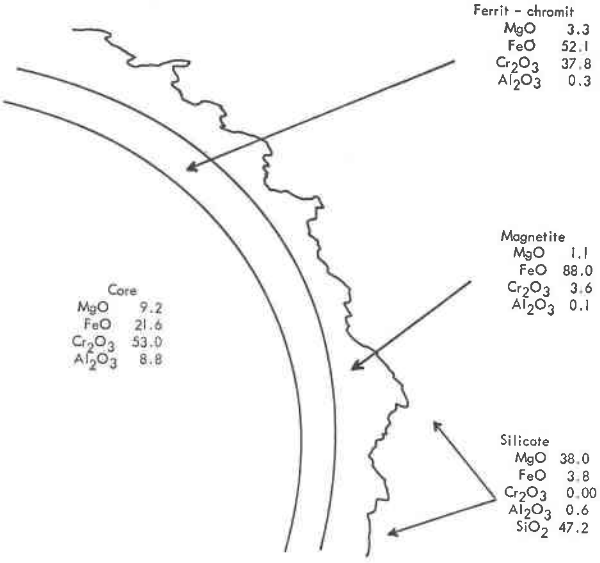

FIG. 5. Typical quantitative electron microprobe analyses of a disseminated chromite grain such as is shown in Figure 4. Data given as weight percent. See discussion in text.

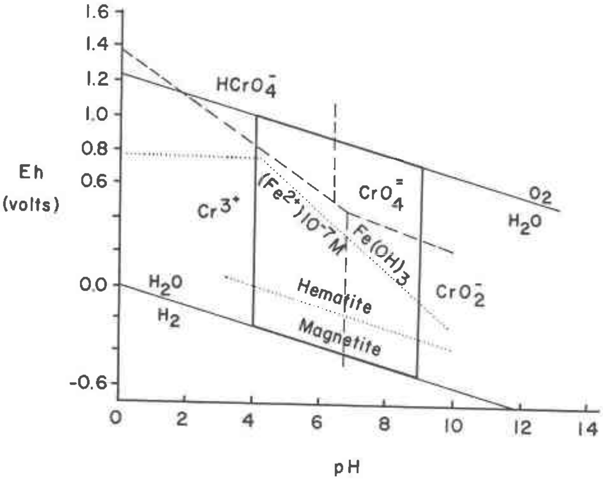

FIG. 6. Eh-pH diagram for chromium and iron species in water at 25°C. Shaded dashed lines give stabilities of chromium species (Klein, 1962, diagram 23); shaded dotted lines give stabilities of some iron species (Krauskopf, 1967); heavy solid lines enclose the range of usual near-surface environments; and light solid lines delimit the stability conditions of water.

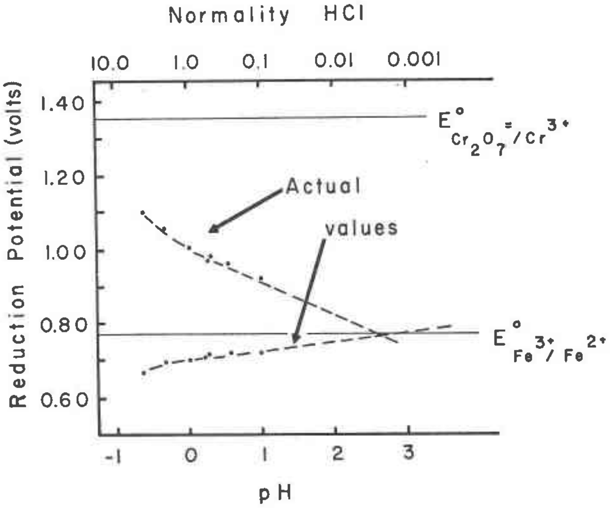

FIG. 7. Formal reduction potentials as a function of pH. Data from Diehl and Smith (1952) are extrapolated with dashed lines by this author. Light solid lines give literature E° values. At pH = 0, $E^\circ Cr_2O_7/Cr^{3+}$ = 1.33 volts compared to actual emf of 1.00 volts and $E^\circ Fe^{3+}/Fe^{2+}$ = 0.77 volts compared to actual emf of 0.70 volts. Extrapolation intersection at the exact value of $E^\circ Fe^{3+}/Fe^{2+}$ is coincidental.

received" Cr_2O_3. Repeated leachings of any given chromite sample gave repeatable Cr^{6+} solubilities.

Disscussion and Conclusion

The significant conclusion of this solubility experiment is that, at a pH of 5.6 and a temperature as low as 25°C, *there is appreciable solubility of chromite* via an Eh-pH effect that produces soluble Cr^{6+} from natural chromites. Although published Eh-pH diagrams calculated from E° values for iron and chromium systems do not predict this result, published chemical data for potentiometric titrations of Cr^{6+} and Fe^{2+} do in fact indicate that Cr^{6+} and Fe^{2+} may become coexisting aqueous species at a pH greater than 2.8.

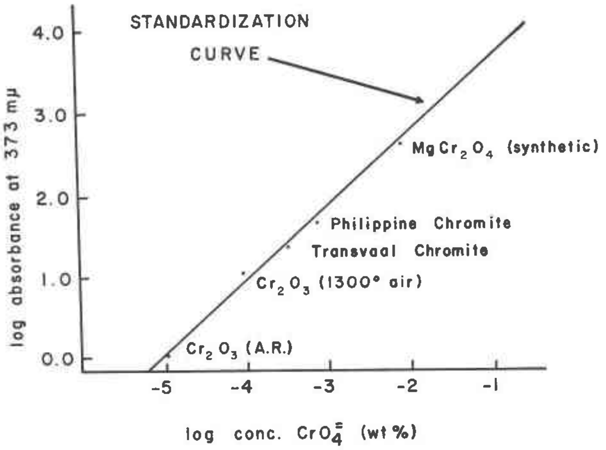

FIG. 8. Beer's Law determination of Cr^{6+} in water equilibrated (pH = 5.6 and 25°C) with various chromium materials. Scatter in the unknown data points was artifically introduced in plotting to give an indication of the uncertainty envelope of data points on the standardization curve. The "Cr_2O_3 (A.R.)" refers to as-received analytical reagent-grade material; "Cr_2O_3 (1300° air)" refers to Cr_2O_3 that has been heated in air at 1300°C.

This low-temperature solubility of chromite, even though in parts per million, is also quite unexpected in terms of geologic interpretation up to this time.

Barnes and O'Neil (1969) have reported that the compositions of run-off waters issuing from dunites and peridotites can best be interpreted as resulting from serpentinization at ambient conditions. Their reported Cr maximum is 0.2 ppm in these waters. The 5–10 ppm values reported here (Fig. 8) for leached pure chromites are high by comparison, but the contrast very likely results from the lower modal percentage of chromite in the dunities and peridotites of their study.

In reviewing the literature, Thayer (1956) found evidence that diagenetic alteration of chromite was minimal—in temperate climates chromite decomposes only slowly. Furthermore, Thayer (1956) states, "The relation that stands out in all descriptions, regardless of the authors' opinions on the genesis of the chromite, is the association of opaque, iron-rich chromite with hydrothermal minerals. There also seems to be general agreement that the opaque portion results from alteration of the original chromite, either by addition or subtraction of material. The presence of two or more spinellid phases, such as translucent chromite cores, opaque chromite border zones, and magnetite in close juxtaposition, is proof that the alteration occurred at temperatures at which solid solution between these phases could take place only very slowly, if at all." Thus, alteration of chromite to produce the zonations in Figure 4 has historically been interpreted as hydrothermal attack on the primary chromite to produce diffusion controlled chromite zoning.

The definite evidence that chromite can become soluble at ambient temperature in natural ground water makes nucleation and precipitation overgrowth of ferrit-chromit at least a theoretical possibility at the State Line deposits. In this scheme, serpentinization would release large amounts of Mg^{2+} and Fe^{2+} from the mafic silicates and, at least initially, produce a small amount of soluble Cr^{6+} from the chromite. As hydrolysis of the silicates continues, the acidity eventually decreases to the point where Fe^{3+} becomes stable, and secondary spinel nucleates and precipitates on residual original chromite—first as ferrit-chomit, at least until the chromium is depleted, and then as magnetite, until the iron is depleted. In the State Line district ferritchromit is common only on the accessory chromite grains. The restriction of ferrit-chromit to disseminated chromite makes sense because, with limited chromium in solution, a thick rind would develop only where the nucleation sites per unit volume of serpentinized rock are rare. A real but microscopically *unnoticeable* thickness of topotaxial ferritchromit may have developed in the schlieren chromite where nucleation sites per unit volume of serpentinized rock are very high. McKague (1964) has mentioned that rimming of any kind is more thinly developed on schlieren chromite than on disseminated chromite grains.

The original dissolution of chromium in this scheme would of necessity leave some aluminum-rich rimming on the chromites. The aluminum-rich rimming has not been found; it too may be unnoticeable with the two-micron beam diameter of the electron microprobe, or may have been "erased" by the redeposition of chromium during the production of ferrit-chromite.

Finally, two conclusions are supported by this study of the State Line chromites: (1) Mobilization of chromium by deuteric solutions may be more likely than has heretofore been considered possible. (2) The ferrit-chromit rind texture in the Pennsylvania-Maryland State Line district can be interpreted to support serpentinization at temperatures as low as 200°C (Bowen and Tuttle, 1949) or even, in part, at ambient conditions, as has been suggested by Barnes and O'Neil (1969) for some western U. S. alpine ultramafics. However, the ferrit-chromit inlaid textures of the Stillwater chromites seem to indicate that fairly high temperatures for serpentinization (auto-metamorphism?) are needed to mobilize the aluminum ion.

Acknowledgments

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