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THE RESPONSE OF CHLORITE TO METASOMATIC ALTERATION IN APPALACHIAN ULTRAMAFIC ROCKS

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ABSTRACT

Seventeen metamorphosed ultramafic bodies in the Precambrian Ashe Formation of the Blue Ridge Province of the southern Appalachians in North Carolina and Virginia were formed from a single protolith, a dunite; differing degrees of metasomatism and recrystallization distinguish the more altered (Todd-type) from the less altered (Edmonds-type) bodies. Chlorite, due to its extensive solid-solution, is a sensitive indicator of the extent of metasomatic alteration. The variation in its Fe/(Fe+Mg) and Al/(Al+Si) values is consistent with differing degrees of the same metasomatic process operating on a single protolith. The linear variation of the two ratios demonstrates concomitant variation of two crystallochemically independent but geologically dependent variables.

Keywords: chlorite, metasomatism, ultramafic bodies, Appalachians, Blue Ridge Province.

SOMMAIRE

Dix-sept massifs ultramafiques métamorphisés de la formation Ashe (Précambrien) de la province dite de Blue Ridge, dans le Sud des Appalaches, en Caroline du Nord et en Virginie, ont été formés aux dépens d'un seul protolithe dunitique. Le degré de métasomatisme et de recristallisation est variable, et distingue les massifs de type Todd, qui sont plus altérés, de ceux qui le sont moins, dit de type Edmonds. Vu les variations possibles dans sa composition, la chlorite s'avère un indicateur sensible du degré d'altération métasomatique. Les variations des rapports Fe/(Fe + Mg) et Al/(Al + Si) étayent l'hypothèse qu'un seul processus a affecté un seul protolithe à divers degrés. La variation linéaire des deux rapports démontre la covariation de deux facteurs cristallochimiquement indépendants mais géologiquement liés.

(Traduit par la Rédaction)

Mots-clés: chlorite, métasomatisme, massifs ultramafiques, Appalaches, province de Blue Ridge.

INTRODUCTION

Scotford & Williams (1983) investigated seventeen metamorphosed ultramafic bodies in the Precambrian Ashe Formation of the southern Appalachians. The bodies are exposed along a 150-km northeast-trending belt from West Jefferson, North Carolina to Floyd, Virginia (Fig. 1). Using results of mineralogical, textural and whole-rock chemical analyses, Scotford & Williams demonstrated that the ultramafic bodies were all derived from the same protolith, most probably an ophiolitic dunite that contained minor amounts of enstatite. The metamorphic mineral-assemblages of individual bodies constitute subgroups drawn from the larger group consisting of olivine, enstatite, tremolite, anthophyllite, antigorite, talc, chlorite, magnetite and dolomite.

Although the ultramafic bodies occur in the garnet, staurolite and kyanite metamorphic zones of the amphibolite facies as recognized in the country rock, no correlation exists between the mineral assemblages in the ultramafic rocks and these metamorphic zones. Trommsdorff & Evans (1974) described a series of mineral assemblages in Alpine ultramafic rocks that have undergone prograde regional metamorphism from an original serpentine-bearing stage. The sequence, applicable to the rocks under study here, is (1) antigorite + talc + tremolite, equivalent to the staurolite–kyanite and lower zones of pelitic rocks, (2) forsterite + talc, equivalent to metamorphism at slightly higher than the kyanite zone, (3) forsterite + anthophyllite + tremolite, a somewhat higher-grade assemblage, and (4) tremolite + forsterite + enstatite, an assemblage roughly equivalent to the sillimanite zone. Although these assemblages occur in some of the ultramafic bodies described here, their distribution does not correspond to the metamorphic grade of the country rock as indicated by the isograds mapped in the Ashe Formation (Fig. 1) by Rankin *et al.* (1972). There is no correspondence between the occurrence of these assemblages and indicated metamorphic grade of the country rock. Moreover, there is no systematic geographic distribution of these assemblages regardless of the grade of the country rock, and in several cases, assemblages representing different grades occur in the same body. Scotford & Williams (1983) concluded that the observed mineral distribution does not reflect a prograde regional metamorphism of serpentinite, but a two-stage retrograde recrystallization of a dunite or harzburgite protolith. Observations that support this assertion are described in Scotford & Williams (1983), but critical to this con-

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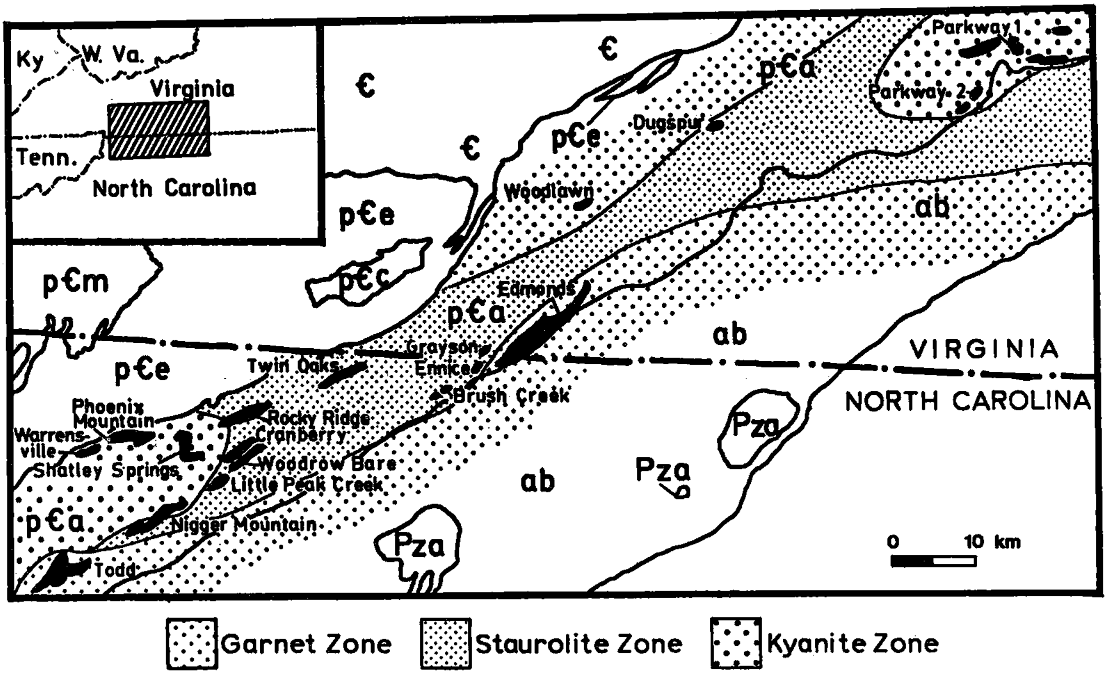

FIG. 1. Location of ultramafic bodies in the eastern Blue Ridge in North Carolina and Virginia. pCe Elk Park Plutonic Group, pCc Crossnor Plutonic Group, pCa Ashe Formation, pCm Mount Rodgers Formation, ab Alligator Back Formation, C Cambrian sediments, and Pza Spruce Pine Plutonic Group. After Rankin *et al.* (1972).

clusion is the occurrence of antigorite pseudomorphs after tremolite. Whether the tremolite, olivine, and chlorite crystallized simultaneously or appeared sequentially, it is quite evident that serpentinization followed rather than preceded their formation.

Scotford & Williams (1983) showed that the rocks from the ultramafic bodies can be divided into two principal petrographic groups on the basis of mineral association and major- and trace-element concentrations. The first group, designated the "Todd type" after the largest body representative of this group, is characterized by high concentrations of tremolite and chlorite, with lesser talc and minor amounts of olivine. The second group is called the "Edmonds type" because that large body is typical of the group. These bodies are characterized by higher concentrations of olivine, antigorite, anthophyllite and talc, and lesser amounts of tremolite and chlorite. The Todd-type bodies characteristically have lower abundances of magnesium and nickel and higher abundances of calcium, aluminum, manganese and zinc as compared to the Edmonds-type bodies. Iron is somewhat more abundant in the Todd-type bodies, and the concentration of cobalt is not significantly different in the two types of bodies. The authors concluded that the contrasting characters of these two types of bodies reflect differing degrees of recrystallization and metasomatism of the original protolith. The following observations support the single-protolith hypothesis: (1) both groups of bodies occur in the same stratigraphic unit (the Ashe Formation) and lie approximately along the same structural trend, (2) both tend to be elongate in the prominent S_1 foliation trend, (3) in several bodies that are dominantly of Edmonds type, samples of Todd-type rocks can be found, and (4) Todd-type samples commonly contain relict olivine and porphyroclasts of tremolite, minerals characteristic of the less recrystallized Edmonds-type rocks. The metasomatism, they concluded, involved the removal of Mg and Ni from the protolith and the addition of Al, Ca, Fe, Mn and K to the ultramafic rocks.

This study of chlorite from all seventeen ultramafic bodies was undertaken to further characterize the composition and degree of alteration of each of the ultramafic bodies. Chlorite was chosen because it is ubiquitous in most metamorphosed ultramafic bodies, including those studied by Scotford & Williams (1983), and also because it exhibits a wide range of solid solution. It was felt that major chemical changes, which resulted from different degrees of metasomatism of the protolith, could be reflected in the composition of the chlorite in the individual metamorphosed ultramafic bodies.

CRYSTAL CHEMISTRY OF THE CHLORITE

Chlorite occurs in both the Edmonds- and Todd-type ultramafic bodies as colorless or faintly green-tan pleochroic grains; the more iron-rich chlorite of the Todd-type samples shows somewhat stronger pleochroism and brown abnormal interference-colors. In the Edmonds-type bodies it occurs as a matrix mineral replacing olivine or, in those that display a foliation, it is concentrated in the foliation planes. In the Todd-type bodies the chlorite is concentrated in the pressure shadows of relict olivine phenocrysts as well as in the foliation planes.

Several X-ray-diffraction methods, based on the response of the chlorite structure to octahedral and tetrahedral substitutions, have been derived to allow rapid determination of the Al/(Al + Si) and the Fe/(Fe + Mg) ratios in chlorite samples. The techniques will not be discussed at length here for they are well summarized by Bailey (1972), who evaluated the several methods then extant. Briefly, the methods are based upon the contraction of the *c* dimension (and thus d_{001}) in response to tetrahedral substitution of Al^{3+} for Si^{4+}, and expansion of the *b* dimension (and thus d_{0k0}) in response to substitution of the ferrous ion for Mg in the octahedral sites.

Chlorite samples from the seventeen ultramafic bodies were analyzed by X-ray diffraction and electron microprobe. X-ray-diffraction data were obtained using chlorite powders and fluorite (*a* 5.4626 Å) as an internal standard. In order to bring planes other than (001) into the diffraction condition, powders were mixed in silica gel to approximate a random orientation. Least-squares unit-cell refinement was performed using the fluorite-corrected 2θ values. The refined *b* and *c* unit-cell parameters of thirty chlorite samples are presented in Figure 2. As seen in that figure, the distinction between the Todd- and Edmonds-type bodies of Scotford & Williams is also revealed in the *b* and *c* parameters of the chlorite in these ultramafic bodies. The less-altered Edmonds-type bodies contain chlorite with a larger *c* cell parameter, indicating lower Al/(Al + Si) values. The range between the mean values of *c* of the two group-averages is 31 times the average estimated standard deviation of the *c* cell parameter. The *b* parameter of the Todd chlorite shows a contraction over that in chlorite from the Edmonds-type bodies, indicating a lower Fe/(Fe + Mg) ratio. The range between the mean values of *b* for the two groups is 11 times the average estimated standard deviation of the *b* parameter.

To support the results of X-ray-diffraction analysis, the electron-microprobe analysis of selected samples was undertaken. Analyses were obtained using an Etec autoprobe and well-characterized standards. Energy-dispersion analyses of elements with *Z* greater than 9 showed that only Mg, Al, Si, Cr and Fe are present. Quantitative analyses for these elements by wavelength dispersion showed no significant difference in concentration among chlorite grains within any thin section; zoning within a single grain was observed only in one sample. Ferric iron contents (calculated knowing [^{IV}Al - ^{VI}Al]) of the chlorite grains average 0.10(8) atoms per half-cell. An average of 0.05(2) Cr atoms per half-cell was also found. The Fe/(Fe + Mg) ratio was calculated using total Fe atoms, and the Al in the ratio

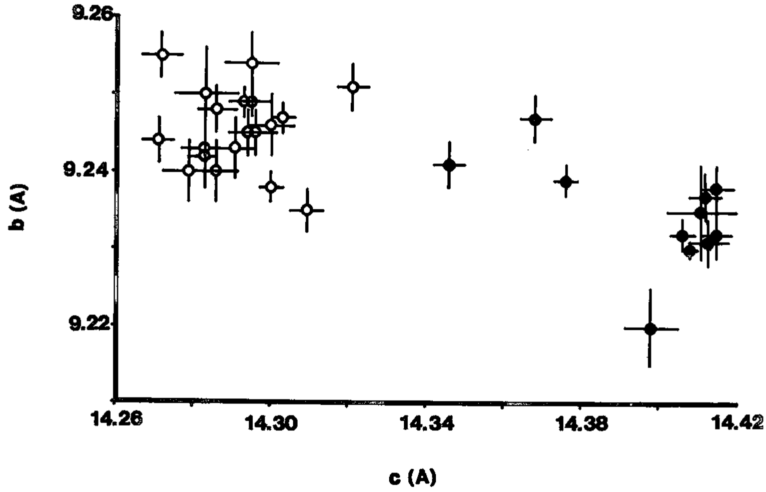

FIG. 2. Least-squares-refined *b* and *c* cell parameters of chlorite. Dark circles represent Edmonds-type bodies, open circles represent Todd-type bodies. Error bars represent one estimated standard deviation.

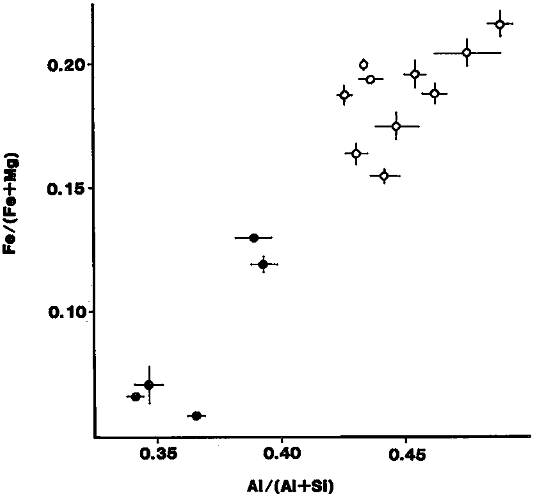

FIG. 3. Fe/(Fe + Mg) *versus* Al/(Al + Si) ratios in chlorite samples. Dark circles represent Edmonds-type bodies, open circles represent Todd-type bodies. Errors bars represent one standard deviation. Where no bars are present, the points enclose one standard deviation.

Al/(Al + Si) is comprised of total (Al + Cr) atoms without distinction between ^{IV}Al and ^{VI}Al.

Figure 3 presents Fe/(Fe + Mg) *versus* Al/(Al + Si) values for the analyzed grains. These microprobe results serve to support the results of X-ray-diffraction analysis; the Edmonds-type chlorite grains exhibit lower Fe/(Fe + Mg) and Al/(Al + Si) values than the Todd-type grains.

DISCUSSION

Figures 2 and 3 support the conclusion of Scotford & Williams that the present chemistry of the ultramafic bodies results from differing degrees of a single metasomatic process operating on the same protolith. Based on whole-rock data, they demonstrated the removal of Mg from and the influx of Fe and Al into the ultramafic protolith. This metasomatism is monitored by the chlorite compositions of the rocks in the two metamorphic groups. The X-ray (*b versus c*) and the microprobe data [Al/(Al + Si) *versus* Fe/(Fe + Mg)] give significance values of < 1% for the *r* statistic, demonstrating concomitant variation of two crystallochemically independent variables (Fe→Mg and 2Al→Mg,Si substitution) that both reflect different intensities of a single metasomatic process operating on the same protolith.

The results of this study demonstrate that chlorite is a sensitive indicator of the extent of metasomatic alteration in the ultramafic bodies. The Fe/(Fe + Mg) and Al/(Al + Si) ratios of chlorite, as determined by X-ray diffractometry and electron-microprobe analysis, seem to monitor the metasomatic exchange of Al, Fe and Mg between the metamorphosed ultramafic rocks and the country rock.

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