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Ionic Substitution in Iron-Magnesium Chlorites*

By

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Introduction

Chemical investigations of chlorites have been made by many workers as reviewed by HEY (1954). TSCHERMAK (1890, 1891) divided them into orthochlorites and leptochlorites, and explained the orthochlorites to be isomorphous mixtures of serpentine and amesite. This explanation has been extended to the leptochlorites by WINCHELL (1926), who has shown that the leptochlorites are oxidized chlorites and not essentially different from orthochlorites. WINCHELL'S interpretation is supported by HEY and others, but HALLIMOND (1939) and MIYASHIRO (1957) believe the actual existence of leptochlorites. TSCHERMAK concluded the solid solution range of orthochlorites is from pennine to amesite, while HALLIMOND has suggested that there exist a gap between corundophilite and amesite. Today it is well known that all of the end-members of WINCHELL'S classification are not of chlorite structure, but of kaolin-type structure. Recent classifications by ORCEL et al. (1950), HEY (1954), and others, however, are made for the wide field, and the solid solution range of chlorites is customarily considered as very wide.

In my recent work (SHIROZU, 1958a) of the well-crystallized chlorites from Japan, it has been clarified that they are orthochlorite, $[(\mathrm{Mg}, \mathrm{Fe}^{2+})_{6-n}(\mathrm{Al}, \mathrm{Fe}^{3+})_n]$ $[\mathrm{Al}_n\mathrm{Si}_{4-n}]\mathrm{O}_{10}(\mathrm{OH})_8$, and their X-ray powder patterns are divided into 14A-monoclinic and 14A-ortho-hexagonal types. Their cell dimensions suggest that they are not so variable in aluminum content and iron chlorites generally have larger aluminum content as compared with magnesium chlorites. This paper presents and discusses these points.

Results

Through the measurements of the cell dimensions and the refractive indices (SHIROZU, in press), the well-crystallized chlorites of iron-magnesium series with various occurrences in Japan (from hydrothermal veins, crystalline schists, serpentinites. etc.) are plotted on a chemical diagram (Fig. 1) together with the chemically analyzed data. Fig. 1 shows the following distinct characters: substitution of Al^{3+} for Si^{4+} (and Mg^{2+} or Fe^{2+}) is limited to a considerably narrow

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range, and there is a general trend from magnesium chlorites to iron chlorites that the aluminum content is greater in the latter than in the former; *n* values of the above formula range from 1.0 to 1.3 for most of magnesium chlorites, and from 1.3 to 1.5 for iron chlorites. The previous data summarized by WINCHELL (1926, 1936), HÖDL (1941), and HEY (1954) bear similar tendencies to the above one, but are not so conspicuous. Many previous analyses which are distant from the present field may probably be either inaccurate analyses or analyses of mixtures or of minerals not having pure or well-crystallized chlorite structure as discussed later.

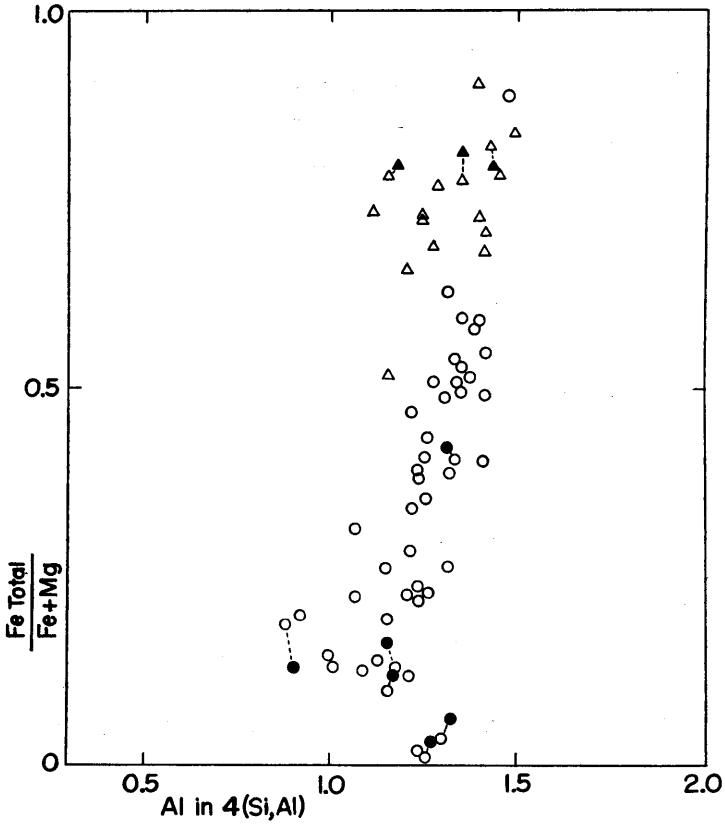

Fig. 1. Chemical composition of well-crystallized iron-magnesium chlorites from Japan. Open marks are plotted through X-ray and optical measurements. Black marks are based on chemically analyzed data, and jointed by broken lines to corresponding open marks in comparison.

△▲ Ortho-hexagonal type. ○● Monoclinic type.

Discussion

The fact that the substitution of Al^{3+} for Si^{4+} and Mg^{2+} (or Fe^{2+}) in the well-crystallized chlorites is limited to a narrow range may be closely related to the stability of chlorite structure. It is well known that the structure of chlorite is of regular interstratification of talc-like layer and brucite-like layer, and is maintained by the ionic bond between these two layers owing to the Al^{3+} substitution. Since this structural scheme is unique as compared with the 1:1 layer silicate minerals having the same-type composition, the above results suggest that this unique structure can be stably maintained under only the situation of the certain range of the ionic bonding forces between the two layers, and it is expected that the more distant from this range the composition is, the chlorite structure may become the more unstable and difficult to crystallize well. The low crystallinity and some bearings of the Usagiyama chlorite and aluminian serpentine (SHIROZU, 1958b), both being inferred to be intermediate between serpentine and well-crystallized chlorite in aluminum content, may be explained from this point of view. Some clay chlorites or pseudo-chlorites may be also explained similarly. Probably these poorly crystalline minerals are neither orthochlorite nor pure chlorite in composition, but may be regarded as " intermediate minerals of the deviation type " of SUDO (1959), probably grading into vermiculites or montmorillonite minerals. Some of leptochlorites may belong to this category of minerals.

The general trend that the aluminum content increases with increasing iron content results in the basal spacings in a trend that the chlorites containing greater iron generally give the smaller values of the spacing. ENGELHARDT's suggestion (1942) that a decrease in basal spacing is related to the substitution of Fe^{2+} for Mg^{2+}, and MARTIN's data (1955) that high iron chlorites have smaller basal spacings than low iron chlorites would be interpreted as the distinct expression of this trend.

This general trend is similar to the facts observed in biotites. Although its causes might be got in geochemical reasons, it is also possible to explain by the proportion between the dimensions of tetrahedral and octahedral layers in the *ab*-plane. Because of the ionic radii of Si^{4+}, Al^{3+}, Mg^{2+}, and Fe^{2+}, increasing in this order, in magnesium chlorites the tetrahedral (Si^{4+} and Al^{3+}) and octahedral (Al^{3+} and Mg^{2+}) layer may fit in each other at about the composition of $n=1.0\sim1.3$ in the above formula, while when Fe^{2+} substitute for Mg^{2+}, the octahedral layer extends so that the simultaneous increasing of Al^{3+} which brings extension of the tetrahedral layer and contraction of the octahedral layer may be favourable to hold the proportion of dimensions. BATES (1959) has concluded that the amounts of misfit between tetrahedral and octahedral layers in chlorites are much smaller than in the most 1:1 layer silicate minerals. The present explanation may be in accordance with his interpretation in the final meaning.

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