along the spectrochemical series for octahedrally co-ordinated $Fe^{2+}X_6$ groups. Consequently Fe^{2+} will tend to avoid sites co-ordinated by F, as suggested by the site populations exhibited by fluor-richterite(34) and (35). This argument is supported by data for micas (Rosenberg & Foit 1977) and humites (Ribbe & Gibbs 1972).

The C.F.S.E. method, as with the Madelung-energy and site-potential methods, predicts ordering on the basis of part of the total structure-energy, with the assumption that the remainder of the structure-energy terms remain constant and thus do not contribute to the ordering process. A much more general method has been suggested (Strens & Wood 1970, Wood & Strens 1970), but considerable difficulties remain to be solved before successful application.

General considerations

There has been considerable confusion between site occupancy, which is an experimental result, and site preference, which is an *interpretation* of an experimental result. Consider the Fe–Mg–Mn amphiboles. In the magnesio-cummingtonite - grunerite series, Fe^{2+} shows the site occupancy $M(4) > M(1) \sim M(2) \sim M(3)$, whereas in the grunerite - dannemorite series, Fe^{2+} shows the site occupancy $M(4) < M(1)$, $M(2)$, $M(3)$; in both cases, the pattern of site occupancy presumably reflects the Fe^{2+} site-preference in the presence of Mg and Mn, respectively. In the ternary Fe–Mg–Mn amphiboles, Fe^{2+} may show the site occupancy $M(4) > M(1)$, $M(2)$, $M(3)$ or $M(4) < M(1)$, $M(2)$, $M(3)$, depending on the amount of Mn in the amphibole; with regard to Mg, Fe^{2+} shows the site preference $M(4) > M(1)$, $M(2)$, $M(3)$; with regard to Mn, Fe^{2+} shows the site preference $M(4) < M(1)$, $M(2)$, $M(3)$, whereas based on the observed site-occupancies, the site preference of Fe^{2+} changes with composition. Similar effects may occur in such combinations of cations as (Mg,Fe^{2+},Mn), (Mg,Fe^{2+},Li) or ($MgFe^{2+},Zn$), and it is probably simpler to refer to cation-ordering patterns rather than site preferences, particularly in amphiboles.

OXIDATION–DEHYDROXYLATION IN AMPHIBOLES

The behavior of amphiboles on heating has been the subject of a large number of studies over the past one hundred years. Early studies were prompted by the similarity of heated hornblende to "basaltic hornblende", and by the controversy concerning the origin of the peculiar optical properties of "basaltic hornblende". Much of the early work is summarized by Barnes (1930), who noted three different views of the changes in hornblende upon heating: (i) oxidation of $Fe^{2+} \rightarrow Fe^{3+}$, (ii) dehydration, and (iii) inversion (phase transformation). Barnes (1930) performed extensive heating experiments on amphiboles both in air and in hydrogen, showing that: (i) iron-poor amphiboles do not change upon heating whereas iron-bearing amphiboles heated in air show a marked conversion of $Fe^{2+} \rightarrow Fe^{3+}$ and a loss of water, generally changing color from green to brown; (ii) the weight loss on heating (to 800°C) is only a fraction of the water obtained by analysis, and (iii) iron-bearing amphiboles do not change when heated in hydrogen. In addition, brown hornblende changes back to green hornblende upon heating in hydrogen. From this, Barnes (1930) concluded that oxidation of Fe^{2+} to Fe^{3+} occurs upon heating iron-bearing hornblende, accompanied by dehydration where hydrogen was given off, allowing the oxidation to proceed.

Addison *et al.* (1962a, b) examined the oxidation of crocidolite by heating in specific atmospheres and measuring the products generated. They heated crocidolite in air, oxygen and vacuum, resulting in partial oxidation of the crocidolite and loss of uncombined water, and proposed that oxidation involves simultaneous oxidation of Fe^{2+} and OH according to the equation

$$4Fe^{2+} + 4(OH)^- + O_2 \rightarrow 4Fe^{3+} + 4O^{2-} + 2H_2O$$

with a secondary surface reaction

$$4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O^{2-}.$$

The surface reaction is maintained by the migration of electrons and protons through the crystal. Incomplete oxidation at the temperature of study (450°C) was attributed to a blocking interaction by Mg cations at the octahedrally co-ordinated sites, hindering electron migration along the Z direction (Addison & White 1968a). Addison *et al.* (1962b) performed rate studies on the oxidation of crocidolite and found that oxidation at constant partial pressure of oxygen proceeds at a constant rate until complete oxidation occurs (between 350 and 480°C). They also proposed that there is a "strongly held" surface layer of water that inhibits oxidation if the temperature and partial pressure of oxygen are too low. Both studies also indicated that fibre formation in crocidolite produces partial oxidation at ambient temperatures. Rate studies were also carried out by Clark & Freeman (1967). Addison & Sharp (1962, 1968) heated both fresh and oxidized crocidolite in hydrogen, and suggested that zero-valent iron is formed as a reaction product in all cases, and that rehydroxylation does occur in some cases.

Hodgson *et al.* (1965) examined in detail the oxidation–dehydroxylation of crocidolite by differential thermal analysis (D.T.A.), thermogravimetric analysis (T.G.A.), dehydration and weight-loss experiments, X-ray diffraction and infrared absorption spectroscopy. They showed that on heating crocidolite in argon, nitrogen, oxygen and air, uncombined water is lost in the range 50–400°C. In addition, heating in argon or nitrogen produces a loss of tensile strength at 300–400°C. At higher temperatures in argon or nitrogen (500–600°C under static conditions, 570–700°C under dynamic conditions), endothermic dehydroxylation occurs, to form what appears to be an amphibole anhydride from the X-ray diffraction and infrared spectral examination. On heating in air, an oxy-amphibole is formed in the ranges 300–450°C (static conditions) and 400–600°C (dynamic conditions). Heating in hydrogen produced no change in the amphibole below 530°C, at which temperature the crocidolite broke down to a mixture of pyroxene, metallic iron, cristobalite and liquid. Hodgson (1965) examined the thermal decomposition of weathered crocidolite, noting that the D.T.A. pattern of decomposition is not affected by weathering but that the final decomposition temperature is a function of the Mg content; this was confirmed for several amphibole types by Freeman (1966). Natural weathering tends to remove ~¼ of the OH groups, with the Fe^{2+}/Fe^{3+} ratio approaching unity; however, the physical characteristics of the fibre are not materially affected.

Gibb & Greenwood (1965) examined natural and oxidized crocidolite and natural cummingtonite by Mössbauer spectroscopy. They showed that the blue color of crocidolite was not due to rapid oscillation of electrons between Fe^{2+} and Fe^{3+}, and that there was no evidence of oxidation states of iron below 2+ in oxidized and reduced amphiboles, as suggested by Addison & Sharp (1962).

Littler & Williams (1965) measured the electrical conductivity of natural and oxidized crocidolite, showing that the amphibole fibres have a high conductivity along the fibre length but very low conductivity across the fibre direction. They suggested that this high conductivity is associated with $Fe^{2+} \longleftrightarrow Fe^{3+}$ charge-transfer and showed the presence of an $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer band in the reflectance spectrum of natural crocidolite; the band disappears upon heating and oxidation.

Extensive studies on the dehydroxylation of crocidolite, asbestiform cummingtonite and tremolite by infrared and X-ray methods were carried out by Patterson (1965) and Patterson & O'Connor (1966). Heating crocidolite in air caused a reduction in the intensity of the principal OH-stretching band(s) and slight band broadening in the range 350–500°C. On further heating, an amphibole-type vibrational spectrum persisted until ~900°C when breakdown of the amphibole occurred. Heating crocidolite *in vacuo* produced dehydroxylation in the range 500–600°C with the same effects as before. The behavior of asbestiform cummingtonite was similar to that of crocidolite. However, for tremolite, no change occurred in the infrared spectrum until dehydroxylation and breakdown at 1000°C (*cf.* Wittels 1951, 1952). Patterson & O'Connor (1966) noted the fine structure of the principal OH band for crocidolite and cummingtonite and suggested that it is due to cation disorder at the M(1) and M(3) sites (*cf.* Burns & Strens 1966, Strens 1966). They also noted the preferential decrease in intensity of the bands at 3633 and 3618 cm^{-1} relative to the 3649 cm^{-1} band and suggested that this is indicative of removal of protons from certain sites in the structure. Wilkins & Vedder (1968) reviewed previous studies and examined heated and deuterated amphiboles by infrared absorption spectroscopy. They concluded that oxidation at temperatures not exceeding 700°C (in actinolite and cummingtonite) may involve donation of electrons by next-nearest-neighbor Fe^{2+} cations, but that no cation exchange needs to be assumed.

Ernst & Wai (1970) have extensively studied oxidation–dehydroxylation relationships in alkali amphiboles using infrared and Mössbauer spectroscopy and X-ray diffraction. They showed that dehydrogenation occurs rapidly (~1–2 hours) at 705°C and atmospheric pressure. Some of the infrared absorption spectra reported by these authors are shown in Figure 103; spectra of the unheated samples show narrow A peaks (MgMgMg–OH configuration) and wide B and C peaks ($MgMgFe^{2+}$–OH and $MgFe^{2+}Fe^{2+}$–OH configurations), the latter resulting from incomplete overlap of the B′ and B″ and C′ and C″ peaks (see Table 53). Upon heating, the B and C peaks (configurations involving Fe^{2+}) are selectively lost whereas the A peak remains unaffected. This provides good evidence for oxidation–dehydoxylation proceeding by the reaction

$$Fe^{2+} + OH \rightarrow Fe^{3+} + O^{2-} + \tfrac{1}{2}H_2$$

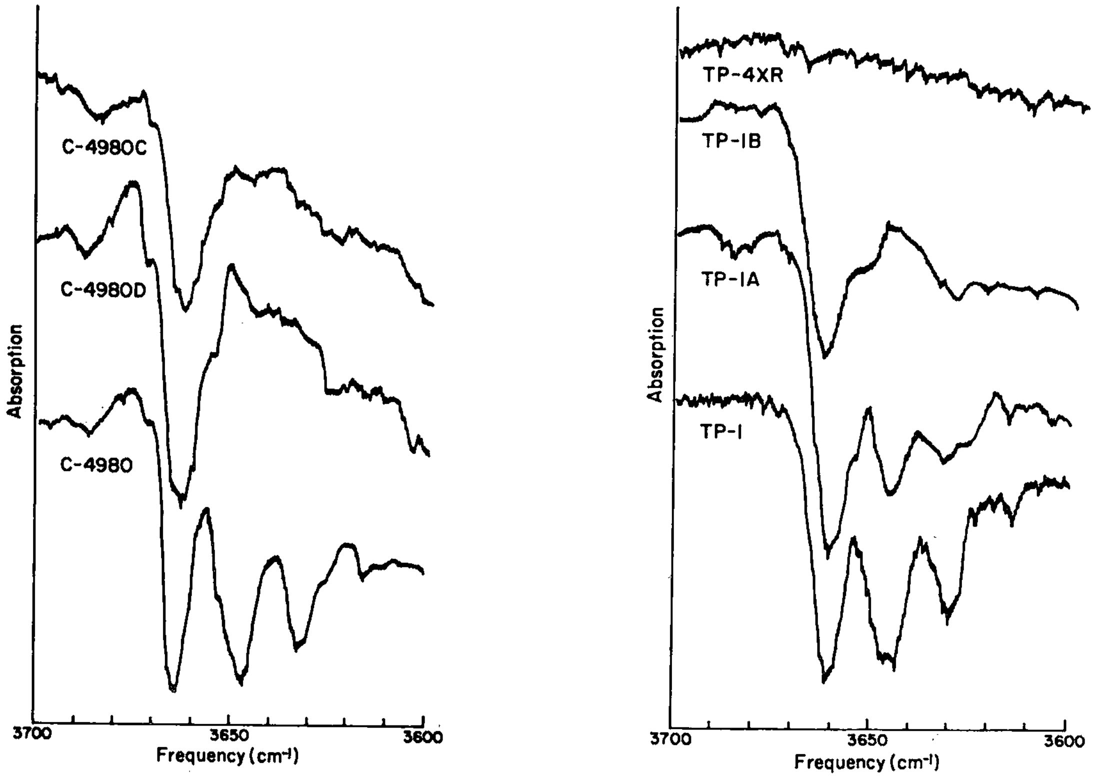

FIG. 103. Infrared absorption spectra of natural and heated magnesio-riebeckite (C–4980) and glaucophane (TP–1) [from Ernst & Wai (1970)]. Specimens C–4980D and TP–1A were heated at one atmosphere, $f(O_2) = 10^{-0.3}$, T = 705°C for one hour; C–4980C and TP–1B were heated at one atmosphere. T = 705°C for 94 hours. TP–4XR was hydrothermally treated at 2 kbar P_{fluid}, $f(O_2) \sim 10^{-22}$, T = 513(10)°C for 15,667 hours. Note the rapid loss of bands due to configurations involving Fe^{2+}.

The Mössbauer spectra of the heated products indicate that dehydroxylation is accompanied by oxidation, with extra Fe^{3+} doublets in the spectra being assigned to Fe^{3+} at the M(1) and M(3) sites. However, there is additional information in the spectra of Figure 103. The A peak is much wider in the spectra of the heated material than in the spectra of the unheated material; this is the result of substitutional broadening that occurs because of the much wider variety of next-nearest-neighbor configurations in the heated material due both to oxidation of Fe^{2+} in next-nearest-neighbor sites and to cation disorder at these sites. Confirming the fact that considerable cation disordering has occurred on heating is the presence of the peak at ~3785 cm^{-1}. This is due to the MgMgMg–OH configuration, shifted to higher frequencies by occupancy of the A site; in line with this assignment, this peak is absent in glaucophane{15}, where the A site is vacant (see Appendix F) and present in calcian magnesio-riebeckite{27}, where the A site is partly filled with Na. Upon heating, this band appears in glaucophane{15} and is intensified in calcian magnesio-riebeckite{27}, indicating that Na is displaced from the M(4) site into the A site; the presence of vacancies at M(4) undoubtedly contributes to the broadening of the A peak in spectra of the heated samples. There are also small peaks in these spectra below 3660 cm^{-1}; these may be assigned to configurations involving Fe^{3+}. Mössbauer spectra of heated amphiboles (Ernst & Wai 1970) show that dehydroxylation is accompanied by oxidation of Fe^{2+} to Fe^{3+}; spectra corresponding to the infrared spectra of Figure 103 are shown in Figure 104. For glaucophane{15} heated at 705°C for 1 hour, the Fe^{2+} at M(1) and M(3) is significantly reduced but still present, the infrared absorption spectra showing the B and C peaks still present but of reduced intensity. After 95 hours at

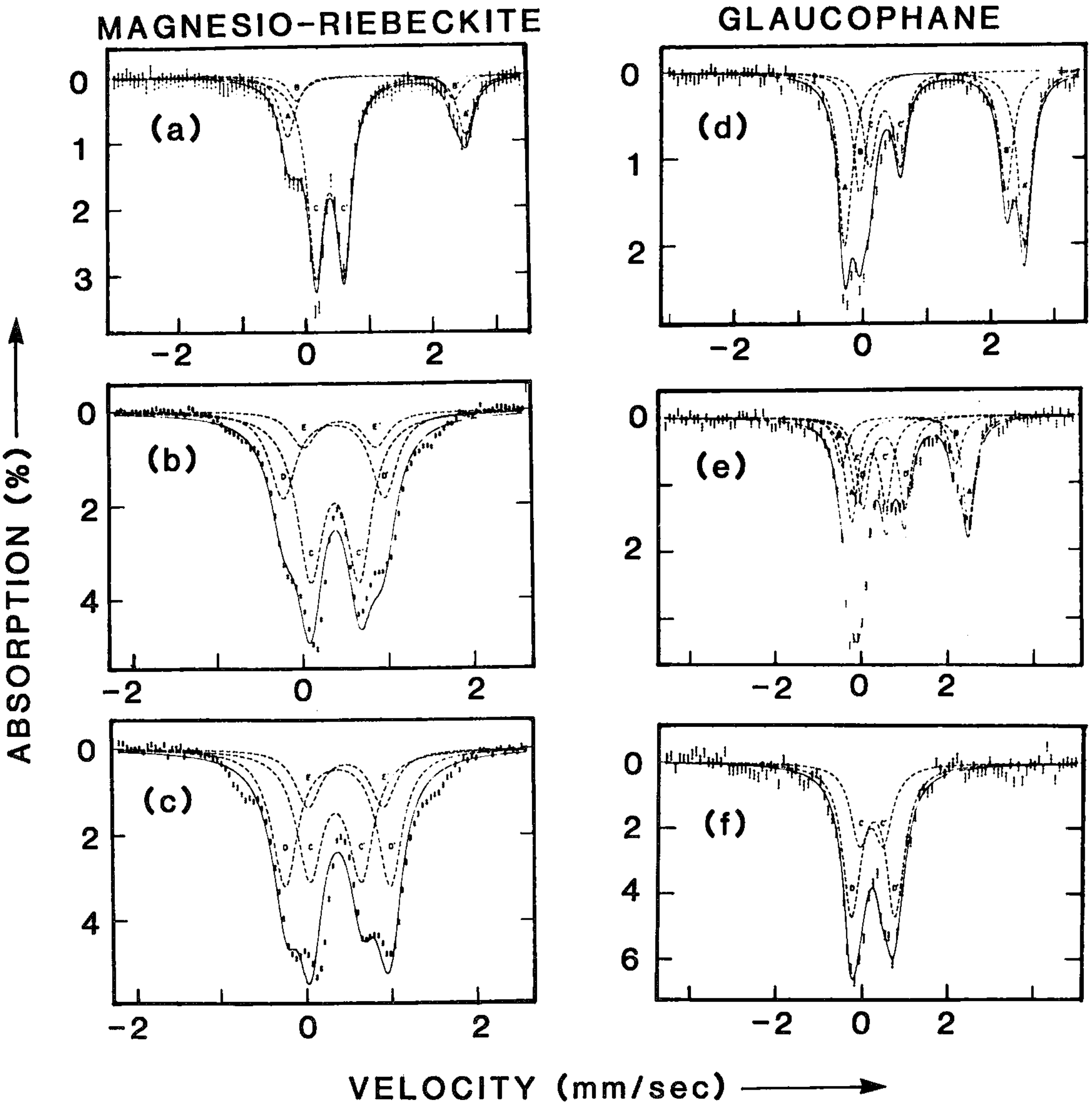

FIG. 104. Mössbauer spectra of natural and heated magnesio-riebeckite (C–4980) and glaucophane (TP–1), corresponding to the infrared absorption spectra of Fig. 103 [from Ernst & Wai (1970)].

707°C, the Mössbauer spectrum of glaucophane{15} shows no Fe^{2+} and the infrared absorption spectrum shows no B or C bands present. It is the same story for calcian magnesio-riebeckite{27}, except that the oxidation–dehydroxylation process seems to have proceeded more quickly, with no Fe^{2+} or B and C bands present after 1 hour at 704°C. Inspection of the Mössbauer spectra for calcian magnesio-riebeckite{27} shows that considerable cation disordering has occurred upon heating. In the unheated material, the Fe (as Fe^{3+}) is strongly ordered at M(2), with only small amounts of Fe (as Fe^{2+}) at M(1) and M(3). In the material heated for 94 hours, all Fe^{2+} is oxidized to Fe^{3+} but the Mössbauer spectrum can be resolved into component Fe^{3+} peaks of much more equal intensity (this is apparent despite the poor fit of the resolved spectrum to the experimental data); thus Fe^{3+} must have migrated from M(2) to the M(1) or M(3) sites (or both) upon heating.

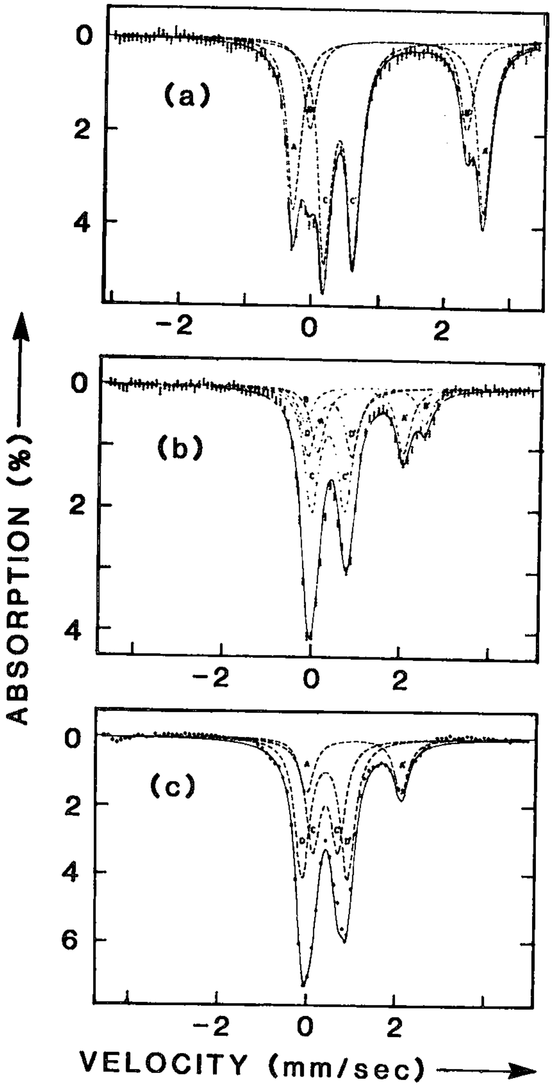

FIG. 105. Mössbauer spectra for natural (top) and heated (bottom) riebeckite [from Ernst & Wai (1970)].

In iron-rich amphiboles, there is insufficient OH to oxidize all the Fe^{2+} by this oxidation–dehydroxylation, and even completely dehydroxylated material contains Fe^{2+}, as shown in Figure 105 for riebeckite{29} (see Appendix F for details). Comparison of the spectra for material heated for 1 hour and 94 hours shows that oxidation of Fe^{2+} still proceeds in the absence of OH, but it is a much slower process with a completely different mechanism. Similarly, in iron-poor amphiboles, dehydroxylation proceeds much more slowly once the oxidation–dehydroxylation mechanism has resulted in complete oxidation of all the Fe^{2+}, but the mechanism of charge compensation (if any) is not known.

Rouxhet *et al.* (1972) examined the progressive oxidation of fibrous grunerite and crocidolite. This process appears to take place continuously over a wide range of temperatures in both materials. In crocidolite, there is a 1:1 correlation between the FeO content and the loss of OH from the sample (measured as the sum of the integrated absorbances of the OH bands), indicating that while OH is present, oxidation proceeds by dehydrogenation. In fibrous grunerite, there is a 3:2 correlation between FeO content and OH content, indicating that dehydrogenation and oxidation occur together (Addison *et al.* 1962a, b, Hodgson *et al.* 1965, Ernst & Wai 1970). Oxidation is accompanied by a loss of tensile strength of the fibres (*e.g.*, Aveston 1969) that "seems to be due to thermal decomposition". When heated under vacuum, oxidation increases with increasing temperature, until it reaches a maximum, above which reduction begins. Below the temperature of maximum oxidation, hydrogen is released by progressive heating; above the temperature of maximum oxidation, oxygen is released. Rouxhet *et al.* (1972) also suggested that the X-ray pattern of crocidolite anhydride reported by Hodgson *et al.* (1965) is actually due to oxy-crocidolite, with crocidolite anhydride being amorphous.

Some preliminary structure-refinement results on oxidized amphiboles have been reported by Ungaretti (1980). Structure refinements before and after heating show a reduction in cell dimensions, considerable shortening of all the bonds to O(3) and disappearance of the H atom in Fourier maps. Of considerable interest is the fact that the oxidation–dehydroxylation process has been accompanied by considerable disordering of cations. In particular, Na has moved from the M(4) site to the A site, leaving vacancies at M(4); this confirms the conclusions drawn from the 3685 cm^{-1} bands in Figure 103. In addition, these results confirm the suggestions of cation reordering over the M(1), M(2) and M(3) sites from the Mössbauer spectra of Figure 104.

HIGH-TEMPERATURE CRYSTALLOGRAPHY

Although a large number of heating studies on amphiboles have been carried out over the past fifty years, these have been concerned mainly with oxidation–dehydroxylation relation-