

Structural adjustments accompanying oxidation-dehydrogenation in amphiboles

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ABSTRACT

Structural changes that accompany oxidation-dehydrogenation in amphiboles are examined using bond-length and bond-strength data from six crystal-structure refinements. These include tschermakitic hornblende (untreated; hydrothermally heated at 650 °C, 1 kbar, 4 d at the magnetite-hematite oxygen buffer; heated in air at 700 °C, 1 atm, 30 min) and literature data for riebeckite (untreated; heated in air at 650 °C, 1 atm, 4 d) and a natural potassian titanian magnesio-hastingsite that contains an appreciable oxy-amphibole component.

These data show that dehydrogenation results in dramatic decreases in bond strength at O(3). About half of the total decrease is compensated by shortening of M–O(3) bond lengths and preferential ordering of trivalent cations at M(1) and M(3). The ordering involves not only the Fe³⁺ produced by oxidation but also trivalent cations originally residing at M(2) in the unoxidized structures.

At least part of the remaining loss of bond strength is offset by interaction of the A-site cation with O(3). In riebeckite, this involves migration of Na from M(4) to the previously vacant A site. In tschermakitic hornblende, there is a slight loss of cations, presumably Na, from M(4) in the air-heated sample. There is also shortening of the A(*m*)–O(3) distances in both heated structures and an increase in the A(*m*) occupancy of the air-heated sample, apparently at the expense of A(2/*m*) and M(4).

Previous investigators have found that in air-heated grunerite, unlike these amphiboles, dehydrogenation is not the only initial oxidation mechanism. This may result from the fact that the availability of compensation mechanisms is limited in grunerite.

INTRODUCTION

Barnes (1930) found that Fe-poor amphiboles exhibited no changes when heated in air at about 850 °C for 3 h, whereas actinolites and hornblendes showed an increase in density, refractive indices, and birefringence, as well as a color change from green to brown. He also found that these changes could be reversed by reheating the sample in H₂. Barnes (1930) concluded that the observed changes are due to the oxidation of Fe, rather than to the decrease in water content that accompanies oxidation. By comparing the percent weight loss on heating with the analyzed water content, he also concluded that during the oxidation process, H₂ and not molecular water is lost. This conclusion suggests the dehydrogenation reaction



In the 1960s, there were a number of studies focusing on rates and mechanisms of oxidation and on the thermal decomposition of fibrous amphiboles, principally fibrous riebeckite (“crocidolite”), although some studies also in-

cluded fibrous grunerite (“amosite”). These investigations involved extensive heating experiments over a wide range of temperatures under a variety of nonhydrothermal conditions. The results of these studies have been reviewed by Hawthorne (1983). Only those points relevant to the present study are included in the following paragraphs.

In alkali amphiboles heated in air or oxygen, initial oxidation of Fe²⁺ occurs rapidly by the dehydrogenation reaction as given above. Ernst and Wai (1970) concluded that extensive dehydrogenation occurs within 1 or 2 h for alkali amphiboles heated at 705 °C in air. Ungaretti (1980) found that changes in cell parameters of several Fe-bearing amphiboles heated in air at 500 °C also indicate that extensive dehydrogenation occurs in less than 2 h. However, there is another much slower process that permits oxidation to continue even after complete dehydrogenation of samples in which the initial molar Fe²⁺ content is greater than the initial molar hydrogen content (Addison et al., 1962a, 1962b; Hodgson et al., 1965; Addison and White, 1968; Ernst and Wai, 1970).

In grunerite, unlike the alkali amphiboles and hornblende, dehydrogenation is not the only significant initial

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oxidation mechanism (Addison and Sharp, 1968; Rouxhet et al., 1972). Based on the relationship between FeO content (which measures the extent of oxidation) and the integrated absorbances of the OH-stretching bands (which measures the extent of dehydrogenation), Rouxhet et al. (1972) found that dehydrogenation could account for essentially all of the initial oxidation in heat-treated fibrous riebeckite, but only about two-thirds of the initial oxidation in heat-treated fibrous grunerite. Ghose and Weidner (1971) found that precession photographs of heated grunerite (30 min at various temperatures between 700 and 800 °C at 500-bars Ar pressure under "relatively oxidizing conditions") indicated the presence of both oxidized and unreacted grunerite. They also found that the heated samples were slightly magnetic, indicating the presence of magnetite (Ghose and Weidner, 1971).

The purpose of this study is to examine the structural implications of dehydrogenation, especially in regard to the oxidation behavior of alkali amphiboles and hornblende as contrasted to that of grunerite. Crystal-structure data for six amphiboles containing varying amounts of oxy-amphibole component are analyzed. These include three refinements of tschermakitic hornblende (Phillips et al., unpub. ms.), along with data for natural and heat-treated riebeckite (Ungaretti, 1980) and a potassian titanian magnesio-hastingsite (Papike et al., 1969; Robinson, 1971).

INFLUENCE OF OXIDATION-DEHYDROGENATION ON CATION DISTRIBUTION

Previous work

From Mössbauer spectra, Ernst and Wai (1970) were able to detect apparent cation migration in a magnesio-riebeckite heated in air for 1 h at 705 °C; appreciable cation migration in a glaucophane and a riebeckite was noted only in samples heated for longer durations. Crystal-structure refinements done before and after heating provide more precise information on cation migration. However, at present, only a few such studies have been done.

Ungaretti (1980) has reported preliminary results for a metamorphic riebeckite heated in air at 650 °C for 4 d. He showed that dehydrogenation accompanied heating, as evidenced by the absence of any significant H peak in the difference-Fourier map of the heated sample, and by a dramatic shortening of the M(1)–O(3) and M(3)–O(3) bond lengths in the structure of the heat-treated sample. This observed bond-length shortening would be expected in order to help compensate for the loss of bond strength at O(3) resulting from dehydrogenation. Ungaretti (1980) found that the number of electrons per octahedral site changed significantly after heating, which means that some migration of octahedral cations was induced by oxidation-dehydrogenation. However, the most dramatic change involved the migration of Na atoms from M(4) to the previously vacant A site, resulting in partial vacancy at M(4). Similar behavior was also observed in a

heated arfvedsonite (Ungaretti, 1980) and calcic amphiboles (Ungaretti, pers. comm., 1986, 1987). Hawthorne's (1983) interpretation of the infrared spectra of Ernst and Wai (1970) for magnesio-riebeckite and glaucophane supports the structural conclusions of Ungaretti (1980). Hawthorne (1983) noted that the band broadening observed after heating is indicative of cation disorder. Furthermore, Hawthorne (1983) attributed the increase in intensity of a small peak at 3685 cm⁻¹ in the spectra of the heated samples to an increase in the Na content of the A site at the expense of M(4).

Structure refinements have been completed by Phillips et al. (unpub. ms.) for a natural tschermakitic hornblende, as well as samples that were heated in air at 700 °C for 30 min and heated hydrothermally at 650 °C, 1 kbar for 4 d at the magnetite-hematite oxygen buffer. Details of the heating experiments are given by Clowe et al. (1988). The amount of oxidation was determined by analysis of Fe³⁺ content using the method of Fritz and Popp (1985). Although the extent of oxidation-dehydrogenation induced in these hornblende samples is considerably less than that in riebeckite (Ungaretti, 1980), similar structural variations were noted. In addition to shortening of the M(1)–O(3) and M(3)–O(3) bond lengths, significant cation migration was observed, particularly in the sample heated for only 30 min in air. A slight loss of electrons from M(4) was evident in the air-heated sample, which suggests a slight migration of cations from M(4) to the A site.

Site-occupancy assignments

Suggested site occupancies for these structures are given in Table 1. For the hornblendes, Ti and octahedral Al were assigned to M(2), and Ca was assigned to M(4) based on chemical analyses. The total occupancies of M(1), M(2), and M(3) were each constrained to 1.0 and Fe/Mg occupancies were refined. M(4) was also assumed to contain some Na, the amount of which was determined by unconstrained site refinement. Phillips et al. (unpub. ms.) found that the apparent electron loss determined for M(4) in the air-heated hornblende varied according to the refinement procedure used for M(4') (see Bocchio et al., 1978; Ungaretti, 1980). For this study, the minimum loss determined was used and was assumed to represent Na, although Ungaretti (pers. comm., 1986, 1987) has found that Ca can also be removed from M(4) (however, less readily than Na) during oxidation-dehydrogenation in air-heated samples. The slight occupancies found at M(4') in all three structures were not considered in the bond-strength calculations. The total Fe³⁺ content of each hornblende was calculated using the ferric-ferrous ratios determined by Clowe et al. (1988) in conjunction with the total octahedral Fe contents determined by site refinement. The Fe³⁺ was distributed among the octahedral sites based on a comparison of observed ⟨M–O⟩ bond lengths and the ideal ⟨M–O⟩ bond lengths proposed by Hawthorne (1981, 1983) for octahedral sites occupied by a single cation. The OH content of O(3) for the natural

TABLE 1. Site-occupancy assignments

	Tschermakitic hornblende								
	Natural			650 °C, 1 kbar, 4 d, MH			700 °C, 1 atm, 30 m, air		
T(1)	0.61Si + 0.39Al			0.61Si + 0.39Al			0.61Si + 0.39Al		
T(2)	1.00Si			1.00Si			1.00Si		
M(4)	0.92Ca + 0.08Na			0.92Ca + 0.08Na			0.92Ca + 0.05Na		
A	0.25Na + 0.09K			0.25Na + 0.09K			0.31Na + 0.09K		
O(3)	0.92OH + 0.05O + 0.03F			0.83OH + 0.14O + 0.03F			0.67OH + 0.30O + 0.03F		
	M(1)	M(2)	M(3)	M(1)	M(2)	M(3)	M(1)	M(2)	M(3)
Mg	0.585	0.321	0.412	0.587	0.251	0.510	0.557	0.279	0.546
Fe ²⁺	0.415	0.032	0.563	0.340	0.137	0.365	0.240	0.150	0.203
Fe ³⁺	—	0.182	0.025	0.073	0.147	0.125	0.203	0.106	0.251
Al	—	0.430	—	—	0.430	—	—	0.430	—
Ti	—	0.035	—	—	0.035	—	—	0.035	—
	Riebeckite						K-Ti-Mg hastingsite		
	Natural			650 °C, 1 atm, 4 d, air			Natural		
T(1)	1.00Si			1.00Si			0.58Si + 0.42Al		
T(2)	1.00Si			1.00Si			0.92Si + 0.08Al		
M(4)	1.00Na			0.67Na			0.82Ca + 0.11Na + 0.06Fe ²⁺ + 0.01Mn		
A	—			0.75Na			0.61Na + 0.39K		
O(3)	1.00OH			0.10OH + 0.90O			0.47OH + 0.49O + 0.04F		
	M(1)	M(2)	M(3)	M(1)	M(2)	M(3)	M(1)	M(2)	M(3)
Mg	0.460	—	0.267	0.081	0.315	0.369	0.650	0.450	0.650
Fe ²⁺	0.508	0.047	0.703	—	—	—	0.140	0.150	0.150
Fe ³⁺	0.032	0.730	0.030	0.770	0.685	0.482	0.060	0.110	0.200
Al	—	0.223	—	0.149	—	0.149	—	0.200	—
Ti	—	—	—	—	—	—	0.150	0.090	—

hornblende was based on the oxy-amphibole content determined from reduction experiments (Clowe et al., 1988). The OH content for each heated hornblende was calculated based on the increase in Fe³⁺ content.

Although Ungaretti (1980) did not give detailed site occupancies for the riebeckites in his preliminary report, he did report the electrons per site in each structure, as well as a detailed chemical formula for the untreated sample, in which Fe³⁺ and Fe²⁺ are distinguished. For the unoxidized riebeckite, Al and Fe³⁺ were initially assumed to reside at M(2), and Na was assigned to M(4). Using the electrons per site reported by Ungaretti (1980), occupancies were calculated using simultaneous equations analogous to those proposed by Ungaretti et al. (1981). This method yielded a composition very close to the chemical analysis reported by Ungaretti (1980). Minor adjustments in the Fe²⁺-Fe³⁺ distributions were then made to improve the agreement between observed and ideal bond lengths. All Fe in the heated riebeckite was assumed to be Fe³⁺. A number of models consistent with the electron distribution reported by Ungaretti (1980) were tested. It was found that in order to obtain reasonable agreement between observed and predicted ⟨M(2)–O⟩ bond lengths, it was necessary to assume no Al at M(2) in the heated structure. This rather radical assumption may or may not be true; however, as noted in the following section, this assignment has little effect on empirical bond-strength calculations.

The structure of a natural potassian titanian magnesiohastingsite (Papike et al., 1969; Robinson, 1971; Robinson et al., 1973) that contains appreciable oxy-amphibole component is also included for purpose of comparison.

Except for minor modifications in the allocation of Fe³⁺ and Fe²⁺, the cation distribution derived for this structure by Hawthorne (1983) is assumed. Hawthorne (1978, 1981, 1983) has emphasized that the type of anion at O(3) exerts a significant influence on ⟨M(1)–O⟩ and ⟨M(3)–O⟩ and he has cautioned that the ideal bond lengths are strictly applicable only to amphiboles in which O(3) = OH. Therefore, in deciding site assignments for the air-heated riebeckite and the hastingsite, good agreement between the observed and ideal mean bond lengths for M(2) was deemed more important than agreement of bond lengths for M(1) and M(3).

VARIATIONS ACCOMPANYING OXIDATION-DEHYDROGENATION

Bond lengths

Although trivalent cations are normally ordered at M(2), a number of studies (Mueller, 1962; Ghose, 1965; Whitaker, 1971) have suggested that, based on charge-balance considerations, trivalent cations might favor M(1) and M(3) in amphiboles with an appreciable oxy-amphibole content. From neutron-diffraction data, Kitamura et al. (1975) found that Ti is preferentially ordered at M(1) in potassium oxy-kaersutite. The mean bond-length data for the hornblendes and riebeckites (Table 2) support these conclusions.

The smaller ⟨M(1)–O⟩ and ⟨M(3)–O⟩ distances in the heated structures imply that some smaller trivalent cations are present at these sites. Even more interesting is the increase in ⟨M(2)–O⟩ that accompanies heating. This indicates that the source of trivalent cations in M(1) and

TABLE 2. Selected bond lengths (Å)

	Tschermakitic hornblende			Riebeckite		Hastingsite
	1	2	3	4	5	6
M(1)–O(1) 2 ×	2.062(1)	2.058(1)	2.057(2)	2.093(2)	2.069(2)	2.047(4)
–O(2) 2 ×	2.146(1)	2.135(1)	2.138(2)	2.093(2)	2.062(2)	2.142(4)
–O(3) 2 ×	2.107(1)	2.092(1)	2.062(2)	2.111(2)	1.954(2)	2.041(4)
Mean (obs.)	2.105	2.095	2.086	2.099	2.028	2.077
Mean (calc.)*	2.095	2.087	2.074	2.098	2.006	2.064
M(2)–O(1) 2 ×	2.035(1)	2.055(2)	2.068(2)	2.115(2)	2.215(2)	2.092(4)
–O(2) 2 ×	2.039(1)	2.048(1)	2.053(2)	2.010(2)	2.044(2)	2.070(4)
–O(4) 2 ×	1.945(1)	1.953(1)	1.959(2)	1.896(2)	1.891(2)	1.980(4)
Mean (obs.)	2.006	2.019	2.027	2.007	2.050	2.047
Mean (calc.)*	2.005	2.013	2.016	2.007	2.042	2.046
M(3)–O(1) 4 ×	2.121(1)	2.104(1)	2.093(2)	2.124(2)	2.079(3)	2.084(4)
–O(3) 2 ×	2.099(2)	2.083(2)	2.071(3)	2.087(3)	1.988(3)	2.068(5)
Mean (obs.)	2.114	2.097	2.086	2.112	2.049	2.079
Mean (calc.)*	2.105	2.091	2.077	2.111	2.035	2.078
T(2)–O(4)	1.607(1)	1.605(1)	1.599(2)	1.598(2)	1.590(2)	1.607(4)

Note: Numbers 1, 4 and 6 are untreated natural samples; 3 and 5 were air-heated; and 2 was hydrothermally treated. Riebeckite data are from Ungaretti (1980), and the potassium titanium magnesio-hastingsite data are from Robinson (1971). Estimated standard deviations are given in parentheses and refer to the last decimal place.

* Calculated using the ideal bond lengths of Hawthorne (1981, 1983) in conjunction with the occupancies given in Table 1.

M(3) is not only Fe³⁺ produced by oxidation-dehydrogenation, but also trivalent cations transferred from M(2) during heating. If Fe²⁺ is initially present in M(1) and M(3), an electron-transfer mechanism (see Wilkins and Vedder, 1969) may contribute to this process. However, the refinement data for both the hornblendes (Phillips et al., unpubl. ms.) and riebeckites (Ungaretti, 1980) demonstrate that appreciable migration of nontetrahedral cations occurs in a relatively short time in air-heated samples.

The three hornblendes (and both riebeckites) are very similar, except for changes induced by oxidation-dehydrogenation. Therefore, the grand mean octahedral bond lengths would be expected to decrease with increasing oxidation because of the smaller size of Fe³⁺. The observed decreases in grand mean octahedral bond lengths are 0.024, 0.002, and 0.005 Å for the heated riebeckite, the hydrothermally heated hornblende, and the air-heated hornblende, respectively. These changes correspond to decreases of 0.013, 0.012, and 0.010 Å per Fe oxidized pfu, respectively, somewhat less than the 0.022 Å predicted by the ideal bond lengths.

Bond strengths

Empirical bond-strength relationships (Brown and Shannon, 1973; Pyatenko, 1973; Ferguson, 1974; Brown and Wu, 1976), which extend Pauling's (1929) original bond-strength concept to account for variation in individual bond lengths, are useful in making structural predictions. Hawthorne (1978) has successfully used this approach to explain individual bond-length variations in a variety of C2/m amphiboles. Although the total bond strength for an oxygen is ideally 2.0 v.u., deviations in the calculations are commonly observed in amphiboles, particularly at O(4) (see Hawthorne, 1978). Nevertheless, the relative "structural stability" among these amphi-

boles should depend somewhat on the extent to which these deviations are minimized.

Bond strengths were calculated for these structures (Table 3) from the occupancies given in Table 1 and the bond-length data from the respective studies, using the empirical constants of Brown and Wu (1976). Because A–O bond-length data were unavailable for the heated riebeckite and because of positional disorder of A cations in the heated hornblendes, bond strengths involving A–O distances were not considered. Bond strengths for O(5), O(6), and O(7), which also belong to the coordination sphere of the A cation, are not considered in Table 3. The H at O(3) is treated in the ideal Pauling (1929) sense, with no consideration given to the H–O(3) distance. The small amounts of F present were added to the values of H in Table 3 in order to assume an ideal bond strength of 2.0 v.u. at O(3).

The number of electrons per site is well characterized for both the riebeckites (Ungaretti, 1980) and the hornblendes. Therefore, the occupancies given in Table 1 should contain no major errors in the assignment of atoms with large differences in scattering powers, i.e., Mg + Al vs. Fe²⁺ + Fe³⁺. The empirical constants of Brown and Wu (1976) are identical for Mg, Al, and Si. Therefore, the assignment of Al and Si at the tetrahedral sites or Al and Mg at the octahedral sites [such as M(1) and M(3) in the heated riebeckite] has no bearing on the calculated bond strengths. Within the octahedral bond-length range observed for these structures, the bond strengths calculated assuming total Fe²⁺ occupancy differ from those of Fe³⁺ by only about 1.5–3%, whereas bond strengths for Mg differ from Fe²⁺ by 13–24%. Hence, it is apparent that errors in assigning Mg and Al or Fe²⁺ and Fe³⁺ occupancies have little or no effect on the calculated bond strengths. Another advantage in using the empirical bond strength approach to interpret the bond-length variations

TABLE 3. Selected empirical bond strengths (s)

	Tschermakitic hornblende				Riebeckite			Hastingsite
	s_1	s_2	s_3	$s_4 - s_3$	s_4	s_5	$s_4 - s_5$	s_6
O(1)-T(1)	0.908	0.912	0.920	-0.012	1.000	0.982	+0.018	0.892
-M(1)	0.376	0.379	0.382	-0.006	0.356	0.399	-0.043	0.395
-M(2)	0.392	0.379	0.366	+0.026	0.355	0.273	+0.082	0.353
-M(3)	0.336	0.345	0.352	-0.016	0.342	0.366	-0.024	0.354
Total	2.012	2.015	2.020		2.053	2.020		1.994
O(2)-T(2)	0.971	0.974	0.971	0.000	0.995	0.971	+0.024	0.939
-M(1)	0.310	0.318	0.317	-0.007	0.356	0.406	-0.050	0.320
-M(2)	0.389	0.385	0.379	+0.010	0.466	0.416	+0.050	0.371
-M(4)	0.271	0.271	0.271	0.000	0.178	0.121	+0.057	0.269
Total	1.941	1.948	1.938		1.995	1.914		1.899
O(3)-M(1)*	0.339	0.350	0.378	-0.039	0.342	0.542	-0.200	0.401
-M(3)	0.354	0.362	0.371	-0.017	0.374	0.457	-0.083	0.367
Subtotal	1.032	1.062	1.127	-0.095	1.058	1.541	-0.483	1.169
O(3)-H	0.95	0.86	0.70	+0.25	1.000	0.10	+0.90	0.51
Total	1.98	1.92	1.83		2.06	1.64		1.68
O(4)-T(2)	1.041	1.046	1.063	-0.022	1.066	1.089	-0.023	1.041
-M(2)	0.483	0.481	0.471	+0.012	0.638	0.627	+0.011	0.458
-M(4)	0.324	0.325	0.317	+0.007	0.206	0.125	+0.081	0.312
Total	1.848	1.852	1.851		1.910	1.841		1.811

Note: s_1 , s_4 , and s_6 are for untreated samples; s_3 and s_5 are for air-heated samples; s_2 is for the hydrothermally treated sample. All values except O(3)-H were calculated using the empirical constants of Brown and Wu (1976). Values for H and F (Table 1) were combined and treated in the classical Pauling (1929) sense.

* There are two symmetrically equivalent O(3)-M(1) bonds.

accompanying oxidation-dehydrogenation is that assumptions regarding exact cation size are not necessary.

Table 3 shows that the directions of change (i.e., increases or decreases) induced by air-heating are the same for the respective individual octahedral bond strengths in both riebeckite and tschermakitic hornblende. The changes tend to be more pronounced in the heated riebeckite because the extent of oxidation is much greater than in the air-heated hornblende. For both amphiboles, there is a decrease in bond strength for all M(2)-O bonds, reflecting the loss of trivalent cations from M(2). An increase is observed for all M(1)-O and M(3)-O bonds, reflecting an increase in trivalent-cation occupancy and, in the case of M-O(3), compensational shortening.

Although the coupled oxidation-dehydrogenation reaction maintains charge balance for the amphibole formula, it creates underbonding at O(3). Whereas the H bonds predominately to O(3), the Fe³⁺ produced by oxidation bonds to six oxygens, only two of which are O(3). To compensate for this undersaturation at O(3), there is dramatic shortening of the M(1)-O(3) distances and, to a lesser extent, the M(3)-O(3) distances (see Table 2). The contraction of M(3)-O(3) bonds is inhibited to some extent because the O(3) oxygens are in a *trans* configuration about M(3). Therefore, extreme contraction would disrupt linkages to the surrounding octahedra (Hawthorne, 1978). In most amphiboles that do not contain appreciable F or O²⁻ at O(3), the M(1)-O(3) bond length is somewhat longer than M(1)-O(1) (see App. B4, Hawthorne, 1983). However, there is progressive shortening of M(1)-O(3) relative to M(1)-O(1) with increasing F and/or O²⁻ at O(3). Therefore, comparison of the difference in bond strengths between M(1)-O(3) and M(1)-O(1) (or M(3)-

O(3) and M(3)-O(1)) for the respective structures gives some measure of the extent of compensational shortening as opposed to the shortening that results from increased occupancy by smaller trivalent cations. For example, in the untreated riebeckite (Ungaretti, 1980), the bond strengths are 0.356 and 0.342 v.u. for M(1)-O(1) and M(1)-O(3), respectively, whereas in the heat-treated sample, the respective values are 0.399 and 0.542 v.u. The large increase in the M(1)-O(3) bond strength (0.200 v.u.) compared to the modest increase for M(1)-O(1) (0.043 v.u., which is presumably due to increased trivalent-cation content), suggests that compensational shortening is extremely important in increasing bond strength at O(3).

The O(4) atom, which is bonded to T(2), M(2), and M(4), tends to be underbonded in most *C2/m* amphiboles (Papike et al., 1969; Hawthorne, 1978). The decrease in the M(2)-O(4) bond strength resulting from loss of trivalent cations during dehydrogenation is more than offset in these structures by a corresponding decrease in the T(2)-O(4) bond length. However, for riebeckite in which there is also a major loss of Na from M(4), O(4) becomes further undersaturated with dehydrogenation.

DISCUSSION

The total increase in the bond strength at O(3) because of increased trivalent-cation content and compensational shortening in the air-heated structures is 0.095 and 0.483 v.u. for tschermakitic hornblende and riebeckite, respectively. These values represent only about half of the decrease (0.25 and 0.92 v.u. for the respective structures) due to dehydrogenation. It seems that at least some of the remaining decrease in bond strength at O(3) is compensated by interaction with the A cation.

A marked increase in apparent thermal anisotropy of the A site was noted as the extent of oxidation-dehydrogenation increased in the hornblende. The values of B_{eq} increased from 7.8(3) in the natural hornblende to 10.2(2) in the hydrothermally heated hornblende to 15.0(4) in the air-heated hornblende. Phillips et al. (unpub. ms.) refined a number of split-atom models involving A(2/m), A(2), and A(m) (see Hawthorne, 1983) in which both site occupancies and isotropic temperature factors were unconstrained. The most successful of these was one in which only A(2) and A(m) were considered to be occupied. However, difference-Fourier syntheses for this model indicated a small electron-density residual at A(2/m) for the natural and hydrothermally heated hornblendes, but not for the air-heated sample. The electrons per formula unit at A(m) are 2.18(9), 2.11(9), and 3.56(20) for the natural, the hydrothermally heated and the air-heated hornblendes, respectively. The increase in electrons at A(m) in the air-heated structure is apparently at the expense of A(2/m) and M(4). The A(m)-O(3) distances in the respective structures are 3.55(2), 3.26(2), and 3.18(2) Å. Ungaretti (pers. comm., 1987) has found even further shortening of the A(m)-O(3) distance in a similar hornblende that was air-heated at 750 °C for 20 h. The decreases in the A(m)-O(3) distances, coupled with the increased occupancy of A(m) in the air-heated structure, suggest that at least a small portion of the bond-strength loss at O(3) that accompanies oxidation-dehydration is offset by interaction with the A(m) cation.

No information about the location or anisotropy of the A site in heated riebeckite was given in the preliminary report by Ungaretti (1980). Papike et al. (1969) were unable to draw conclusions concerning the exact behavior of A-site cations in the potassian titanian magnesio-hastingsite; however, the relatively large isotropic temperature factor (5.47) suggests that there is substantial positional disorder of A cations. Therefore, although there is no direct evidence for A-O(3) bonding in either structure, it provides a plausible explanation for both the behavior of the A cation and the "apparent" underbonding at O(3).

Because they are hydrous phases, all amphiboles are inherently unstable when heated in air at these temperatures. It is possible to produce amphiboles with a high oxy-amphibole content by air-heating only because the oxidation-dehydrogenation reaction in these samples occurs at a much faster rate than thermal decomposition (see Clowe et al., 1988). It is quite possible that extensive oxidation-dehydrogenation and the structural adjustments it induces act to destabilize the structure; this is consistent with the experimental results of Clowe et al. (1988), but further studies will be necessary to substantiate this possibility.

Preliminary results from a study of grunerite (Phillips et al., unpub. data) suggest that the extent of dehydrogenation observed in a grunerite heated at 700 °C in air for 30 min is insufficient to account for the amount of Fe³⁺ determined by chemical analyses. Although tentative, these results are in accord with earlier studies (Addison

and Sharp, 1968; Ghose and Weidner, 1971; Rouxhet et al., 1972). In grunerite, there are no trivalent cations present at M(2), little or no Ca or Na at M(4), and A is vacant. Therefore, underbonding at O(3) resulting from dehydrogenation can be offset only by the Fe³⁺ at M(1) and M(3) produced by oxidation and by bond-length shortening of M(1)-O(3) and M(3)-O(3). Because the compensation mechanisms in grunerite are limited, extensive dehydrogenation should have a much greater destabilizing effect (as gauged by the empirical bond strengths) than in amphiboles such as hornblende or riebeckite, in which other mechanisms are available. Therefore, it is not unreasonable to expect that oxidation by the dehydrogenation reaction cannot proceed as far in grunerite as in other amphiboles.

SUMMARY

The rapid oxidation-dehydrogenation observed in air-heated hornblende and riebeckite results in a dramatic change in bond strength at O(3), which is offset by a variety of structural adjustments. Fe³⁺ produced by oxidation, as well as some pre-existing trivalent cations at M(2), are preferentially ordered at M(1) and M(3). There is also marked compensational shortening of O(3) bonds to M(3) and, particularly, M(1). These mechanisms offset only about half of the loss of bond strength at O(3) resulting from dehydrogenation.

At least part of the remaining loss of bond strength is offset by interaction of A-site cations with O(3). In hornblende, this is evidenced by a marked decrease in the A(m)-O(3) distances and an increase in the A(m) occupancy of the air-heated sample. In riebeckite, the A site is initially vacant, but with oxidation-dehydrogenation, there is a significant migration of Na from M(4) to A (Ungaretti, 1980).

In air-heated grunerite, unlike other amphiboles, dehydrogenation is not the only mechanism contributing to oxidation (Addison and Sharp, 1968; Rouxhet et al., 1972). This may be due, in part, to the limited availability of mechanisms necessary to compensate for the underbonding at O(3) that arises from dehydrogenation.

ACKNOWLEDGMENTS

The original manuscript was improved by comments and suggestions from Luciano Ungaretti and Frank Hawthorne. Jeff Kaspar aided in checking calculations and the manuscript was typed by Karen Bird. This work was supported in part by NSF Grant EAR 8312878 to R.K.P.

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MANUSCRIPT RECEIVED MAY 28, 1987

MANUSCRIPT ACCEPTED JANUARY 14, 1988