

UNIT-CELL PARAMETERS AND OPTICAL PROPERTIES
OF TALC ON THE JOIN $Mg_3Si_4O_{10}(OH)_2$ - $Fe_3Si_4O_{10}(OH)_2$ WARREN C. FORBES, *University of Illinois at Chicago Circle,
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ABSTRACT

Values of $d(003)$, $d(060)$, and γ were measured for talcs of varying Fe/(Fe+Mg) ratios synthesized under controlled conditions of temperature, pressure, and oxygen fugacity. The effect of iron on the $d(003)$ spacing is strongly dependent on oxygen fugacity. Iron substitution produces an increase in the c dimension, with the amount of increase greatest for the hematite-magnetite (HM) buffer series and lowest for the magnetite-wüstite, magnetite-iron series (MW-MI). The b dimension increases regularly with iron content only on the MW-MI buffer. At higher relative oxygen fugacities, $d(060)$ may be slightly larger than that of iron-free talc, but does not vary significantly with further iron substitution. The index, γ , increases with iron content, but there is no apparent correlation between γ and oxygen fugacity.

A substitution of the type $Fe^{3+}+H^+=Si^{4+}$ is proposed to explain the observed variations. The increase in c may result from the formation of hydroxyl ions on the basal surface. The extent of this substitution is apparently greatest on the HM buffer and decreases at lower oxygen fugacities.

The pronounced effect of oxygen fugacity on the cell dimensions of iron-bearing talc suggest that talc may be of some use as an indicator of oxygen fugacity in natural environments.

INTRODUCTION

The effect of iron substitution on the unit cell parameters and optical properties of talc was determined as part of a study of the phase equilibria of the system $Mg_3Si_4O_{10}(OH)_2$ - $Fe_3Si_4O_{10}(OH)_2$. These data were required for determining the iron content of fine grained talc coexisting with other iron-bearing phases. The values of $d(003)$, $d(060)$, and γ were used as parameters and were measured for talcs of varying Fe/(Fe+Mg) ratios synthesized under controlled conditions of temperature, pressure and oxygen fugacity.

Minnesotaite, $Fe_3Si_4O_{10}(OH)_2$, has long been considered as the iron analog of talc. However, as will be shown below, the solution of iron in talc is complex and generally does not conform to the simple $(Mg,Fe)_3Si_4O_{10}(OH)_2$ solid solution series. Iron content therefore, is expressed as Fe/(Fe+Mg), rather than in terms of mole fraction minnesotaite.

EXPERIMENTAL PROCEDURE

Talc compositions of varying iron content were synthesized under controlled conditions of temperature, pressure and oxygen fugacity. Magnesium was weighed out as periclase (Mallinckrodt, lot KVE). High purity Fe_2O_3 (Spex, lot 08661) was used as the source of iron. SiO_2 was used in the form of silica gel (Spex, lot 08661). All chemicals were heated at 1200°C for 24 hours to drive off adsorbed water.

Reagent mixtures in the requisite proportions were mechanically ground under acetone

in an agate mortar for at least four hours. The resulting grain size as measured optically averaged five microns or less. Since it is possible that starting materials may affect both the reaction rates and the nature of the phase(s) produced, three different starting materials utilizing various forms of iron, were produced. Magnesio-wüstite solid solutions were prepared to insure complete homogenization of iron and magnesium in the starting material. Iron was also introduced as Fe_2O_3 . Finally, a reduced starting material was prepared by passing hydrogen over the Fe_2O_3 -mix at 650°C for 1 hour. Both the mix made with magnesio-wüstite and the reduced assemblage proved to be very reactive and produced identical results. The "oxidized" assemblage reacted at a somewhat slower rate but yielded the same values as the other mixes if given sufficient time. The reduced starting material was used in all experiments reported here.

Oxygen fugacity was controlled by the buffer technique, which has been described by Eugster and Wones (1962). Fugacities (hydrogen and oxygen) were controlled using the hematite-magnetite (HM), nickel-nickel oxide (NNO), quartz-fayalite-magnetite (QFM), and magnetite-iron, magnetite-wüstite (MI-MW) buffer series. Water was added in excess of that required to oxidize the buffer. Wones (1953) has pointed out that iron may be lost to platinum under reducing conditions. Therefore in later stages of the study, the charge was placed in silver-palladium tubing to eliminate iron loss.

The solubility of iron in talc is limited, thus variation of talc parameters with iron content could be determined only over a small compositional range. Compositions equivalent to atomic ratios $[\text{Fe}/(\text{Fe}+\text{Mg})]$ 0.01, 0.015, 0.025, 0.035, 0.05, 0.075, 0.1 and 0.20 were prepared corresponding to 0.58, 0.88, 1.47, 2.06, 2.94, 4.36, 5.81, and 11.62 weight percent "FeO".

Synthesis of talc of varying iron content was carried out under conditions necessary to produce talc as the only phase. It proved impossible to synthesize talc containing more than approximately 3.75 weight percent "FeO" at oxygen fugacities defined by the HM buffer. Quartz was present in all charges synthesized on the HM buffer and in several formed on the NNO buffer.

Charges were examined optically and by x-ray techniques. Indices of refraction were determined in white light by oil immersion techniques and are considered accurate to ± 0.003 . Index oils were calibrated on an Abbé refractometer using a sodium light source. For talc, $\gamma \simeq \beta$, and birefringence was usually 0.002 or less. The flakes usually lay on a basal surface, prohibiting measurement of α .

Unit cell parameters were obtained by powder techniques, using smear mounts and a powder diffractometer. Reflection positions were carefully determined by use of either Lake Toxaway quartz or silicon as internal standards. The (003) talc reflection was calibrated against the (101) quartz reflection ($26.662^\circ 2\theta, \text{CuK}\alpha$). The (060) talc reflection was calibrated using the silicon (311) peak ($56.124^\circ \text{CuK}\alpha$). Uncertainties shown are the standard deviations from at least six measurements. The effect of iron content on the a dimension could not be evaluated because of the low intensity of (hk0) and (hk l) reflections.

Full sample data are presented in Table 1.

RESULTS

Basal spacing. The change in basal spacing of talc as a function of iron content is shown in Figure 1 and in Table 1. It is evident that change in $d(003)$ with increasing iron content is strongly dependent on oxygen fugacity. The rate of increase is lowest for talcs synthesized on the MW-MI buffer, increases on the QFM and NNO buffers, and is highest for those formed on the HM buffer. The maximum iron content of the talc

TABLE 1. SYNTHESIS CONDITIONS AND PHYSICAL PROPERTIES OF COMPOSITIONS ON THE JOIN $Mg_3Si_4O_{10}(OH)_2$ AND $Fe_3Si_4O_{10}(OH)_2$

Fe/ (Fe+Mg)	Temp (°C)	P (kbars)	Time (hrs)	Buffer	$d(003)(\text{Å})$	$d(060)(\text{Å})$	γ
0.010	580	1	242	HM	3.1199(10)	1.5274(2)	1.572
.015	500	1	260	HM	3.1215(12)	1.5268(1)	n.d.
.025	425	1	216	HM	3.1297(10)	1.5275(1)	1.574 ^a
.062	373	1	240	HM	3.1544(25)	1.5270(7)	1.562 ^a
.010	620	1	384	NNO	3.1180 (6)	1.5277(1)	1.568
.025	500	1	479	NNO	3.1224 (8)	1.5279(2)	1.570
.050	440	1	477	NNO	3.1276 (9)	1.5279(1)	1.572 ^a
.10	400	1	556	NNO	3.1406(15)	1.5278(4)	1.578 ^a
.015	570	1	163	QFM	3.1169 (5)	1.5265(5)	1.566
.035	550	1	168	QFM	3.1215 (3)	1.5274(1)	1.569
.050	525	1	166	QFM	3.1220 (5)	1.5277(1)	1.568
.075	475	2	162	QFM	3.1242(11)	1.5271(1)	1.572
.010	625	1	242	MW	3.1157 (6)	1.5262(2)	1.568
.015	600	1	605	MW	3.1151(11)	1.5265(3)	1.570
.025	565	2	218	MI	3.1153 (8)	1.5267(2)	1.570
.035	560	1	576	MI	3.1168 (9)	1.5269(1)	1.572
.075	510	1	220	MI	3.1188 (5)	1.5275(2)	1.580
.20	500	2	336	MI	3.1262 (8)	1.5301(3)	n.d.
.00	675	1	245	—	3.1151 (5)	1.5260(2)	1.566

^a Quartz appears.

varies with the buffer used. The range on the HM buffer is particularly restricted because of failure to synthesize a talc containing more than 3.75 weight percent FeO. Talc of higher iron content could be produced at lower oxygen fugacities. Talc with a Fe/(Fe+Mg) ratio of 0.2 was synthesized on the MI buffer. The $d(003)$ value, $3.1262 \pm .0008$, fits a straight line extrapolation of the MI-MW curve as shown in Figure 1.

The straight line fit of these data allows calculation of least square equations of the form $d(003) = A + Bx$, where $x = \text{Fe}/(\text{Fe} + \text{Mg})$. Regression coefficients are given in Table 2.

The c dimension of Fe-bearing talc formed on the MI and MW buffer is dependent on synthesis conditions. Initially, the $d(003)$ spacing is significantly larger than the final value, the amount of deviation being dependent on temperature, pressure and run duration. On the MW-MI buffer, at pressures less than 1000 bars, runs of up to 20 days duration were required to produce talc with a stable $d(003)$ spacing. The initially

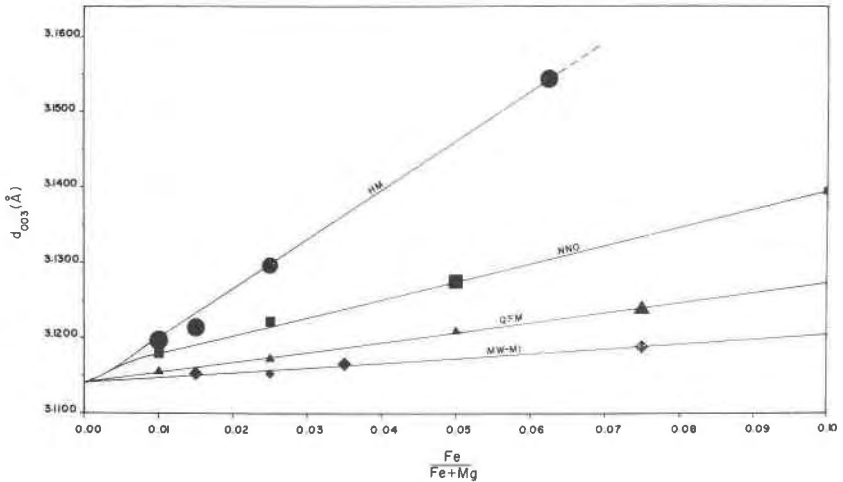


FIG. 1. Plot of iron content of talc versus $d(003)$. The vertical dimension of the symbols equals the experimental uncertainty.

large basal spacing is probably due to grain size effects. Ross (1968) has shown that for several layer silicates, anomalous basal spacings may be expected for crystals only a few unit cells thick. With longer run duration, and/or higher temperatures and pressures, the crystals would increase in thickness, yielding normal $d(003)$ spacings. It is puzzling however, that this behavior does not occur in Fe-talc formed on the QFM, NNO, or HM buffers.

b axis variation. As shown in Fig. 2, a systematic correlation between $d(060)$ and iron content is apparent only for compositions synthesized on the MW-MI buffer. For samples formed on the other buffer series, $d(060)$ may be slightly larger than that of iron-free talc and does not appear to vary with increasing iron substitution. However, because of the large scatter in the data and the small change in $d(060)$ these observations

TABLE 2. REGRESSION COEFFICIENTS FOR THE LEAST SQUARES EQUATION
 $d(003)(\text{\AA}) = A + Bx$. $x = \text{Fe}/(\text{Fe} + \text{Mg})$

Buffer	A	B	Standard Error
HM	3.1143	0.651	± 0.0005
NNO	3.1147	.248	.0005
QFM	3.1150	.104	.0006
MI	3.1141	.064	.0003

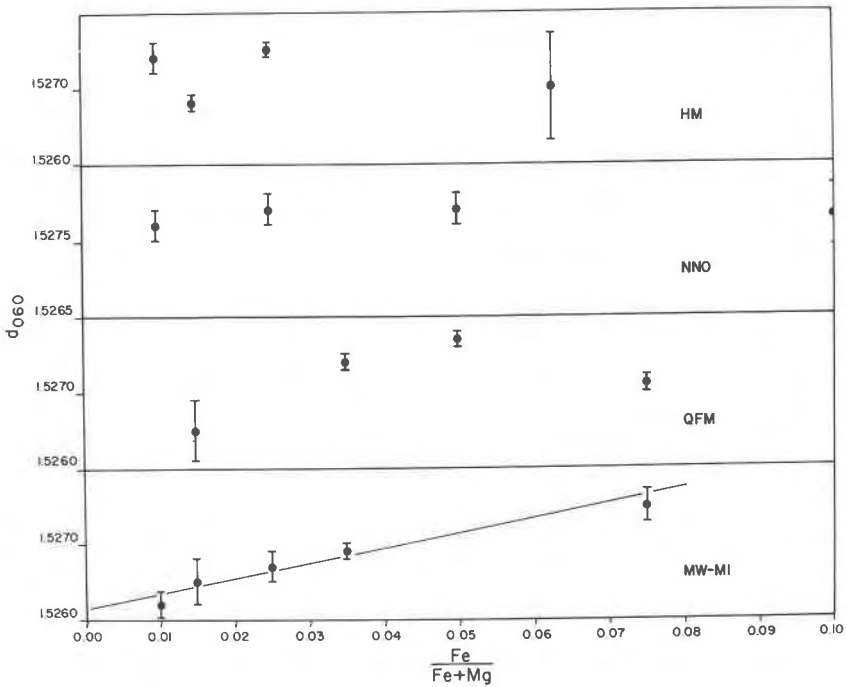


FIG. 2. Plot of iron content of talc versus $d(006)$ for the HM, NNO, QFM and MW-MI buffer series. Uncertainties are shown by error bars.

must be regarded as tentative. An additional complication is the overlap of the (060) with $(\bar{3}31)$ and $(\bar{3}\bar{3}1)$ (Malcolm Ross, pers. comm.).

These data do indicate that except for talc formed on the MI-MW buffer, $d(060)$ is of little value for determination of the iron content of talc.

Optical properties. Differences between the buffer series are small and may be non-existent over the small compositional range because of uncertainties. No correlation between γ and oxygen fugacities is apparent.

DISCUSSION

The variation in basal spacing with iron content and oxygen fugacity provide some insight into the nature of Fe-substitution in talc. Possible substitutions in the octahedral layer are $\text{Fe}^{2+} \rightleftharpoons \text{Mg}^{2+}$ and $2 \text{Fe}^{3+} \rightleftharpoons 3 \text{Mg}^{2+}$ and in the tetrahedral layer ferric iron may replace silicon ($\text{Fe}^{3+} \rightleftharpoons \text{Si}_4^+$).

Previous work on sheet silicates has shown that little or no increase in the basal spacing is to be expected when Fe^{2+} replaces Mg^{2+} in the octa-

hedral layer. Donnay, *et al.* (1964), have shown that Fe^{2+} - Mg^{2+} substitution in the ferriphlogopite-ferriannite series causes a flattening of the octahedral layer resulting in a reduced basal spacing and increased b dimension. Complete replacement of Mg^{2+} by Fe^{2+} results in a decrease in c of 0.09 Å and an increase in b of 0.11 Å. Similarly, the biotite data of Wones (1963a) show that for the MW buffer series, the basal reflection position remains constant with increasing iron substitution. Biotites synthesized by Wones on the HM buffer show a contraction in c with increased iron content. In the above work, the (060) position was found to be a sensitive indicator of the amount of annite solid solution. Therefore, progressive Fe^{2+} - Mg^{2+} substitution should either produce a slightly decreased basal spacings or not affect c at all.

Wones (1963a) attributed the observed variations in biotite cell parameters with oxygen fugacity (or in this case hydrogen fugacity) to the formation of an "oxy-biotite" component. This involves the oxidation of octahedral iron to the +3 state with a resultant loss of hydrogen to maintain charge neutrality. The unit cell dimensions decreased with increasing oxygen fugacities at constant iron content. Therefore formation of an "oxy-talc" component $\text{Mg}_{3-y}\text{Fe}_y^{3+}\text{Si}_4\text{O}_{10+y}(\text{OH})_{2-y}$ would not explain the observed increase in $d(003)$ with increasing f_{O_2} .

The increase in c may be explained by tetrahedral substitution of Fe^{3+} for Si^{4+} . An increase may be expected because of the substantially larger ionic radius of Fe^{3+} (0.64 Å) as compared to Si^{4+} (0.41 Å). However the variation in $d(003)$ appears to be too large to be explained by simple Fe^{3+} - Si^{4+} substitution. Talc, containing 0.2 atoms of Fe per unit cell, synthesized on the HM buffer has a c dimension approximately 0.1 Å larger than talc of identical composition formed on the MI buffer. The dimensional effect of Fe^{3+} tetrahedral substitution in talc therefore is at least five times that observed for Fe^{3+} - Al^{3+} replacement in the biotite series (Donnay, *et al.*, 1964; Wones, 1963b). From consideration of bond length changes and percentage of Fe^{3+} in tetrahedral coordination, one would expect an increase in c of approximately 40 percent of that found in biotite.

It is suggested that a substitution of the type $\text{Fe}^{3+} + \text{H}^+ \rightleftharpoons \text{Si}^{4+}$ is occurring. The hydrogen ion, required for charge balance, may be added to a bridging oxygen between adjacent Si^{4+} - Fe^{3+} tetrahedra. The oxygen atom accepting the hydrogen would be overbonded, receiving bonds of 4/4, 3/4, and 1 from Si^{4+} , Fe^{3+} , and H^+ respectively so that its sum of electrostatic bond strengths is 2.75. As a result of this overbonding, the Si-OH and Fe-OH bonds should be considerably longer than the average Si-O (bridging) length of 1.63 Å and the Fe^{3+} -O length of 1.90 Å. The effect of electrostatic bond strengths on bond lengths has been pointed

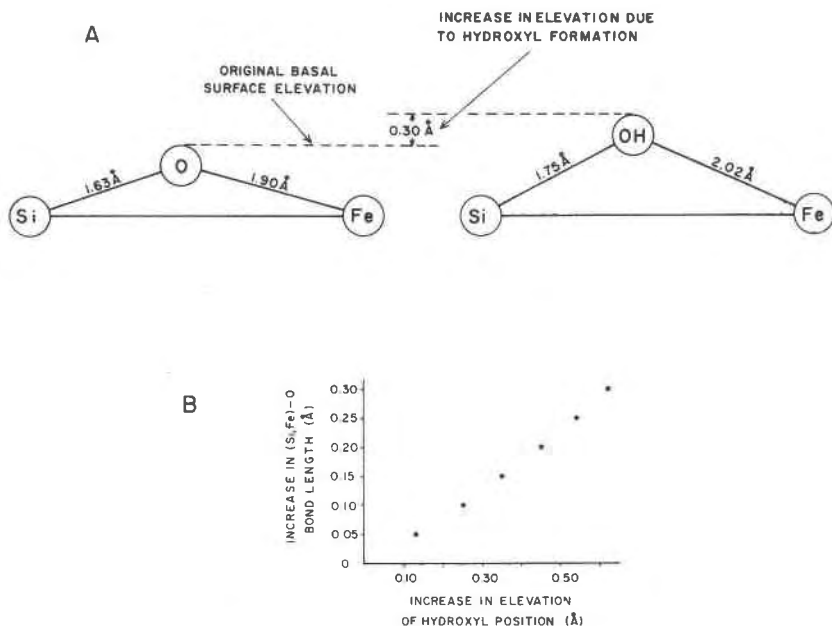
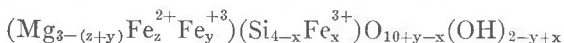


FIG. 3. A Increase in the elevation of the hydroxyl ion by a lengthening of the Si-OH and Fe-OH bond lengths. B. Plot relating increase in hydroxyl elevation to bond length increases. Note that relatively small increases in bond lengths produce a substantial elevation increase. The points were obtained graphically from part A.

out by Baur (1961). Examination of the bond length data of datolite $\text{CaBSiO}_4(\text{OH})$, (Pant and Cruickshank, 1967), pectolite $\text{Ca}_2\text{NaHSi}_3\text{O}_9$, (Prewitt, 1967) and $\beta\text{-Na}_2\text{Si}_2\text{O}_5$ (Pant, 1968), indicate that an increase in bond length of 0.12 \AA should be expected for an overbonding of 0.75 (Baur, pers. comm.). As shown in Figure 3, one effect of increased Si-OH and Fe-OH bond lengths would be to elevate the hydroxyl above the basal sheet. For a bond length increase of 0.12 \AA , the bridging OH is raised about 0.30 \AA above its former position. This height increase must be considered as a maximum as lateral displacement of Fe^{2+} and Si^{4+} parallel to the basal sheet will reduce this elevation. The presence of additional hydrogen in the talc structure therefore may result in the formation of isolated domes on the formerly planar basal surface. The displacive effect of these domes between adjacent sheets should result in an increase of layer thickness of at least the same order of magnitude as that observed.

Therefore it is probable that the solid solution of iron in talc is complex. Taking into account the possible formation of oxy-talc at high rela-

tive oxygen fugacities, a structural formula of the type



is possible. The dimensional effects due to oxy-talc (if present) are masked by the comparatively large changes caused by the $\text{Fe}^{3+} + \text{H}^+ \rightleftharpoons \text{Si}^{4+}$ substitution.

The presence of quartz in runs synthesized on the HM and NNO buffers strongly indicates that $\text{Fe}^{3+} \rightleftharpoons \text{Si}^{4+}$ substitution has occurred. The Si content in these talc samples must be less than that required by the simple talc formula.

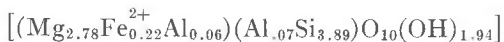
The progressively larger slopes of the $d(003)$ curves in Figure 1, can be attributed to increasing amounts of the proposed $\text{Fe}^{3+} + \text{H}^+ = \text{Si}^{4+}$ substitution at higher relative oxygen fugacities. The slight slope of the MW-MI spacing curve suggests that tetrahedral Fe^{3+} occurs even under very low oxygen fugacity.

The presence of tetrahedral Fe^{3+} in natural talc is not well documented. Many talc analyses indicate Fe_2O_3 but the actual presence and location of the Fe^{3+} within the structure is uncertain. Talc very often contains chlorite and/or magnetite as impurities and these minerals may be the source of the ferric iron. However, the occurrence of tetrahedral Fe^{3+} in other layer silicates is well known and there is little to suggest that it does not occur in talc as well.

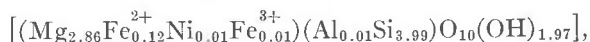
The presence of excess hydrogen in layer and chain silicates has been noted by several workers (Gilberg, 1964; Deer *et al.*, 1962, 1963). Nicholls and Zussman (1955) have shown that hydroxyl ions replace oxygen within the silicate structure of a hornblende. McConnell (1950) has proposed that excess hydroxyl ions occur in montmorillonite. Thus it appears reasonable to assume that formation of additional hydroxyl ions is a valid mechanism for the maintenance of charge neutrality.

GEOLOGICAL APPLICATIONS

The pronounced effect of oxygen fugacity on the basal spacing of iron-bearing talc indicates that estimates of f_{O_2} during the crystallization of natural talc can be made. Determination of oxygen fugacity, relative to the four buffer series used in this study, is possible if the total iron content and unit cell dimensions of a talc are known. These data were obtained for two talc samples (kindly supplied by A. H. Chidester) from a serpentinite near Waterbury, Vermont. Steatitization of the ultra-mafic produced a steatite—talc+carbonate—serpentinite zonation with the body. Sample W-89 [$\text{Fe}/(\text{Fe} + \text{Mg}) = 0.074$]



represents talc in the talc-carbonate zone, while W-83 [$\text{Fe}/(\text{Fe} + \text{Mg}) = 0.04$]



is from a talc vein cutting the serpentinite. Talc analyses and the geology of the deposit were taken from Chidester (1962). For W-89, $d(003) = 3.1179(3) \text{ \AA}$, $d(060) = 1.5275(2) \text{ \AA}$, and for W-83, $d(003) = 3.1167(3) \text{ \AA}$, $d(060) = 1.5269(2) \text{ \AA}$. Application of these data to Figures 1 and 2 suggest that these samples were formed under oxygen fugacities equivalent to those defined by the MW-MI buffer. Coincidence of the $d(003)$ and $d(060)$ values with the MW-MI curves is nearly perfect. The presence of other elements, particularly aluminum, in these samples may effect the talc unit cell dimensions. Aluminum substitution in talc of the type $\text{MgSi} \rightleftharpoons \text{AlAl}$, produces a decrease in $d(003)$ (Fawcett and Yoder, 1966). Thus the oxygen fugacities suggested may be too low. However the coincidence of both the $d(003)$ and $d(060)$ values with the MW-MI curves indicates that the dimensional effect of aluminum is minor. Collaborative evidence of f_{O_2} during crystallization of talc is scant. Magnetite is present as fine grained particles and fractured grains partially invaded by talc. Quartz and olivine are absent. The presence of a quartz-magnetite assemblage would indicate oxygen fugacities above those defined by the QFM buffer. Element distribution data presented by Chidester (p. 102, 126) suggest that Fe^{2+} increased slightly at the expense of Fe^{3+} during formation of the talc-carbonate rock. This at least suggests a reducing environment. Clearly, other talc parageneses, in which oxygen fugacity can be independently determined, need to be studied in order to evaluate this method.

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