

RE-EXAMINATION OF THE WOLLASTONITE-HEDENBERGITE (CaSiO_3 - $\text{CaFeSi}_2\text{O}_6$) EQUILIBRIA

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ABSTRACT

The equilibria for the iron-rich wollastonite solid solution \rightleftharpoons less iron-rich wollastonite solid solution + hedenbergite reaction has been determined in the temperature interval 600°–995°C, $P_{\text{H}_2\text{O}} = 1\text{ kbar}$, and f_{O_2} defined by the QFM buffer. The equilibria develops an inflection around 800°C for a composition of $(\text{Ca}_{0.88}\text{Fe}_{0.12})\text{SiO}_3$. The flattening continues until a composition of $(\text{Ca}_{0.80}\text{Fe}_{0.20})\text{SiO}_3$ at approximately 815°C. The slope then changes smoothly to a composition of $(\text{Ca}_{0.5}\text{Fe}_{0.5})\text{SiO}_3$ at 980°C. X-ray diffraction analysis of the wollastonite solid solutions from the inflected region show development of multiple reflections analogous to all previously occurring major reflections.

The X-ray data and infrared spectra measurements (Rutstein and White, 1971) indicate the equilibria inflection and double reflections are due to the co-existence of a wollastonite structure and a bustamite structure. These structures coexist with hedenbergite as a function of bulk composition and temperature.

Crystal chemical considerations require that both pyroxenoid structural variants undergo a series of ordered and disordered state as a function of composition and temperature.

INTRODUCTION

The major previous phase equilibria studies on the CaSiO_3 - $\text{CaFeSi}_2\text{O}_6$ join were conducted by Bowen, Schairer, and Posnjak (1933) as part of their pioneering study of the CaO - FeO - SiO_2 system. Their dry synthesis were made at an atmospheric pressure and at an oxygen partial pressure approximating that of the fayalite-quartz-iron buffer. As far as this work is concerned, there are two major points of interest from their study. The first is the inversion of hedenbergite at 865°C to a wollastonite solid solution which is in no way different from other wollastonite solid solutions. The second is the large extent of hedenbergite solid solution in wollastonite. This extends to approximately 62 weight percent hedenbergite at 800°C. (Their solvus is reproduced as part of Figure 4.)

Because of extremely sluggish reactions and the limitations of their equipment, this solvus is based upon two 48-hour heating experiments, both of identical composition (60:40 weight percent wollastonite:hedenbergite). Thus, even though this is very scanty evidence, their solvus has largely been accepted without confirmation. However, the possibility that this solvus is incorrect develops when comparison is made between the phase equilibria determined for the hedenbergite-ferrosilite ($\text{CaFeSi}_2\text{O}_6$ - FeSiO_3) join by Munoz and Lindsley (1968) with that determined by Bowen, Schairer, and Posnjak (1933). This was most pronounced in regard to the location and slope of the reaction iron-rich

hedenbergite solid solution \rightleftharpoons less iron-rich hedenbergite solid solution + fayalite (Fe_2SiO_4) + quartz (SiO_2). The differences were explained as reflecting a lack of attainment of equilibrium in the experiments of Bowen *et al.* Therefore, one might expect similar effects on the system under study here.

In addition, interpretation of the experimental work by Bowen *et al.* (1933) suggests that medium to high grade metamorphic environments, up to 25–50 weight percent hedenbergite component could be found in solid solution with wollastonite. However, most available analyses of natural wollastonite samples only contain traces of the hedenbergite component. Hence, the lack of agreement between naturally occurring compositions and those predicted from the experimental study suggest a need for re-examination.

EXPERIMENTAL METHODS

Starting materials were reagent grade CaCO_3 , Fe_2O_3 , and silicic acid ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$) which were carefully dehydrated before weighing. These materials in the desired proportions were mixed for three hours in a mechanical shaker, fired in air at approximately 925–950°C for fifteen minutes in a silver foil-lined silica glass boat, and hand ground under acetone in an agate or synthetic sapphire mortar for approximately one hour. The resulting mixture was extremely reactive and gave yields of almost 100 percent within a few hours. Compositions were prepared along the pseudobinary join wollastonite-hedenbergite ($\text{CaSiO}_3\text{-Ca}_{0.5}\text{Fe}_{0.5}\text{SiO}_3$). Replicate mixes were made for several compositions to check reproducibility of technique and method.

Synthesis and reaction were carried out using standard hydrothermal techniques in Tuttle-type “cold-seal” pressure vessels and using the oxygen buffer technique of Eugster and Wones (1962). Temperatures reported are believed accurate to $\pm 5^\circ\text{C}$ and represent the maximum temperature deviation in the course of a run. Similarly, reported pressures are believed to be ± 10 bars.

Products from these experiments were examined using a petrographic microscope equipped with phase contrast and by X-ray diffraction techniques. The use of phase contrast methods was extremely useful in the identification of the fine-grained run products produced at lower temperatures.

For routine identification of phases and for precise determination of d values, a Phillips high angle diffractometer equipped with curved crystal monochromer and a Tem-Pres diffractometer were used. In both cases copper radiation was used.

Smear mounts were prepared using KCl as an internal standard. This had been previously standardized with Lake Toxaway quartz ($a=4.9131 \text{ \AA}$ and $c=5.4946 \text{ \AA}$) and silicon ($a=5.4306 \text{ \AA}$). Two or four oscillations were made over the interval $22^\circ\text{-}32^\circ 2\theta$ using a goniometer speed of $\frac{1}{4}^\circ 2\theta$ per minute and chart speed of $\frac{1}{2}''$ per minute for the Phillips instrument, and a goniometer speed of $1\frac{1}{2}^\circ 2\theta$ per minute and chart speed of $1''$ per minute for the Tem-Pres instrument. Measured uncertainties were generally within $0.010\text{-}0.020^\circ 2\theta$. Replication between both instruments was excellent. However, intensities and resolution were of course lower without the use of the monochromer.

No significant improvement in precision was obtained by making more than two oscillations. The compositions of wollastonite solid solution determined from the average of five peaks has a precision of ± 4 mole percent hedenbergite or better.

The nature of the equilibria as a function of temperature and composition was determined using synthesis runs determined to represent steady state conditions and solution and exsolution runs of previously prepared end members and intermediate solid solutions.

RESULTS

Wollastonite solid solutions containing the hedenbergite component synthesized at 750°–995°C, 1 Kb $P_{\text{H}_2\text{O}}$ and f_{O_2} defined by the QFM buffer resulted in a smooth variation of d in the composition interval $(\text{Ca}_{1.0}\text{Fe}_{0.0})\text{SiO}_3$ to $(\text{Ca}_{0.90}\text{Fe}_{0.10})\text{SiO}_3$.¹ The data for the two strongest of the 5 major reflections are shown in Figure 1. The data for the remaining reflections are all similar in appearance. The values given in the ASTM literature by Hellner and Taylor do not agree with values calculated using Appleman *et al.*'s program and the cell data of Prewitt and Peacor (1964). Hence, until this ambiguity and some unusual X-ray effects described below are clarified, the reflections in the interval 31°–22° 2θ will be referred to here in order of decreasing 2θ as d_1 , d_2 , d_3 , d_4 , d_5 .

In the interval CaSiO_3 – $(\text{Ca}_{0.90}\text{Fe}_{0.10})\text{SiO}_3$, the least squares equations for $d_{(hkl)}$ as a function of composition are:

$$d_1 = 2.8840 + 0.0009x \quad (1)$$

$$d_2 = 2.9910 + 0.0010x \quad (2)$$

$$d_3 = 3.2276 + 0.0009x \quad (3)$$

$$d_4 = 3.4080 + 0.0011x \quad (4)$$

$$d_5 = 3.7106 + 0.0013x \quad (5)$$

where x is mole fraction CaSiO_3 in $(\text{Ca}_x\text{Fe}_{1-x})\text{SiO}_3$.

The data from $(\text{Ca}_{0.90}\text{Fe}_{0.10})\text{SiO}_3$ to $(\text{Ca}_{0.60}\text{Fe}_{0.40})\text{SiO}_3$ appears linear within experimental error. For more iron-rich compositions, the curves describing all d values show a sudden break around $\text{Ca}_{0.90}$. Note that Boyd and Schairer (1964) and Davis and Boyd (1966) also encountered the phenomenon of an abrupt change in slope in their determination of $d_{(31\bar{1})}$ and $d_{(220)}$, respectively, as a function of composition along the diopside-enstatite join. They were unable to explain the cause of this effect. While it is true that their system dealt with ortho-pyroxene-clinopyroxene ($\text{Mg} \leftrightarrow \text{Fe}$) equilibria and this system deals with pyroxenoid-clinopyroxene ($\text{Ca} \leftrightarrow \text{Fe}$) equilibria, the underlying causes of the effect in these chain silicates may well be similar.

¹ To obtain a copy of the tables listing the experimental conditions for the synthesis of these materials and measured d values order NAPS Document No. 01606 from ASIS National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 866 Third Avenue, New York, N.Y. 10022, remitting \$2.00 for microfiche or \$5.00 for photocopies, in advance, payable to CCMIC-NAPS.

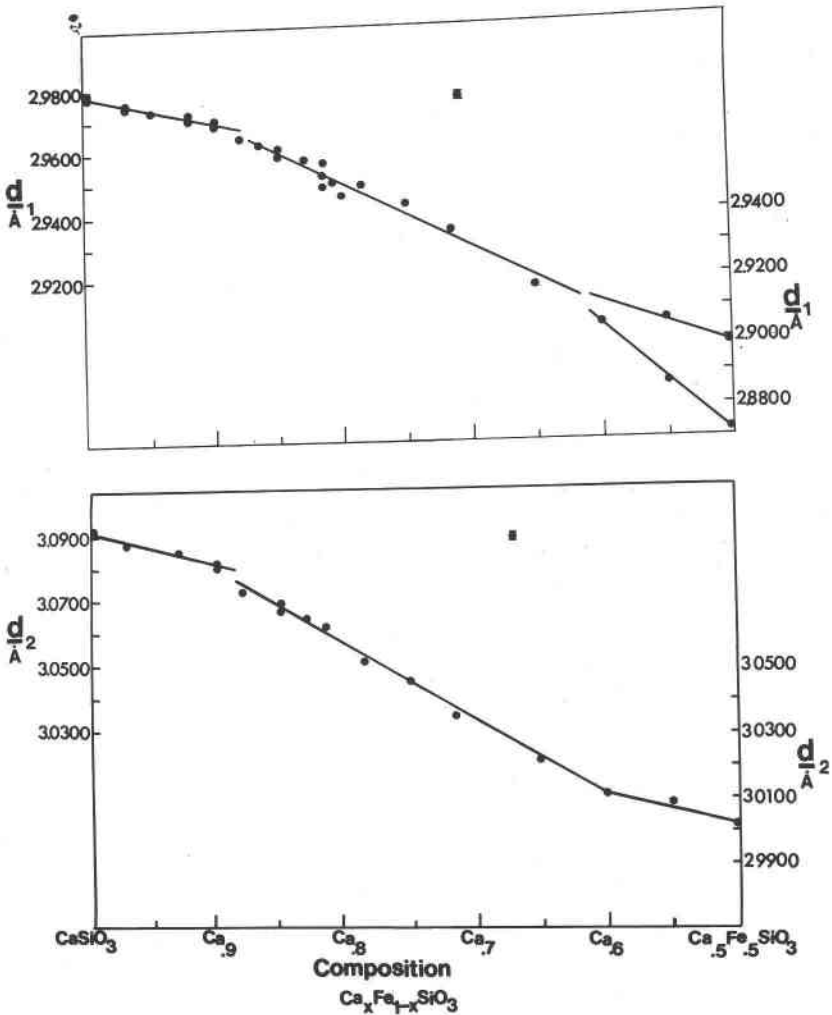


FIG. 1. d_1 and d_2 versus composition for wollastonite solid solution ($\text{Ca}_x\text{Fe}_{1-x}$) SiO_3 synthesized on the QFM buffer.

From $\text{Ca}_{0.60}$ to $\text{Ca}_{0.50}$ the major reflection d_1 splits into two well-defined reflections. These continue to more iron-rich compositions and are presumably those used by Lindsley and Munoz (1969) in derivation of spacing curves for wollastonite-ferrosilite solid solutions.

Other than the change in slope around $\text{Ca}_{0.90}$, the variation in all d values with composition appears to be straightforward. However, more careful examination of all reflections in the interval ($\text{Ca}_{0.90}\text{Fe}_{0.10}$) SiO_3 to

$(\text{Ca}_{0.78}\text{Fe}_{0.22})\text{SiO}_3$ reveals the development of subsidiary reflections accompanying those reflections already present.

Figure 2 shows the isothermal development of these subsidiary reflections for d_2 (the second major reflection) as a function of composition. The reflection for KCl, the internal standard is also shown. All compounds were synthesized at 850°C , 1 kb $P_{\text{H}_2\text{O}}$ and f_{O_2} defined by the QFM buffer. The subsidiary peak begins on the high 2θ or low d side. With increasing iron content it changes 2θ and continues to develop in intensity to a composition of $(\text{Ca}_{0.86}\text{Fe}_{0.15})\text{SiO}_3$. The original peak has now de-

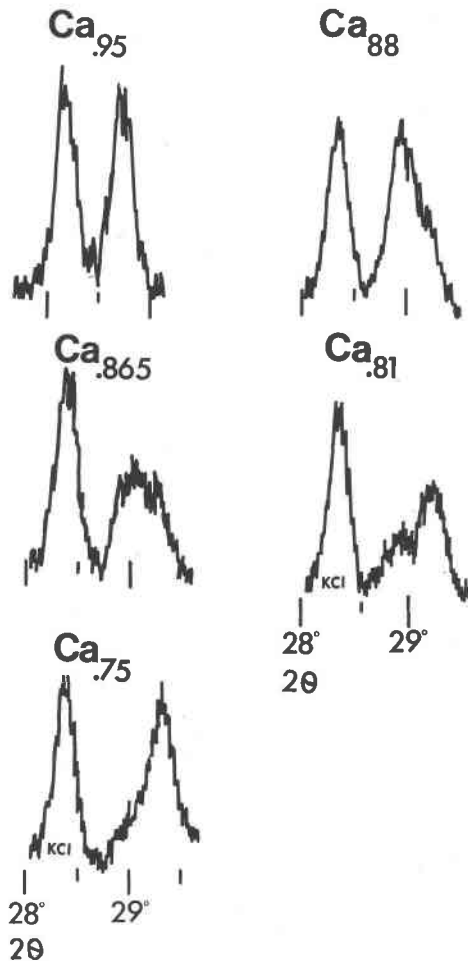


FIG. 2. Isothermal ($T = 850^\circ\text{C}$) development of d_2 as a function of composition $(\text{Ca}_x\text{Fe}_{1-x})\text{SiO}_3$. The internal KCl standard peak is also included.

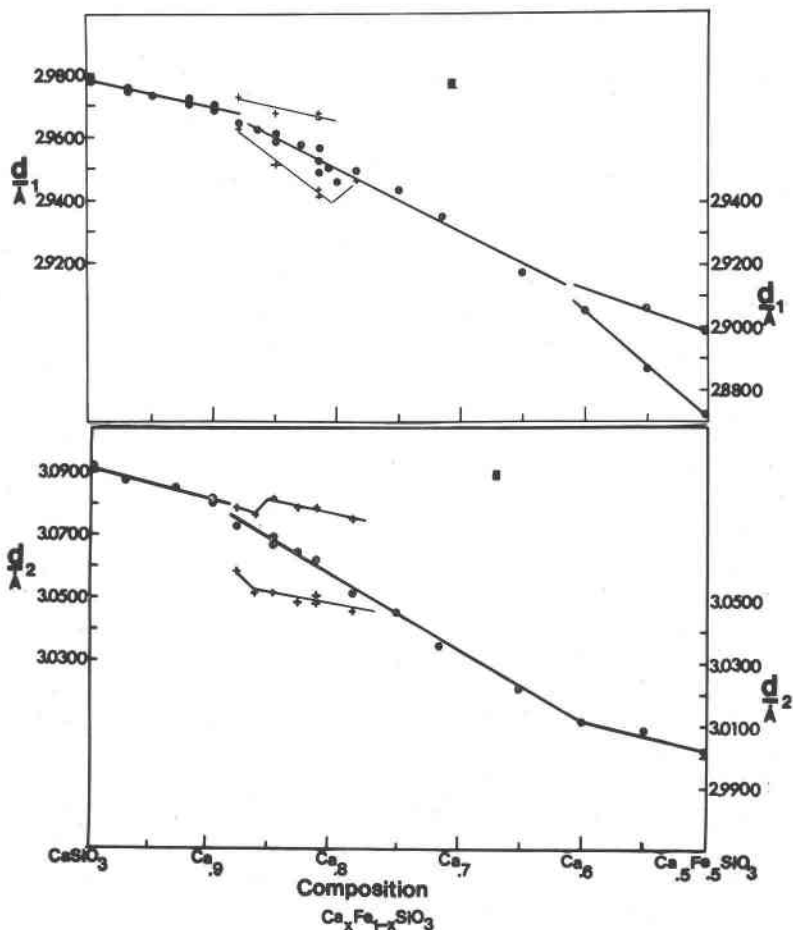


FIG. 3. d_1 and d_2 versus composition for wollastonite solid solutions ($\text{Ca}_x\text{Fe}_{1-x}$) SiO_3 synthesized on the QFM buffer. The crosses represent measurements of the twin reflections comprising the "bulk" peak denoted by the solid circles.

creased in intensity. With increasing iron content, the intensity of the subsidiary reflection increases and the intensity of the original reflection decreases until no trace of the latter remains at a composition of approximately $(\text{Ca}_{0.75}\text{Fe}_{0.25})\text{SiO}_3$. All other reflections show similar development.

The peak measurements for d_1 and d_2 as a function of composition are plotted in Figure 3. Graphs of the data for the remaining peaks have essentially the same form as that of d_1 and d_2 . The figures show two types of measurements for the split reflections. The crosses denote measurements of the separate reflections comprising a double reflection for iso-

thermal ($T=850^{\circ}\text{C}$) samples. The solid circles represent the measured average of the two reflections as given in Figure 1. Since there was considerable overlap in many instances, it was extremely difficult to measure the position of reflection accurately. However, the values given represent the most likely locations of the centers of the reflection peaks.

Given the extreme uncertainty in measurement, it is uncertain whether the values represent a change in d as a function of composition. The apparent decrease of the low d_1 reflection may just as well be due to the decrease in intensity (with concomitant overlap) of the high d_1 reflection. Within the reproducibility of measurement ($0.0010\text{--}0.0030\text{ \AA}$), all other split portions appear to remain constant with changing composition.

Experiments were made at varying temperatures for a few compositions which displayed this splitting effect. These showed that the intensity of the split portions of a given reflection was indeed related to temperature. However, coupled with the marked overlap and interaction at lower temperatures, little could be determined about precisely how the intensity or position of the reflections varied.

For compositions synthesized on the HM buffer, no splitting was observed. Instead, andradite co-existing with wollastonite solid solution developed for bulk compositions beginning at $(\text{Ca}_{0.90}\text{Fe}_{0.10})\text{SiO}_3$ at 850°C and 1 kb $P_{\text{H}_2\text{O}}$.

The above diffraction effects could simply be ascribed to a two-phase field. However, there is no optical (oil immersion and phase contrast) evidence for the presence of two phases. Further, the set of d values do not fit any known phase or combination of phases other than a mixture of $(\text{Ca}_x\text{Fe}_{1-x})\text{SiO}_3$ and $(\text{Ca}_y\text{Fe}_{1-y})\text{SiO}_3$ (where x and y refer to different cation proportions derived from one bulk composition). However, given the measured d values and the relative sizes of the Ca and Fe cations, it is believed that the stoichiometric coefficients indicate two types of pyroxenoid phases as follows. A type with large d representing a more Ca-rich phase and a type with small d representing a more Fe-rich phase. The exact nature of the more Fe-rich phase is not known from these studies. However, from other work (Rutstein and White, 1971), it is probably due to an ordering effect. This will be discussed below.

PHASE EQUILIBRIA

The boundary determined experimentally using X-ray and optical microscopic techniques for the wollastonite solid solution + hedenbergite field and the wollastonite solid solution field is shown in Figure 4 for 1 kb $P_{\text{H}_2\text{O}}$ and f_{O_2} defined by the QFM buffer. The data points represent solution and exsolution runs of previously synthesized end members, complete reversal of the reaction using previously synthesized end mem-

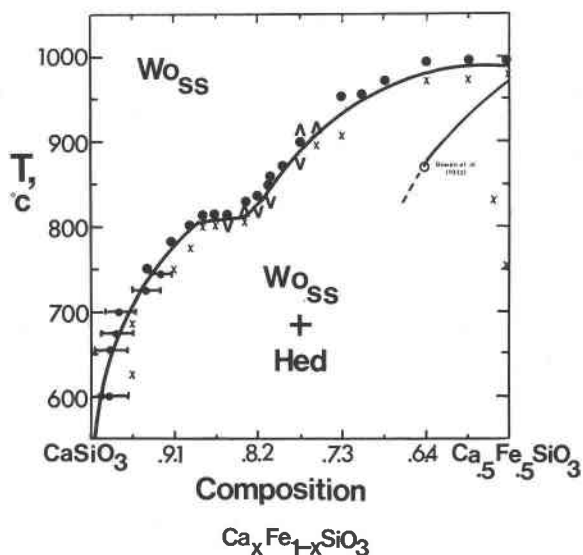


FIG. 4. Temperature—composition relations for wollastonite solid solutions and hedenbergite at 1 kb $P_{\text{H}_2\text{O}}$ and f_{O_2} defined by the QFM buffer. The synthesis experiments are denoted by solid circles indicating one phase and crosses indicating two phases. Solution and exsolution experiments are denoted by a solid circle with an error bar representing the spread of measurements. Complete reversal of reaction, is denoted by a V pointing in the direction of reaction reversal. See text for discussion. The solvus determined by Bowen *et al.* (1933) is shown for comparison.

bers or intermediate solid solutions, and steady state synthesis runs yielding one of two phases.² Compositions for the solution and exsolution experiments were determined using the spacing curves discussed above. Since the spacing curves could not be applied reproducibly at varying temperatures for compositions having doublet reflections, this technique for equilibria determination was restricted to the less iron-rich solid solutions. The data for complete reaction reversal represent wollastonite solid solution starting product \rightarrow wollastonite solid solution + hedenbergite run products (denoted by ∇); and wollastonite solid solutions + hedenbergite starting product \rightarrow wollastonite solid solution run product (denoted by \wedge). The determination of the steady state approximation for the synthesis experiments was made on the basis of no change in run products for experiments up to four weeks duration ($T = 750^\circ$) as compared to experiments of a week's duration. Note that all of the data ob-

² For directions to obtain a copy of the tables listing the hydrothermal experiments used to determine the solvus, see footnote on page 2042.

tained by the various techniques are reproducible and internally consistent. This, in itself, is an additional criterion that the results represent equilibrium conditions.

No differences in equilibria position were discerned for $\frac{1}{2}$, 1, or 2 kb experiments. Similarly, no differences were observed for experiments made on the WI or NNO buffers. At values of oxygen fugacity higher than NNO, hedenbergite is replaced by andradite, wollastonite solid solution, and quartz.

The solvus determined by Bowen *et al.* is also shown for comparison. The differences between it and the redetermined equilibria given here are believed due to lack of attainment of equilibrium in the experiments of the earlier workers (*e.g.*, see Lindsley and Munoz, 1969, p. 303). Note that the present phase diagram goes far in explaining the paucity of iron-rich wollastonites in the natural environment. Further discussion of this point will be presented elsewhere (Rutstein, in preparation). Suffice it to say that the relocation of the equilibria, coupled with the effects of the diopside component upon this equilibria, explains the majority of natural wollastonite compositions.

DISCUSSION

The phase equilibria results of the present study reveal yet another example of what appears to be an inflected subsolidus solvus, (*e.g.*, see Davis and Boyd, 1966; Lindsley and Munoz, 1969). However, the present system displays these effects at much lower pressures than either of the others.

The inflected appearance of the solvus can be explained as being due to either one of two causes (*e.g.*, see Lindsley and Munoz, 1969, pp. 308–309). First, the cause may be shown as in Figure 5. Here, the inflection arises due to the interference of two different elements of pyroxene-pyroxenoid equilibria. That is, a miscibility gap in the wollastonite solid solutions and a pyroxene-pyroxenoid transition loop. This explanation requires a continuous shift between the wollastonite structure and the hedenbergite structure.

However, for the reaction $(Ca_xFe_{1-x})SiO_3 \leftrightarrow CaFeSi_2O_6 + (Ca_yFe_{1-y})SiO_3$ there are three sites of concern in wollastonite solid solutions, but only two in hedenbergite. Therefore, for the conversion of wollastonite solid solutions to hedenbergite, or vice versa, a disordered intermediary phase would be predicted.

In addition, there is no evidence for a Ca- or Fe- deficient hedenbergite co-existing with wollastonite solid solutions for the bulk compositions studied here. Comparison of $d_{(221)}$ and $d_{(220)}$ values for pure hedenbergite and hedenbergite co-existing with wollastonite solid solutions

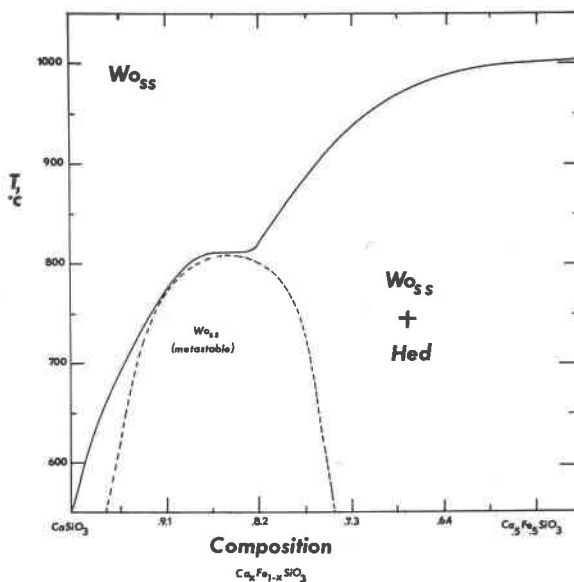


FIG. 5. Possible explanation for inflected solvus shown in Fig. 4. A metastable miscibility gap interfering with a pyroxene-pyroxenoid transition loop.

reveal that both sets of values are essentially identical. Also, Papike (personal communication) had indicated that an Fe-deficient hedenbergite is not structurally stable. Hence, this explanation is not preferred.

An alternative explanation is shown in Figure 6b. Here the cause of the inflection is due to the equilibria between one pyroxene phase (hedenbergite) and *two* pyroxenoid phases. According to optical and X-ray studies, there appears to be very little difference between the properties of these two pyroxenoid phases. Further, the sizes of these phases is unknown although they must be of at least sufficient magnitude to produce X-ray diffraction effects. However, on the basis of infrared spectroscopic measurements presented elsewhere (Rutstein and White, 1971), the second pyroxenoid phase actually has the bustamite ($\text{CaMnSi}_2\text{O}_6$) structure. To a first approximation, this structure can be considered as the ordered analogue of disordered iron-rich wollastonite structures. Thus, although schematic, Figure 6b was drawn to correspond as closely as possible to the X-ray data presented above, but yet be consistent with the spectroscopic data cited.

The interpretation of the interaction of the two pyroxenoid structural types explains the X-ray diffraction effects discussed above. The doublets then represent distinct and separate coexisting crystals of very similar composition but in an ordered-disordered relationship to one another.

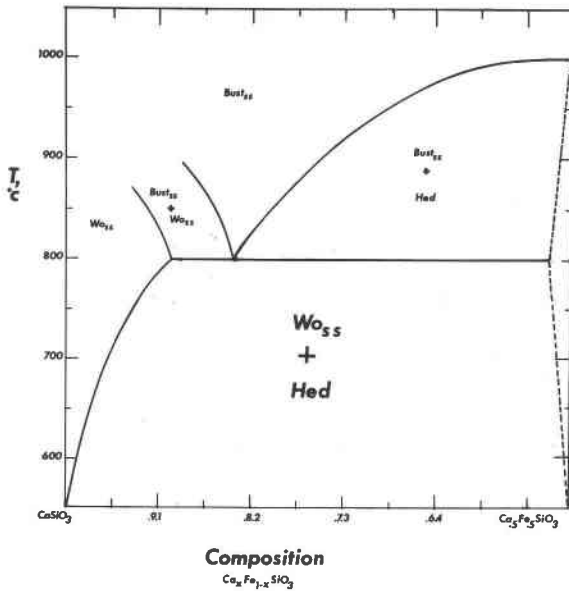


FIG. 6. Preferred explanation for inflected solvus shown in Fig. 4. Hedenbergite coexists with a pyroxenoid with either the wollastonite or the bustamite structure. The details of the phase boundaries are schematic and, in the case of the field of hedenbergite solid solution, highly exaggerated.

Note that the effects observed could be equally explained by a "mixed crystal" containing regions (or chain sections) of bustamite structure and regions (or chain sections) of wollastonite structure. Clarification of this can be gained by consideration of the nature and relationships of the two pyroxenoid structures as follows.

In pure triclinic wollastonite, the calcium atoms are distributed over three general positions (Prewitt and Buerger, 1963). The retention of the wollastonite structure with the addition of iron requires that the iron and calcium both be distributed randomly. However, given cation size considerations, it is probable that this random distribution is confined to the smaller $\text{Ca}_{(1)}$ and $\text{Ca}_{(2)}$ sites and the bridging $\text{Ca}_{(3)}$ site is restricted to calcium.

On the other hand, in the pure bustamite structure, the calcium and iron must be ordered. By analogy with the manganese analogue (Prewitt and Peacor, 1964) this Fe-bustamite (1:1 Ca:Fe) must have one Ca and one Fe on inversion centers and two Ca and two Fe in general positions. Additionally, this ordering requires a shifting of the octahedral bands relative to the wollastonite structure.

For intermediate compositions (*e.g.*, approximately $(\text{Ca}_{0.88}\text{Fe}_{0.12})\text{SiO}_3$ to $(\text{Ca}_{0.5}\text{Fe}_{0.5})\text{SiO}_3$) at 850°C), the bustamite structure is observed spectroscopically (Rutstein and White, 1971). However, since Fe and Ca are no longer in equal proportions, the probability of a "disordered" bustamite arises; this is, a random distribution of iron and calcium over the general positions. The detailed nature and extent of disorder (relative to bustamite) or order (relative to wollastonite) is not clear and must await single crystal characterization.

What is clear, however, is that the distribution of iron in low-iron wollastonite solid solutions proceeds in a random fashion as discussed above. At a certain temperature-composition dependent boundary, the substituting iron becomes ordered with the resultant development of a new structural variant—the bustamite type—coexisting with the wollastonite structural type. With increasingly iron-rich bulk compositions, the development of an ordered structure predominated over the disordered structure and the bustamite variant is stable alone. With increasing temperature, a given composition can interact to produce a variety of ordered and disordered phases relative to *both* the wollastonite and the bustamite structural types. The details of these variances and their interactions with the high temperature α -wollastonite modification and with liquidus-solidus equilibria of the system remain to be determined.

CONCLUSIONS

It is apparent from this work and the work of others (Kushiro, 1969, and Davis and Boyd, 1966, for the MgSiO_3 - $\text{CaMgSi}_2\text{O}_6$ join; Lindsley and Munoz, 1969, for the FeSiO_3 - $\text{CaFeSi}_2\text{O}_6$ join; and work underway on the CaSiO_3 - $\text{CaMnSi}_2\text{O}_6$ join) that more careful characterization of the phases is needed for those reactions involving chain silicates. It appears that routine applications of optical and X-ray powder diffraction techniques will not always suffice for phase characterization. Instead, supplementary techniques are often necessary (in this case, infrared spectroscopy). Hence, until the structure and crystal chemistry of the reactants and intermediate phases is more clearly understood, one must use caution in accepting the results of phase equilibria studies.

Application of a variety of characterization tools and crystal chemical considerations to the subsolidus wollastonite-hedenbergite (CaSiO_3 - $\text{CaFeSi}_2\text{O}_6$) equilibria has revealed the following:

1. The correct equilibria lies to much less iron-rich compositions than previously thought. This removes much of the apparent contradiction between iron content of compositions of natural wollastonites and those predicted by experimental studies.
2. Where only a single simple structural variant was considered to

exist, actually a variety of ordered and disordered wollastonite and bustamite structural types exist as a function of composition and temperature.

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