

Stability Relations of Andradite-Quartz in the System Ca-Fe-Si-O-H

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Abstract

Isobaric $\log f_{O_2}$ - T phase relations for the reaction andradite + quartz = hedenbergite + wollastonite + $1/2 O_2$ in the Ca-Fe-Si-O-H system were experimentally determined at 500 and 2000 bars P_{fluid} and temperatures from 400° to 900°C using conventional techniques with solid phase oxygen buffers to control f_{O_2} . With f_{O_2} values defined by the Ni-NiO buffer, the assemblage andradite + quartz + fluid is stable up to 600°C at 500 bars and 680°C at 2000 bars P_{fluid} . In the lower f_{O_2} range, the assemblage hedenbergite + wollastonite + fluid is stable above about 350°C. The high-temperature and high- f_{O_2} assemblage of equivalent composition is wollastonite + magnetite (or hematite) + quartz + fluid. The low-temperature assemblage is ilvaite + wollastonite (or xonotlite) + fluid. Combined with the previously determined equilibria for wollastonite, andradite, hedenbergite, and ilvaite, chemographic analyses interrelating the phases andradite (Ad), hedenbergite (Hd), wollastonite (Wo), ilvaite (Iv), magnetite (Mt), calcite (Cc), and quartz (Qz) in saturated SiO_2 conditions in the system Ca-Fe-Si-C-O-H permits the locations of invariant points on a $\log f_{O_2}$ - T diagram. It also delineates isobaric T - f_{O_2} conditions of formation for the assemblages Ad+Iv+Qz, Hd+Iv+Qz, Ad+Qz+Mt, Ad+Hd+Qz, Ad+Wo+Qz, Ad+Wo+Cc, Ad+Mt+Cc, Wo+Mt+Qz, and others applicable to an analysis of Ca-Fe-Si skarn formation.

Introduction

The purpose of this study is to continue investigations on the stability relations of some common mineral assemblages found in skarns. To date, andradite has been synthesized in the laboratory, and its stability has been determined by numerous workers (Flint, McMurdie, and Wells, 1941; Coes, 1955; Jagitsch, 1956; Swanson *et al.*, 1960; Ernst, 1966; Huckenholz and Yoder, 1970; Gustafson and Ernst, 1971). The most detailed and comprehensive experimental study of the f_{O_2} - T - P_{fluid} relations for andradite, hedenbergite, and ilvaite bulk composition in the system Ca-Fe-Al-Si-O-H is that of Gustafson (1971; 1974). It was recognized that the upper thermal stability limit and the breakdown products of andradite are strongly f_{O_2} dependent. Two reactions—(1) andradite = magnetite + wollastonite + O_2 ; and (2) andradite = kirschsteinite + wollastonite + O_2 —were found to define the stability limit of andradite. However, kirschsteinite is not stable in the presence of excess SiO_2 , and these reactions are inappropriate for most geologic environments (*e.g.*, for f_{O_2} less than those defined by the HM buffer) and the andradite stability limit greatly shifts towards lower temperatures and higher f_{O_2} values. Most previous andradite investigations have been confined

to the bulk composition $Ca_3Fe_2Si_3O_{12}$. Except for reconnaissance experiments performed by Kurshakova (1970, 1971a), whose results will be commented upon later in the present report, the laboratory study of the reaction: andradite + 2 quartz = hedenbergite + wollastonite + O_2 has not been previously undertaken.

Burt (1971a) has recently deduced mineral stabilities in the system Ca-Fe-Si-C-O-H on several different types of phase diagrams by employing mineral incompatibilities observed in natural skarns. The stability diagrams resulting from his analyses were found to work very well as a petrogenetic grid for skarn deposits. However, because experimental data were not available, all his diagrams were drawn for arbitrary unspecified T , P_{fluid} , f_{O_2} , and μCO_2 . The experimental data for the reaction andradite + quartz = wollastonite + hedenbergite + O_2 obtained in the present study, combined with Gustafson's earlier work and with the well-determined reaction calcite + quartz = wollastonite + CO_2 (Harker and Tuttle, 1956; Greenwood, 1967) may be employed to define T - f_{O_2} coordinates for an invariant point (point 9 of Figs. 38 and 39 of Burt, 1971a) from which radiate univariant curves for two other reactions—(1) andradite + quartz + CO_2 = hedenbergite +

calcite + O₂; and (2) andradite + wollastonite + CO₂ = hedenbergite + calcite + O₂.

The effect of SiO₂ on the andradite stability is geologically significant because of the fact that in thermally metamorphosed impure limestone and in metasomatic skarn formation, andradite-rich garnet is almost always found in association with quartz (*e.g.*, see Burt, 1971b). Although end-member andradite is not common, knowledge of its physicochemical behavior is important as a limiting case for petrogenetic discussion of complex natural garnet solid solutions. Examples of conversion of hedenbergite to andradite in siliceous skarns are numerous (Kurshakova, 1968; Burt, 1971b). Such metasomatic alteration has even been reported in the Allende meteorite (Fuchs, 1971). Because of the petrologic significance of the reaction: andradite + quartz = hedenbergite + wollastonite + O₂, an experimental study was begun in 1970 as part of a project investigating phase relations in the system Ca-Fe-Al-Si-C-O-H, and the results will be discussed in this report.

Experiments

Method

The starting materials used corresponded to the composition andradite + 2 quartz (3CaO·Fe₂O₃·5SiO₂). They were oxide + carbonate mixtures made of reagent grade hematite (fired 24 hours at 1000°C in air), CaCO₃, and cristobalite. In order to decarbonate the starting mix, it was fired at 1000°C in a controlled CO - CO₂ atmosphere for one hour. The oxide mixtures were then sealed with excess H₂O in 0.22" O.D. Au capsules and subjected to experiments at 800°C and 600°C, 2 kbar P_{fluid} for a week in order to synthesize high-temperature (hedenbergite + wollastonite) and low-temperature (andradite + quartz) assemblages, respectively. Crystalline mixtures consisting of synthetic high- and low-temperature assemblages in subequal proportion were then used for the reversal experiments. Phase relations were deduced by observing which assemblage grew

at the expense of the other, *i.e.*, the reactions were reversed.

Conventional hydrothermal apparatus and procedures as described in previous reports (Liou, 1973; Gustafson, 1971, 1974; Liou, Kuniyoshi, and Ito, 1974) were used. Experiments were all performed in the presence of excess H₂O; the solid-oxygen-buffer techniques described by Eugster and Wones (1962) and by Huebner (1971) were employed throughout the investigation. The $P - T$ fluctuations for each run were within $\pm 5^\circ\text{C}$ and ± 30 bars. The abbreviations for oxygen buffer assemblages and synthetic phases are shown in Table 1.

Run products were determined microscopically and by powder X-ray diffraction methods using CuK α radiation. The identification of andradite, quartz, hedenbergite, and wollastonite could be made unambiguously under the microscope. The relative change of phase proportions in runs very close to the equilibrium boundary, however, was not always possible to determine because the rate of reaction, usually in the direction of decreasing temperature (*e.g.*, conversion of hedenbergite to andradite), was exceedingly slow at temperatures lower than 600°C and at 500 bars P_{fluid} . Therefore, in many cases run products had to be rerun under the same conditions before the direction of reaction could be ascertained, and several other runs under closely similar $P_{\text{fluid}} - T - f_{\text{O}_2}$ conditions were made in order to demonstrate unequivocally the reaction direction.

Compositions of phases considered in the present study are shown on a CaSiO₃-FeO_x-SiO₂ plot (Fig. 1) and listed together with their abbreviations in Table 1. The bulk composition investigated was 3CaO·Fe₂O₃·5SiO₂ + excess H₂O (square of Figure 1). However, platinum charge capsules were used for the NNO buffer runs, and it is believed that iron loss in Pt at low oxygen fugacity is so serious that charge compositions could be changed appreciably. Similarly, iron loss to the Ag₂₅Pd₇₅ capsules with the QFM and IW buffer was also detected, in that the run products (on the high-temperature side of the

TABLE 1. Abbreviations and Compositions for Synthetic Phases and Oxygen Buffer Assemblages

Ad = Andradite, Ca ₃ Fe ³⁺ ₂ Si ₅ O ₁₂	Mt = Magnetite, Fe ₃ O ₄
Hd = Hedenbergite, CaFe ²⁺ Si ₂ O ₆	Qz = Quartz, SiO ₂
Wo = Wollastonite, CaSiO ₃	HM = Hematite - Magnetite
Iv = Ilvaite, CaFe ²⁺ Fe ³⁺ Si ₂ O ₈ (OH)	NNO = Nickel - Nickel Oxide
Kr = Kirschsteinite, CaFe ²⁺ SiO ₄	QMF = Quartz + Magnetite - Fayalite
Xo = Xonotlite, Ca ₆ Si ₆ O ₁₇ (OH) ₂	MW = Magnetite - Wustite
Fa = Fayalite, Fe ₂ SiO ₄	IM = Iron - Magnetite
Cc = Calcite, CaCO ₃	F = Fluid

reaction) usually show a thin colorless wollastonite and/or quartz rim around the charge at the contact with the capsule. Therefore, the charge composition could shift away from the FeO_x apex, as shown by the arrow in Figure 1. Thus quartz and wollastonite, respectively, could be present in minor quantity in the high- and low-temperature assemblage in the reversal experiments. The amount of iron loss has not been determined in the present study. Evidently, it is a function of P , T , f_{O_2} , run duration, charge composition, mineral assemblage and the nature of the charge capsule.

Results

Andradite + quartz were readily synthesized to 100 percent purity within a week from an oxide mixture in an unbuffered run at 600°C , 2 kbar P_{fluid} . The high-temperature assemblage, hedenbergite + wollastonite, was crystallized from the oxide mixture in an unbuffered run at 800°C or with f_{O_2} defined by the MW buffer at 600°C . The products of unbuffered experiments invariably contain some quartz + andradite (less than 20 percent) with hedenbergite + wollastonite. The assemblage hedenbergite + wollastonite (+quartz) could only be obtained in experiments with f_{O_2} controlled by the NNO, QFM, and MW buffers. However, for the purpose of the present study, minor amounts of andradite + quartz present

in the high-temperature assemblage do not affect the determination of the andradite + quartz stability because the reversed experiments were conducted by using the crystal mixtures consisting of high- and low-temperature assemblages in subequal proportions.

In many of the high-temperature experiments starting from either an oxide mixture or a crystal mixture, zoning in the condensed run products was observed: a greenish hedenbergite + wollastonite core coated with a thin colorless wollastonite + quartz layer (less than 50μ thick) at the contact with the capsule. This zoning was very distinctive in the run products in which a platinum capsule was used for the NNO buffer. This phenomenon evidently is related to the depletion of iron into the Pt capsule, thus changing the bulk composition significantly.

The descriptions of synthetic andradite, hedenbergite, and wollastonite obtained in the system Ca-Fe-Si-O-H have been given in detail by Gustafson (1971, 1974), so only a brief summary will be given here. Andradite formed crystals 2-10 μ in diameter which often exhibit {110} crystal faces; they are light green in color and commonly contained numerous minute inclusions. The cell constant (a_0) and refractive index (n_D) of synthetic andradite (600°C , 2 kbar P_{fluid} , unbuffered)— $12.064 \pm 0.004 \text{ \AA}$ and 1.887 ± 0.003 —are in good agreement with earlier measurements reported in the literature (for detailed review, see Gustafson, 1971). It should be pointed out that both the lattice constant and the refractive index of andradite are highly dependent on the starting material, run temperature, and $P_{\text{H}_2\text{O}}$. It has been suggested that some synthetic andradite crystallized in the anhydrous condition may contain minor substitution of Fe^{2+} for Ca, and andradite formed hydrothermally at temperatures less than 500°C may form hydroandradite-andradite solid solutions.

Synthetic hedenbergite crystallized from oxide mixtures, both unbuffered and with the QFM buffer, are light green in color and occur as thin prisms 10-30 μ in length, whereas those crystallized under f_{O_2} defined by the MW buffer are very light green and much finer grained ($< 10 \mu$). The average cell dimension and refractive indices are $a_0 = 9.85 \pm 0.02 \text{ \AA}$, $b_0 = 9.03 \pm 0.01 \text{ \AA}$, $c_0 = 5.25 \pm 0.01 \text{ \AA}$, and $\beta = 104.8^\circ \pm 0.1^\circ$; $N_\alpha = 1.730 \pm 0.005$; and $N_\gamma = 1.755 \pm 0.005$. No systematic change in the properties of hedenbergite from the hedenbergite-wollastonite assemblage was found. This fact, along with the observation made by the previous investigators (Rutstein and Yund, 1969; Gustafson, 1971,

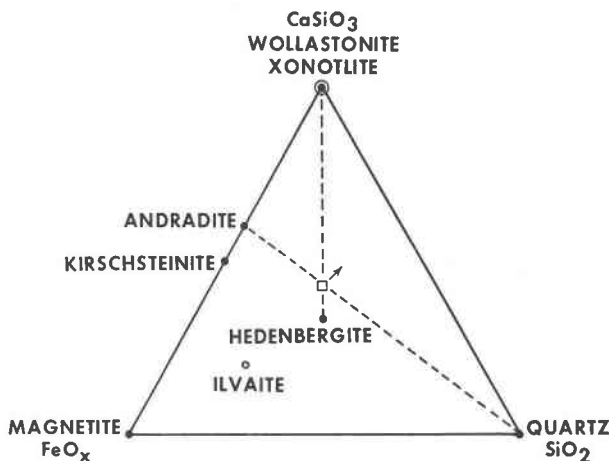


FIG. 1. Compositions of crystalline phases in the system $\text{FeO}_x - \text{CaSiO}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ projected onto the anhydrous plane. Solid circles: anhydrous phases; Open circles: hydrous phases; Square: ideal bulk composition of the charge in the present study. The dashed lines indicate the reaction relation between andradite + quartz and hedenbergite + wollastonite. Arrows shows the charge compositional shift for runs at the low f_{O_2} conditions.

TABLE 2. Reversal Experimental Run Data for the Reaction: Andradite + Quartz = Hedenbergite + Wollastonite + O₂

Run No. (Ad)	Starting mix*	Temp. (°C)	P _{fluid} (bars)	Buffer	Duration (hours)	Condensed run products**
19	(1)	786	2000	NNO	117	Hd + Wo (+Qz)
37	(2)	730	2000	NNO	240	Hd + Wo (+Ad + Oz)
22	(2)	723	2000	NNO	278	Hd + Wo (+Ad + Qz)
34	(2)	711	2000	NNO	312	Hd + Wo (+Ad + Qz)
21	(2)	696	2000	NNO	278	Hd + Wo (+Ad + Qz)
40	(2)	683	2000	NNO	550	Hd + Wo (+Ad + Oz)
20	(2)	676	2000	NNO	430	Ad + Qz (+Wo)
50(2)	(2)	572	2000	NNO	1440	Ad + Qz (+Hd + Wo)
50	(2)	650	2000	NNO	762	Ad + Qz (+Hd + Wo)
48(2)	(2)	623	2000	NNO	768	Ad + Qz (+Hd + Wo)
25(2)	(2)	404	2000	NNO	1446	Ad + Qz (+Hd + Wo)
23	(2)	695	2000	QFM	305	Hd + Wo (+Qz)
5	(1)	676	2000	QFM	312	Hd + Wo (+Qz)
17	(2)	674	2000	QFM	576	Hd + Wo (+Ad + Qz)
24	(2)	657	2000	QFM	240	Hd + Wo (+Ad + Qz)
13	(2)	652	2000	QFM	426	Hd + Wo (+Ad + Qz)
46	(2)	645	2000	QFM	580	Hd + Wo (+Ad + Qz)
47	(2)	627	2000	QFM	606	Hd + Wo (+Ad + Qz)
48	(2)	610	2000	QFM	861	Hd + Wo (+Ad + Qz)
12	(2)	596	2000	QFM	428	Ad + Qz (+Wo)
47(2)	(2)	583	2000	QFM	811	Ad + Qz (+Hd + Wo)
11	(2)	547	2000	QFM	428	Ad + Qz (+Hd + Wo)
10	(2)	500	2000	QFM	428	Ad + Qz (+Hd + Wo)
26(2)	(2)	394	2000	QFM	1446	Ad + Qz (+Hd + Wo)
35	(1)	655	2000	Mw	259	Hd + Wo (+Qz)
16	(1)	574	2000	IM	480	Hd + Wo (+Qz)
31	(2)	698	500	NNO	304	Hd + Wo (+Ad + Qz)
30	(2)	667	500	NNO	385	Hd + Wo (+Ad + Qz)
44	(2)	647	500	NNO	596	Hd + Wo (+Ad + Qz)
41	(2)	621	500	NNO	576	Ad + Qz (+Hd + Wo)
44(2)	(2)	607	500	NNO	1441	Ad + Qz (+Hd + Wo)
45	(2)	597	500	NNO	504	Ad + Qz (+Hd + Wo)
42	(2)	590	500	NNO	1577	Ad + Qz (+Hd + Wo)
32	(2)	673	500	QFM	324	Hd + Wo (+Ad + Qz)
33	(2)	653	500	QFM	385	Hd + Wo (+Ad + Qz)
42	(2)	620	500	QFM	600	Hd + Wo (+Ad + Qz)
43	(2)	606	500	QFM	602	Hd + Wo (+Ad + Qz)
49	(2)	592	500	QFM	504	Hd + Wo (+Ad + Qz)
42(2)	(2)	570	500	QFM	860	Ad + Qz (+Hd + Qz)
43(2)	(2)	539	500	QFM	860	Ad + Qz (+Hd + Qz)

*Starting mix (1) is synthetic assemblage of andradite + 2 quartz + excess H₂O and starting mix (2) is crystalline mixture consisting of (Andradite + 2 quartz): (hedenbergite + wollastonite) in subequal proportion.

**Phase or phases within parentheses are interpreted as metastable.

1974) that there is no noticeable difference in hedenbergite cell parameters with variation in f_{O_2} , indicates that hedenbergite solid solution toward the wollastonite component (Fe-deficient hedenbergite) does not exist or is not structurally stable (Rutstein, 1971).

However, Rutstein (1971, Fig. 4) demonstrated experimentally that wollastonite solid solution extends to the composition (Ca_{0.88}Fe_{0.12})SiO₃ at 800°C with f_{O_2} defined by the QFM buffer. At temperatures lower than 600°C, the hedenbergite component in wollastonite is negligible. This relation is consistent with the analyzed naturally-occurring compositions of metamorphic wollastonites. Thus, it is reasonable to assume that wollastonites encountered in the present study possess compositions ranging from stoichiometric CaSiO₃ to (Ca_{0.9}Fe_{0.1})SiO₃. Wollastonite is colorless, acicular, and fine-grained (less

than 15 μ). Due to the presence of other phases such as hedenbergite, quartz, and andradite in the run products, it was difficult to determine accurately cell dimensions for wollastonite because of peak interference. In addition, due to the fine grain size and intimate association of synthetic phases, measurements of index of refraction were difficult to reproduce. Reliable measurements could only be made on the wollastonite coating the inner capsule walls in iron-leached samples (the NNO buffer at 700°C, oxide mix). Results are as follows: $a_o = 7.906 \pm 0.006 \text{ \AA}$, $b_o = 7.190 \pm 0.008 \text{ \AA}$, $c_o = 7.068 \pm 0.007 \text{ \AA}$, $\alpha = 90.38 \pm 0.05^\circ$, $\beta = 95.24 \pm 0.09^\circ$, $\gamma = 102.50 \pm 0.05^\circ$, $\alpha = 1.620 \pm 0.005$, and $\gamma = 1.628 \pm 0.005$.

The T - f_{O_2} values for the reaction andradite + quartz = hedenbergite + wollastonite + O₂ was determined at $P_{\text{fluid}} = 500$ and 2000 bars. Two starting materials were used: (1) synthetic andradite + quartz; and (2) crystalline mixtures of reactants and products in subequal proportions. Table 2 presents all reversible run data for this reaction; the results are plotted on conventional isobaric log f_{O_2} - T diagrams (Figs. 2 and 3).

At 2 kbar P_{fluid} and above 750° (670°C) with f_{O_2} defined by the NNO (the QFM) buffer, the assemblage andradite + quartz was readily converted to hedenbergite + wollastonite. At lower temperatures

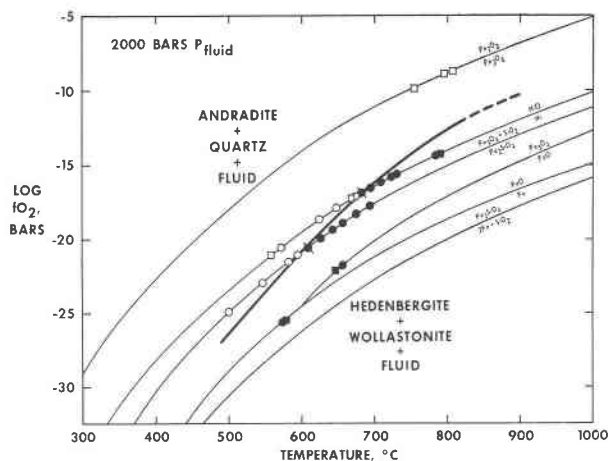


FIG. 2. Log f_{O_2} - T diagram for the andradite + quartz bulk composition (Ca₃Fe₂Si₅O₁₆) + excess H₂O at 2000 bars P_{fluid} (data from Table 2). Buffer curves are from Huebner (1971, Table 5-3, p. 146-147). Symbols indicate starting materials as follows: circles: crystalline mixtures of (andradite + quartz) and (hedenbergite + wollastonite) in subequal proportion; squares: oxidized iron oxide mixture; circles with bar: no reaction has taken place.

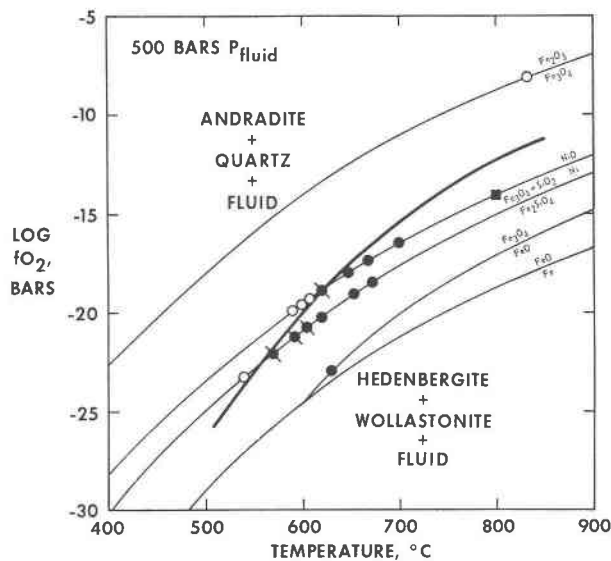


FIG. 3. $\log f_{O_2}$ - T diagram for the andradite + quartz bulk composition + excess H_2O at 500 bars P_{fluid} (data from Table 2) (Symbols, same as Figure 2).

andradite + quartz persisted. However, andradite + quartz apparently is not stable at any temperature along the MW and IM buffers: the two phases readily reacted until andradite was exhausted, leaving the stable assemblage hedenbergite + wollastonite + quartz. The presence of quartz, as mentioned previously, is probably due to the iron loss in the capsule and thus a minor change in the bulk composition occurred.

By using the crystalline mixtures at 2 kbar P_{fluid} , andradite + quartz greatly decreased in the reversal runs over 700°C when the NNO buffer was used. At temperatures lower than 700°C, the reaction is sluggish and 4 phases always remained even after one month's duration. However, slight variations between the peak heights of andradite and hedenbergite in the charge enabled delineation of the reaction direction. The nearly complete andraditization of hedenbergite was found in two long experiments (Ad#20 and Ad#12) at 2 kbar P_{fluid} , which provides confidence in the location of the equilibrium boundary for this reaction. As shown in Figure 2, this boundary crosses the NNO buffer curve at $678^\circ \pm 5^\circ C$ and the QFM buffer at $605^\circ \pm 10^\circ C$.

At 500 bars P_{fluid} , the reaction takes place exceedingly slowly. None of the charges have shown total depletion of andradite (or hedenbergite) in the high (or low) temperature side of the reaction. Therefore, special care had to be taken in detecting the reversal

reaction, and charges under T - f_{O_2} conditions in the vicinity of the equilibrium boundary were run long enough to ensure that reaction had indeed taken place; most of these runs had durations of 20 days to 2 months. The reaction was reversed, and the equilibrium boundary is shown in Figure 3. The reaction crosses the NNO buffer curve at about 620°C and the QFM buffer curve at about 550°C.

A T - P_{fluid} diagram for this reaction is shown in Figure 4, in which circles represent reversals with f_{O_2} defined by the NNO buffer curve and squares, f_{O_2} defined by the QFM buffer curve. When lowering the fluid pressure from 2000 bars to 500 bars, the upper limit for the stable coexistence of andradite + quartz decreases from 678°C to 620°C with f_{O_2} defined by the NNO buffer and from 605°C to 550°C for f_{O_2} defined by the QFM buffer.

Comparison with Previous Studies

The results of this investigation on the reaction (a) andradite + quartz = hedenbergite + wollastonite + O_2 are compared with previous studies in Figure 5. Ernst (1966, Fig. 11) first showed the T - f_{O_2} relations between andradite and hedenbergite at 3 kbar P_{fluid} on the basis of synthetic results utilizing the relatively CaO-poor ferrotremolite bulk composition. The inferred boundary curve of Ernst for the univariant reaction (b) involving conversion of andradite + quartz + magnetite = hedenbergite +

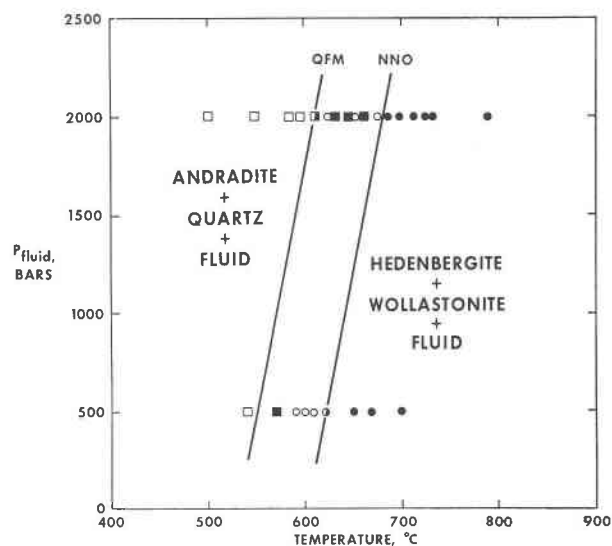


FIG. 4. P_{fluid} - T diagram for the reaction: andradite + quartz = hedenbergite + wollastonite + $1/2 O_2$ at oxygen fugacities defined by the QFM (squares) and NNO buffers (circles).

O₂ was located between the HM and QFM buffer curves and essentially parallel to them. Reactions (b) and also (c), andradite = wollastonite + magnetite + O₂, were later determined experimentally by Gustafson (1971) with results as in Figure 5. Reaction (b) has been reversed although difficulty has been encountered due to the exceedingly slow rate for the andradization of hedenbergite. The univariant curve (b) intersects the NNO buffer curve at about 450°C and 2 kbar P_{fluid} and terminates at high temperature at an invariant point from which radiate reactions (a), (b), (c), and (d)—hedenbergite = wollastonite + magnetite + quartz. Reactions (a) and (b) were experimentally located by different operators and are consistent with the geometrical relationship which will be discussed in detail in the next section. The isobaric invariant point lies at about 920°C, 2 kbar and at f_{O_2} value between the HM and NNO buffers.

Recently, Kurshakova (1970, 1971a, b) published experimental results for reactions (a) and (b), shown as dashed curves in Figure 5. Her curves differ in T - f_{O_2} locations but not in topology compared to the results of Gustafson (1971, 1974) and the present study. However, differences shown in Figure 5 are mainly attributed to differences in starting materials, in run duration, and in experimental methods.

Kurshakova (1970) used chemical mixtures $3CaO \cdot 2FeO \cdot 5SiO_2$ and $3CaO \cdot Fe_2O_3 \cdot 5SiO_2$ as well as mineral mixtures consisting of natural andradite, hedenbergite, and wollastonite selected from calcareous skarn deposits for starting materials. Compositions of these natural minerals were not known. Anhydrous silicic acid was used instead of quartz. These selected minerals + silicic acid were ground into powder and mixed in the stoichiometric proportions to form hedenbergite + wollastonite and andradite + quartz. The starting mixtures, thus, were either andradite + silicic acid or hedenbergite + wollastonite but not the mixture of both reactant and product. Such starting material was then sealed in platinum capsules and subjected to experiments of 750-1000 atm for about 10 days duration. The reaction was detected by the growth of newly formed assemblages in a specific T - f_{O_2} field, *i.e.*, growth of andradite + quartz from chemical mixtures or mineral mixture hedenbergite + wollastonite or *vice versa*. Kurshakova (1970) concluded that "phase transformations in the chemical mixture proceed much more rapidly than in the mineral mixture" and "experiments with chemical mixtures are more

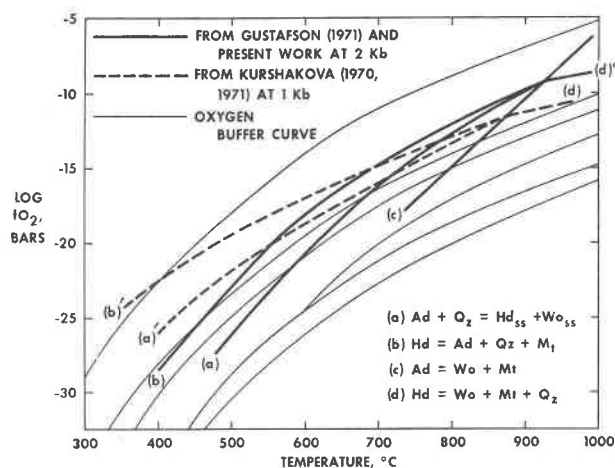


FIG. 5. Comparison of some experimentally determined curves from the present and previous studies on reactions (a) $Ad + Qz = Hd + Wo + 1/2 O_2$; (b) $Hd + O_2 = Ad + Qz + Mt$; (c) $Ad = Wo + Mt + O_2$; and (d) $Hd = Wo + Mt + Qz$.

successful than with mineral mixtures." Thus, her results are in good concordance with the synthetic data of Ernst (1966). Therefore, Kurshakova (1971a, b) used chemical mixtures to study the reaction (b) andradite + quartz + magnetite = hedenbergite, and the results shown in Figure 5 were on the basis of synthetic run products.

Much of the uncertainty in experimental studies between minerals in subsolidus regions arises over the question of whether or not equilibrium has been attained. Fyfe (1960), in a critical discussion of this problem, stated that synthetic results should never be considered as equilibrium results and that the term "equilibrium diagram" should not be used unless it is justified by both experimental and geological criteria. The experiments performed by Kurshakova (1970, 1971a, b) have not been successfully demonstrated as equilibrium, and her results were essentially based on the synthesis data. As mentioned previously, the reverse process involving conversion of hedenbergite + wollastonite to andradite + quartz is extremely sluggish. Seeds of andradite in the mineral mixture and longer experiments are necessary for such conversion at temperatures in the vicinity of the equilibrium boundary if the andradization is to be detected within a reasonable experimental period.

As shown in Figure 5, at constant f_{O_2} and P_{fluid} values, the presently determined equilibrium boundary lies at higher temperatures than the results of Kurshakova (1970) indicate. Her use of silicic acid

instead of quartz could partially account for the difference. The presence of very reactive silicic acid, which possesses a much higher free energy than quartz, must have greatly shifted towards lower temperatures the equilibrium curve of the reaction, andradite + quartz = hedenbergite + wollastonite + O_2 . Moreover, the possible iron loss to the platinum capsules, as discussed in the previous section, as well as possible chemical impurities present in the natural andradite, hedenbergite, and wollastonite of her starting materials may account for the presence of unknown phases in some of her run products (sample 59, Table 4 of Kurshakova, 1970).

Discussion and Applications

Prior to the present investigation, phase equilibria relating most common skarn-forming minerals in the system Ca-Fe-Si-C-O-H have been depicted in many different types of phase diagrams including T - P_{fluid} , isobaric $\log f_{O_2}$ - T , and various isobaric, isothermal $\log f_{O_2}$ - $\log f_{CO_2}$, μ_{O_2} - μ_{CO_2} , and μ_{H_2O} - μ_{CO_2} diagrams where μ is the chemical potential (Kurshakova, 1971b; Gustafson, 1971, 1974; Burt, 1971a, 1972b). These types of phase diagram have been used to show the topological stability relations of mineral assemblages observed in the field (e.g., Burt, 1971b). In the undersaturated and CO_2 -free system, andradite was found to break down to magnetite + wollastonite and kirschsteinite + wollastonite respectively under oxidizing and reducing conditions (Gustafson, 1971, 1974). Using the phases Ad, Hd, Wo, Mt, Kr, Xo, Iv, Qz, and F, Gustafson (1971, Fig. 25) developed a petrogenetic grid with 14 "stable" isobaric invariant points. However, this petrogenetic grid is too complicated for visualization of phase relations; in fact, the stability of many of his 14 isobaric invariant points have not been proven with respect to other calcium-iron-silicates such as ferrobustamite, ferrotremolite, babingtonite, etc (Burt, 1971c).

Using experimentally determined f_{O_2} - T - P_{fluid} stabilities of andradite, hedenbergite, ilvaite, and xonotlite (Gustafson, 1971, 1974; Figs. 2 and 3, present study) and Schreinemaker's principle (for details, see Zen, 1966), the sequence of assemblages relating these phases may be quantitatively located in an isobaric T - f_{O_2} plane. To make the discussion as simple as possible, 3 assumptions were made: (1) fluid (considered as essentially pure H_2O) and quartz are present in excess in the pseudobinary system $CaSiO_3$ - FeO_x ; (2) the only iron oxide is

magnetite; and (3) andradite, hedenbergite, ilvaite, and wollastonite possess ideal compositions (Table 1).

Paragenetic relations resulting from this analysis are shown in Figure 6, where heavy lines indicate experimentally determined reactions. Xonotlite decomposition at about 200°C (Gustafson, 1971, 1974) is of the hydration-dehydration type; because it is iron-free, it is not affected by oxygen fugacity ($P_{fluid} = \text{const.}$) for oxygen fugacities greater than those of the QFM buffer. Accordingly, it is shown as a vertical line in the T - f_{O_2} plot of Figure 6. The T - f_{O_2} breakdown of ilvaite to hedenbergite + magnetite + fluid was also determined by Gustafson (1971), who found that ilvaite is stable at temperatures lower than 450°C under a wide range of oxygen fugacity values. The isobaric invariant point at 2 kbar P_{fluid} , from which three experimentally determined reactions—(1) andradite = magnetite + wollastonite + $1/2 O_2$, (2) hedenbergite + $1/2 O_2$ = andradite + quartz + magnetite; and (3) andradite + quartz = hedenbergite + wollastonite + $1/2 O_2$ —radiated is located at $T = 920^\circ \pm 30^\circ C$, $f_{O_2} = 10^{-8}$ bars.

From the positions of the univariant lines and invariant points of Figure 6, it is apparent that the reaction, andradite = wollastonite + magnetite, in the SiO_2 -excess system is restricted to higher f_{O_2} conditions, and kirschsteinite is no longer stable. The assemblage Wo + Mt + Qz is restricted to high T - f_{O_2} conditions; Ad + Qz + Mt is stable at high f_{O_2} values in the temperature range of 400°-900°C; Ad + Hd + Qz is stable within a well defined T - f_{O_2} range; and the assemblage Hd + Wo + Qz is stable under fairly reducing conditions over a wide temperature range. Ilvaite-bearing assemblages are stable below approximately 450°C and xonotlite below 200°C.

It must be kept in mind that these relations are based on experimental and geometric results for pure end-member compositions. Because of the actual compositional variability of these phases in nature, such as Al in andradite and Mg in the clinopyroxene, considerable overlap of the phase boundaries is to be expected. Moreover, Figure 6 is applicable only under the condition that $P_{H_2O} = P_{fluid} = P_{total}$ and the composition is confined to the system Ca-Fe-Si-O-H. In natural skarns, important additional components which are not considered here included Al, Mg, Mn, and CO_2 . These additional components could give rise to additional phases such as epidote, calcite, siderite, tremolite, cummingtonite, diopside, etc. In such

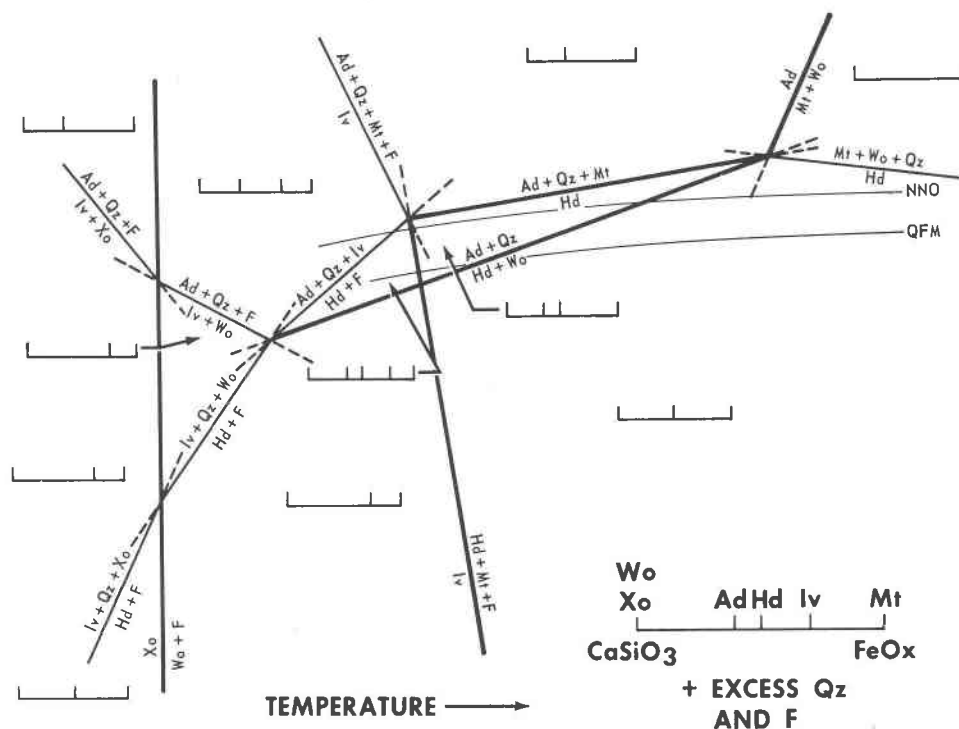


FIG. 6. Schematic isobaric $\log f_{O_2}$ - T relations of andradite, wollastonite, hedenbergite, ilvaite, magnetite, xonotlite, quartz, and vapor in the presence of excess SiO_2 and fluid in the system $CaSiO_3 - FeO_x - SiO_2 - H_2O$. Heavy lines are experimentally determined reactions. For abbreviations, see Table 1.

environments with CO_2 in the fluid phase or introduction of Al_2O_3 and MgO into the system, the stability relations shown in Figure 6 would, of course, be significantly modified. Detailed schematic relations with the addition of epidote and prehnite in the Ca-Fe-Al-Si-O-H (Liou, 1973, Fig. 7) and with the effect of other components in the fluid phase (Chatterjee, 1967; Burt, 1971a, 1972a, b) have been previously discussed.

Calcite is ubiquitous in the skarn formations. The topological relations of mineral stabilities due to the introduction of calcite into the system are depicted in an isobaric $\log f_{O_2}$ - T diagram of Figure 7. This diagram (derived from Figure 6) has been constructed using the experimentally determined stabilities of wollastonite, andradite, and hedenbergite and the chemographic relations determined by Burt (Fig. 39, 1971a). The reaction, calcite + quartz = wollastonite + CO_2 , was located on the T - f_{O_2} diagram (2 kbar P_{fluid}) with the assumed fluid composition of $X_{CO_2}/(X_{H_2O} + X_{CO_2}) = 0.75$. It appears that X_{CO_2} in the skarn-forming fluid may be less than this value and increasing X_{H_2O} greatly displaces the equilibrium toward lower temperatures (e.g., Green-

wood, 1967). Thus, Figure 7 presents the maximum stabilities for calcite + quartz, andradite, and hedenbergite in skarn formation. The T - f_{O_2} values of invariant point 9 (of Burt, Fig. 39, 1971a) and G (of Gustafson, 1971) could be estimated with great certainty if X_{CO_2} of the fluid phase could be determined. For example, at 2 kbar with fluid of $X_{CO_2}/(X_{H_2O} + X_{CO_2}) = 0.75$, the invariant point 9 is located at about $700^\circ C$ and an f_{O_2} of 10^{-16} bars.

Although the T - f_{O_2} diagram in Figure 7 is topologically consistent and in agreement with the available experimental data, not all possible reactions have been included in such an idealized system. Furthermore, f_{O_2} , T , P , and X_{CO_2}/X_{H_2O} are not the only variables that influence the stabilities of Ca-Fe-Si skarn minerals; differential movement of Ca, Fe, Si, and Al across the silicic plutonic and impure limestone contact must have existed in order to develop the zoned skarns (e.g., Brock, 1972; Vidale, 1968, Vidale and Hewitt, 1973). Nevertheless, Figure 7 indicates that the formation of the andradite-quartz assemblage requires a strongly oxidizing condition and skarns containing hedenbergite + wollastonite + quartz require a more reducing environment. This

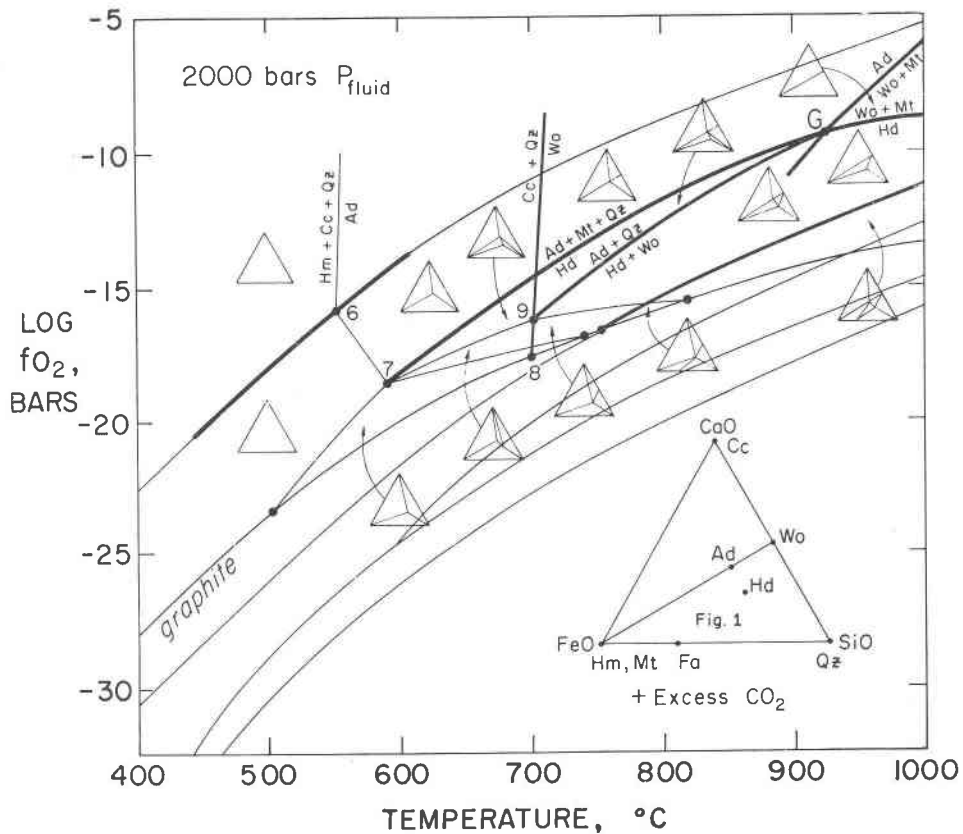


FIG. 7. Log f_{O_2} - T diagram showing the relations of andradite, hedenbergite, wollastonite, magnetite, quartz, and calcite at 2 kbar P_{fluid} in the presence of excess H_2O and CO_2 in the system Ca-Fe-Si-C-O-H. Heavy lines are experimentally determined reactions from Figure 6 and calcite + quartz = wollastonite + CO_2 located at $X_{CO_2}:X_{H_2O} = 0.75:0.25$ from Greenwood (1967). Invariant points 6, 7, 8, and 9 are identical to those of Burt (1971a) and G located by Gustafson (1971). The T - f_{O_2} curve for graphite is from Huebner (1971).

requirement satisfactorily explains why andradite + quartz + graphite and hedenbergite + wollastonite + hematite have never been reported in skarns. Figure 7 also shows that the reaction andradite + quartz = hedenbergite + wollastonite + $1/2 O_2$ is bounded by two experimentally located invariant points 9 and G. The present results together with the data of the reaction hedenbergite = andradite + magnetite + quartz investigated by Gustafson (1971, 1974) and Kurshakova (1971b) define a very narrow f_{O_2} range for the stable coexistence of andradite + hedenbergite + quartz. For example, at 2 kbar P_{fluid} and $700^\circ C$, this assemblage is stable between f_{O_2} values of 10^{-14} and 10^{-16} bars and at $800^\circ C$ between 10^{-12} and 10^{-13} bars of f_{O_2} . In such overlapping segments of andradite and hedenbergite (+ quartz) regions, the following mineral assemblages are stable: Ad + Wo + Cc, Ad + Wo + Qz, Ad + Hd + Qz, Hd +

Mt + Qz, Ad + Hd + Mt, and Ad + Mt + Cc. The occurrences of such mineral assemblages in Ca-Fe-Si skarns have been described (e.g., Burt, 1971b) and the present results provide limiting T - f_{O_2} conditions for their formation.

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