# The breakdown of hercynite at low f_{O_2}

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ABSTRACT

Experimental data on the stability of hercynite yield very large discrepancies in the derived values of its free energy. We attempted to resolve these discrepancies through an electrochemical study of the equilibrium

$$2 \text{ FeAl}_2\text{O}_4 = 2 \text{ Fe} + 2 \text{ Al}_2\text{O}_3 + \text{O}_2. \tag{1}$$

<center>hercynite   metal   corundum</center>
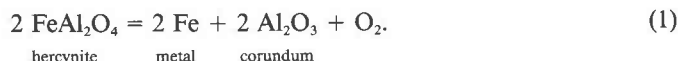
These measurements proved, however, also to give a wide range of apparent free energies, so we have made a detailed phase equilibrium study of the Fe-Fe$_2$O$_3$-Al$_2$O$_3$ system at 1 atm pressure.

Our results demonstrate that difficulties in measuring the position of Equilibrium 1 in T-f_{O_2} space are due to the appearance of a new phase, a defect spinel of approximate composition Fe$_{0.5}$Al$_{2.33}$O$_4$ and a cell edge $a_0 = 8.00$ Å. This phase appears to be stable at 1 atm at temperatures below 1175 °C and at f_{O_2} 1–2 log units below the buffer of quartz + iron + fayalite (QIF). The low values of f_{O_2} involved probably explain why the defect spinel has not been previously reported. Furthermore, the Fe$_{0.5}$Al$_{2.33}$O$_4$ spinel is destabilized relative to hercynite-corundum by increasing pressure and (probably) by the addition of Fe$_2$O$_3$.

The data show that previous experiments at 1 atm measured either the hercynite-corundum-Fe equilibrium or various equilibria involving the defect spinel phase, and hence the apparent discrepancies in the hercynite free energy. The results also indicate that hercynite is more stable at 1 atm than would be predicted from high pressure phase-equilibrium experiments. This appears to be due to the solution of excess Al$_2$O$_3$ in hercynite at low pressure.

INTRODUCTION

Because of hercynite's widespread occurrence in metamorphic rocks and its importance in steelmaking, its stability and crystal chemistry have been investigated extensively. Above 875 °C, FeAl$_2$O$_4$ forms a complete solid solution with magnetite and, as a consequence, Al-bearing spinel is stable over a range in excess of 8 log units in f_{O_2} (Turnock and Eugster, 1962; Meyers et al., 1980). Spinel of hercynitic composition is therefore a potentially useful monitor of f_{O_2} in rocks. The phase relations between spinel solid solutions and corundum, hematite, and wüstite were investigated at low temperatures by Turnock and Eugster (1962) and at high temperatures by Richards and White (1954), Atlas and Sumida (1958), and Roiter (1964). The initial purpose of our study was to determine the free energy of end-member hercynite with the minimum Fe^{3+} content. This is best done, in principle, by investigating the low f_{O_2} boundary of its stability field.

The hercynite reduction reaction, defining the low f_{O_2} boundary of hercynite stability,

$$2 \text{ FeAl}_2\text{O}_4 = 2 \text{ Fe} + 2 \text{ Al}_2\text{O}_3 + \text{O}_2, \tag{1}$$

<center>hercynite   metal   corundum</center>

has been investigated by many workers (Schenk et al., 1929; Cirilli, 1946; Lebedev, 1962; Rezukhina et al., 1963; McLean and Ward, 1966; Chan et al., 1973). There are however large discrepancies, on the order of 17 kJ/mol, in the free energy of Reaction 1 among the results of these studies. The results are also inconsistent with values of the free energy of hercynite derived from reversed phase-equilibrium experiments on reactions involving almandine and hercynite (Bohlen et al., 1986; Shulters and Bohlen, 1989). For example, at 900 °C, there is a difference of ~12 kJ/mol in the free energy of Reaction 1 between the phase-equilibrium experiments and the electrochemical measurements of Chan et al. (1973). We attempted therefore to resolve the discrepancies by redetermining the position of Reaction 1 in T-f_{O_2} space. This was initially done electrochemically by placing a mixture of hercynite + corundum + Fe inside a ZrO$_2$ oxygen electrolyte cell and determining the apparent f_{O_2} of the sample relative to a reference mixture of either Fe and wüstite or Ni and NiO. The results were then amplified by making phase-equilibrium measurements at temperatures of 900–1100 °C and 1 atm pressure.

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SAMPLE PREPARATION AND EXPERIMENTAL METHOD

Synthetic hercynite was produced by sintering pellets composed of the correct stoichiometric proportions of reagent-grade Fe metal and Al_2O_3. The Al_2O_3 was obtained by dehydrating aluminum hydroxide in air at 1300 °C for 2 d. Sintering was a two-step process. The first step was to react the Fe-Al_2O_3 mixture under relatively oxidizing conditions (log f_{O_2} = −4) at 1300 °C for 9 h in order to produce a single phase cation-deficient spinel. The second stage was to reduce the mixture at a log f_{O_2} of −11.4 at 1300 °C (~0.7 log units below the Fe-wüstite buffer) for about 12 h. The sample was ground and held again at the same conditions until only spinel peaks were detected upon X-ray analysis. Without the first step, Fe metal and corundum were found to persist even after numerous grindings and firings. The cell edge of the hercynite was determined from the average of ten scans of $1/4°$ 2θ per min across the (511) and (422) peaks using Si metal as an internal standard and is a_o = 8.1527(11) Å. This is in good agreement with the result of Hill (1984), who reported a_o = 8.15579(6) Å. Coprecipitated Fe_2O_3-Al_2O_3 mixes were used for some synthesis experiments. They were prepared by dissolving ferric ammonium sulfate and aluminum nitrate in dilute nitric acid and then precipitating hydroxides with ammonia. The hydroxide mixture was decomposed at 600 °C, giving a fine-grained reactive oxide mix.

Coarse-grained synthetic corundum for the electrochemical measurements was the same material (Alundum 60RR, Fisher) as that used for the solubility measurements of Ragnarsdottir and Walther (1985). Electrolytic Fe was treated by passing H_2 over it at 600 °C for several hours to remove any oxide coating. Electrochemical measurements were made by grinding together hercynite, corundum, and Fe under acetone and pressing the mixture into pellets using a very small amount of butyl acetate binder. The pellets were then dried overnight at 110 °C and then placed in an yttria-doped ZrO_2 electrolyte cell, with a pellet of either Fe-wüstite or Ni-NiO placed on the outside. Thereafter, measurements of the apparent f_{O_2} of the mixture hercynite + corundum + Fe followed the procedures described by Woodland and Wood (1989).

Phase-equilibrium measurements were made by using pellets of pure hercynite, corundum + iron, fine-grained oxides, or various reaction products produced during the study. These pellets were placed either singly or together in a Pt basket so that they were not in mutual contact and lowered into the hot zone of a controlled-atmosphere vertical furnace. The desired f_{O_2} was achieved by using CO-CO_2 mixtures in the proportions indicated by the tables of Deines et al. (1974) while maintaining a flow velocity close to 1 cm sec^{-1}. The f_{O_2} was monitored during the experiments with an yttria-doped ZrO_2 oxygen specific electrolyte cell. Proper behavior of the cell was checked by measuring the emf when running air on both sides of the cell. The residual emf never measured more
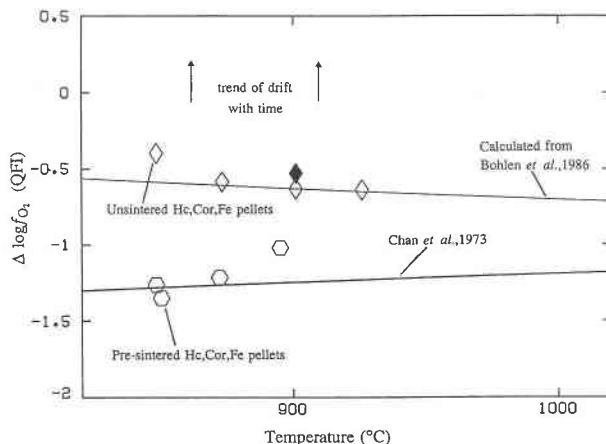

Fig. 1. Comparison of measurements of the equilibrium hercynite = corundum + Fe with electrochemical data obtained in this study. Data of Chan et al. (1973) are electrochemical measurements, whereas the curve labeled Bohlen et al. (1986) is derived from high pressure experiments (see text). Diamonds refer to electrochemical measurements on unsintered hercynite + corundum + Fe mixtures. Open diamonds refer to data taken during a cycle of increasing T and the closed diamond indicates measurements taken during a cycle of decreasing T. These measurements tended to drift to higher f_{O_2} (see text). Hexagons refer to sintered mixtures of hercynite + corundum + Fe. QFI is the quartz-iron-fayalite buffer.

than 2 mV (<0.04 log units in f_{O_2}). The cell was also checked against the Fe-wüstite buffer and was found to be within 0.1 log units of the calibration of O'Neill (1987). The duration of the experiments was between 15 and 24 h. The pellets were quenched in the reducing atmosphere by pulling the basket to the top of the work tube. They were removed from the furnace after cooling in the gas mixture for approximately 20 min. The pellets were then X-rayed to ascertain the direction and extent of reaction.

RESULTS AND DISCUSSION

Electrochemical measurements on mixtures of synthetic hercynite + synthetic corundum + Fe produced rather unusual results. Generally they yielded apparent f_{O_2} close to the QIF buffer and tended to drift to higher f_{O_2} values. In only one experiment did we obtain results that were reproducible in cycling from low temperature to high temperature and back again. These results, shown in Figure 1, are in approximate agreement with the position of Reaction 1 predicted from the high pressure experiments of Bohlen et al. (1986) and Shulters and Bohlen (1989) (see below).

We interpreted the general drift in f_{O_2} values as due to difficulty in establishing intergranular equilibrium among the three phases hercynite, corundum, and Fe, possibly because of the refractory nature of corundum. We therefore tried sintering the pellets at 1000 °C and an f_{O_2} just inside the hercynite stability field, as deduced from the high pressure experiments. After sintering for 12 h in the CO-CO_2 atmosphere, the samples were quenched

TABLE 1. Experimental results

Experiment no.	Mixture*	T °C	log f_{O_2}	Δlog f_{O_2}(QIF)	End products*
42188	hc	899	−17.78	−0.14	hc
42288a	hc	903	−18.59	−1.10	hc
42288b	oxides	903	−18.59	−1.10	hc + Fe
42588a	hc	900	−18.77	−1.56	hc
42588b	oxides	900	−18.77	−1.56	dsp + Fe
42888	oxides	901	−18.85	−1.25	dsp + Fe + hc?
72388a	hc	907	−18.09	−0.63	hc
72388b	cor + Fe	907	−18.09	−0.63	cor + Fe
72688a	cor + Fe	905	−17.71	−0.20	hc
72688b	oxides	905	−17.71	−0.20	hc
72888	cor + Fe	900	−18.00	−0.39	hc
72988a	hc	902	−18.92	−1.35	hc + dsp + Fe
72988b	cor + Fe	902	−18.92	−1.35	cor + Fe
80288a	hc	906	−18.36	−0.87	hc
80288b	cor + Fe	906	−18.36	−0.87	cor + Fe
90888	dsp + Fe	904	−18.18	−0.65	hc
91488	dsp + Fe	906	−18.41	−0.92	hc
92288	dsp + Fe	908	−18.28	−0.84	hc
91587	hc + cor + Fe	1004	−16.75	−1.20	dsp + hc + cor + Fe
92187	hc + cor + Fe	1004	−16.70	−1.15	dsp + hc + cor + Fe
101287	hc	999	−16.96	−1.32	dsp + Fe
31688	oxides	1000	−16.82	−1.19	dsp + Fe + cor + hc
32488	oxides	1000	−16.80	−1.17	Fe + cor + dsp?
32888	oxides	1001	−16.60	−0.99	cor + Fe
33088	oxides	1000	−16.50	−0.87	cor + hc
41988	oxides	1000	−16.80	−1.17	cor + Fe + hc + dsp?
42088	oxides	1000	−16.75	−1.12	cor + Fe + hc + dsp?
70788a	cor + Fe	992	−16.34	−0.57	hc
70788b	hc	992	−16.34	−0.57	hc
70988a	cor + Fe	991	−16.50	−0.71	hc + cor + Fe
70988b	hc	991	−16.50	−0.71	hc
71088a	cor + Fe	991	−16.80	−1.01	cor + Fe
71088b	hc	991	−16.80	−1.01	hc
71288	cor + Fe	994	−16.70	−0.96	cor + Fe
71588	cor + Fe	991	−16.66	−0.87	cor + Fe
71888	hc	991	−17.35	−1.56	dsp + Fe
72088	hc	995	−17.52	−1.80	dsp + Fe + cor
90888	hc	1005	−16.96	−1.43	dsp + Fe
92088	hc	1007	−16.80	−1.30	dsp + Fe
92188	dsp + Fe	1010	−16.44	−0.99	hc
51188a	cor + Fe	1045	−15.45	−0.62	hc
51188b	hc	1045	−15.45	−0.62	hc
51388	cor + Fe	1052	−15.22	−0.51	hc
61788a	hc	1047	−16.30	−1.50	dsp + Fe + hc
61788b	cor + Fe	1047	−16.30	−1.50	cor + Fe
62088	hc	1047	−16.07	−1.27	dsp + Fe + hc
62188a	hc	1047	−15.84	−1.04	hc
62188b	cor + Fe	1047	−15.84	−1.04	cor + Fe
62288	cor + Fe	1047	−15.59	−0.79	cor + Fe
62988a	hc	1047	−16.68	−1.88	cor + Fe
62988b	oxides	1047	−16.68	−1.88	cor + Fe
63088a	hc	1047	−16.47	−1.67	cor + Fe
63088b	oxides	1047	−16.47	−1.67	cor + Fe
70188	cor + Fe	1047	−15.49	−0.69	hc + cor + Fe
60688a	hc	1105	−14.84	−0.98	hc
60688b	cor + Fe	1105	−14.84	−0.98	cor + Fe
60788a	hc	1105	−14.57	−0.71	hc
60788b	cor + Fe	1105	−14.57	−0.71	hc + cor + Fe
60888	hc	1104	−15.22	−1.35	dsp + Fe + cor
60988	hc	1095	−15.18	−1.17	dsp + Fe
91788	dsp + Fe	1104	−14.82	−0.95	hc
92988	dsp + Fe	1096	−15.01	−1.01	hc

* hc = hercynite, dsp = defect spinel, cor = corundum, Fe = iron metal.

in the gas stream and X-rayed to check that the three phases were present. The sintered pellets were then placed inside the electrochemical cell. Apparent f_{O_2} were approximately 0.5 log units more reduced than those observed with the unsintered pellets and were in better agreement with the results of Chan et al. (1973) than with those of

Bohlen et al. (1986) and Shulters and Bohlen (1989). We interpreted the shift in f_{O_2} as possibly being due to the appearance of an additional phase and so began a series of phase equilibrium experiments to test the possibility.

The results of the phase equilibrium experiments are presented in Table 1 and in Figure 2. As discussed above,

TABLE 2. Microprobe analysis of defect spinel

	Wt%
Al_2O_3	79.97(2.54)
FeO	22.73(2.87)
Total	102.70
On basis of four O atoms	
Al	2.35(7)
Fe	0.47(6)
Total	2.82

Note: The analysis is an average of 11 spots. Values in brackets are one standard deviation.
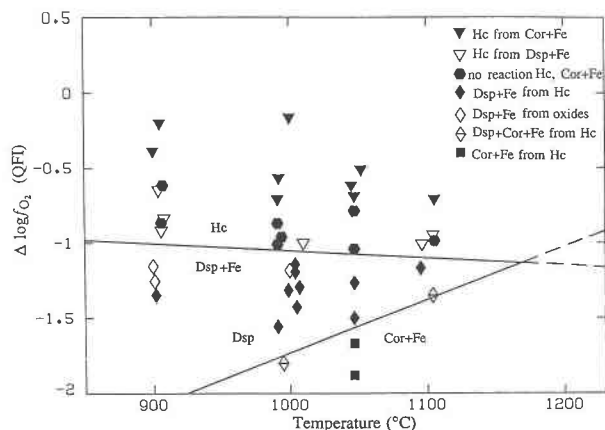

Fig. 2. Phase-equilibrium experimental data on the stability of hercynite, defect spinel, and corundum + Fe at 1 atm pressure. Results are plotted relative to the quartz-iron-fayalite buffer (QFI). Solid lines are approximate positions of Reaction 2 (upper) and Reaction 4 (lower).

identification of the stable phases was based upon the X-ray diffraction patterns obtained for the reaction products. For a number of experiments the two most intense hercynite peaks, at $d = 2.884$ Å and $d = 2.459$ Å, were observed to have shifted dramatically to 2.83 Å and 2.41 Å, respectively, implying a cell edge of 8.00 Å instead of 8.15 Å. In some cases, additional peaks were observed that could not be attributed to any of hercynite, corundum, or Fe. In several experimental products, we were able to analyze this additional phase with the electron microprobe (Table 2) and found that it is close to an Fe^{2+} end-member högbomite in composition (McKie, 1963; Grew et al., 1987). Although we originally reported it as a högbomite-like phase (Woodland and Wood, 1988) an electron diffraction study has now shown it to be a spinel (D. Peacor, personal communication). Our experiments demonstrate that this is a previously unreported defect spinel on the join FeO-Al_2O_3 and that it is of approximately constant composition $Fe_{0.5}Al_{2.33}O_4$. The electron diffraction results will form the basis of a future communication.

The results of our experiments are shown in Figure 2 relative to the position of the QIF buffer (O'Neill, 1987). That the defect spinel has never been reported from any previous experimental study is a consequence of the low f_{O_2} needed to stabilize it relative to hercynite. In addition, most previous investigations were performed at high temperature, where the assemblage hercynite + corundum + Fe is stable. The very refractory nature of corundum may also, in some instances, inhibit the formation of the defect spinel. This contention is supported by several hercynite synthesis experiments in which Fe and corundum persisted for numerous cycles of grinding and firing despite the f_{O_2} being held well within the hercynite stability field. In addition, mixtures of corundum and Fe commonly showed no evidence of reaction when held for long times in the hercynite stability field (Table 1).

There are two possible interpretations of the electrochemical and phase-equilibrium data. One is that Reaction 1 lies approximately at the position deduced from the high pressure data (see below) and that all of the reactions involving the defect spinel are metastable. We note that all our experiments that produced hercynite from corundum and Fe are consistent with this interpretation but that the corundum-Fe stability field appears to be at

much lower f_{O_2} at 1 atm (Fig. 2). In this interpretation all the previous experiments at 1 atm would have measured metastable defect spinel equilibria. The alternative interpretation is that at 1 atm Reaction 1 is in a different position from that predicted by the high pressure experiments and that the defect spinel equilibria are stable. In support of this, we cite our electrochemical measurements on sintered mixtures of hercynite + corundum + Fe. These yielded f_{O_2} in agreement with the results of Chan et al. (1973), about 0.5 log units in f_{O_2} below the position of Equilibrium 1 predicted from high pressure data. If the results of Chan et al. were truly metastable, they should not have been reproduced from the stable assemblage of hercynite + corundum + Fe.

It is clear that between 900 °C and 1100 °C, hercynite does not break down by means of Reaction 1 but by

$$7\ FeAl_2O_4 = 6\ Fe_{0.5}Al_{2.33}O_4 + 4\ Fe + 2\ O_2 \quad (2)$$

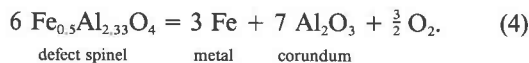hercynite $\qquad$ defect spinel $\qquad$ metal
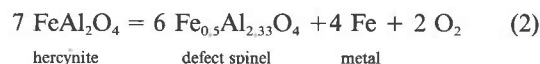
This appears to be a univariant reaction involving hercynite and defect spinel of essentially fixed composition, rather than a divariant reaction involving one spinel solid solution. This is supported by numerous chemical analyses made in concert with the electron diffraction investigation, which revealed two distinct spinel compositions. Several experiments were made with defect spinel and Fe in an attempt to reverse the T-f_{O_2} position of Reaction 2. The results of these reversals constrain the reaction to be 1.05 ± 0.1 log units in f_{O_2} below the QIF buffer (O'Neill, 1987) at 1000 °C and 1100 °C (Fig. 1). This yields a value for the equilibrium constant (K_2) as follows:

$$\log K_2(\pm 0.25) = 2 \log f_{O_2} = 16.45 - \frac{74040}{T}$$

$$(1173-1450\ K). \quad (3)$$

The lower limit of the stability field of the defect spinel

is constrained by its reduction to Fe and corundum:

$$6 \ \text{Fe}_{0.5}\text{Al}_{2.33}\text{O}_4 = 3 \ \text{Fe} + 7 \ \text{Al}_2\text{O}_3 + \tfrac{3}{2} \ \text{O}_2. \quad (4)$$
$$\underset{\text{defect spinel}}{} \qquad \underset{\text{metal}}{} \quad \underset{\text{corundum}}{}$$

The position of this reaction is approximately fixed by two experiments that produced defect spinel, corundum, and Fe from hercynite and two that produced corundum and Fe from hercynite. Since within the defect spinel stability field it is easy to produce the defect phase plus Fe from hercynite, generation of corundum plus Fe means that Reaction 4 has been overstepped to lower f_{O_2}. Further investigation of the reaction was hampered by the inability to buffer f_{O_2} to lower values with CO-CO_2 mixes (Deines et al., 1974), and we were not able to produce the defect spinel from mixtures of corundum + Fe. The approximate position shown in Figure 1 gives, for log K_3,

$$\log \text{K}_3 = \tfrac{3}{2} \log f_{O_2}$$

$$\approx 23.2 - \frac{73760}{T} \quad (1273\text{–}1450 \ \text{K}). \quad (5)$$

The apparent stability of a defect spinel at low f_{O_2} adds a new phase that must be taken into account when considering subsolidus phase relations in the system Fe-Fe_2O_3-Al_2O_3. Schreinemakers analysis of four phases, corundum, defect spinel, hercynite, and Fe, at 1 bar pressure indicates that there is one invariant point if O is considered an intensive variable and two stable spinels coexist, as identified by our experiments. The four univariant reactions that radiate from this point are 1, 2, 4, and the metal-absent reaction:

$$\text{defect spinel} = \text{hercynite} + \text{corundum} \quad (6)$$

A consistent set of phase relations is shown in Figure 3. Note that although Reaction 6 is shown as independent of f_{O_2}, solution of Fe^{3+} in hercynite and defect spinel will actually cause the reaction to be a function of f_{O_2}, the sense of which depends on which phase more readily dissolves Fe^{3+}. In view of the occurrence of hercynite$_{ss}$ + corundum in contact metamorphic rocks (e.g., Tilley, 1924) it is likely that Fe^{3+} prefers hercynite over the defect spinel. The experimental data indicate that the invariant point is near 1175 °C with an $f_{O_2} \sim 1.1$ log units below QIF. Above 1175 °C, the defect spinel is unstable and the stable reaction becomes Reaction 1. If our interpretation of the phase equilibrium data is correct, the metastable extension of Reaction 1 must lie within the defect spinel stability field between Reactions 2 and 4 (Fig. 3).

The phase boundaries determined in this study are shown in Figure 4 together with curves for Equilibrium 1 derived from literature. Our electrochemical measurements on sintered mixtures of hercynite + corundum + Fe and the electrochemical measurements of Chan et al. (1973) correspond to the position of the metastable extension of Equilibrium 1. We therefore interpret their data as referring to metastable Equilibrium 1. In view of the
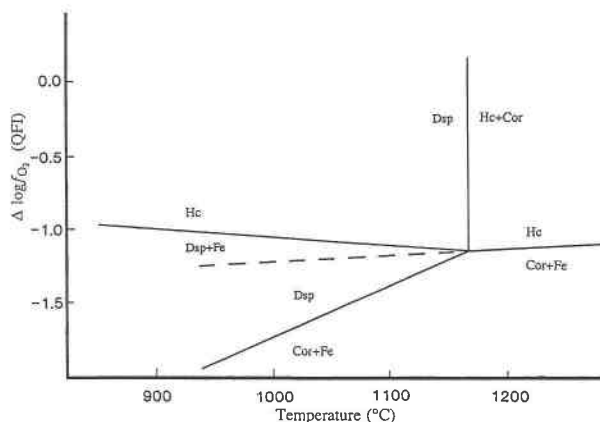

Fig. 3. Probable phase relations among hercynite, defect spinel, corundum, and Fe at 1 atm pressure. QFI is the quartz-iron-fayalite buffer.

refractory nature of Fe and corundum mixtures this appears to be a reasonable interpretation. Furthermore, the ability to measure metastable equilibria electrochemically has been effectively demonstrated by Woodland and Wood (1989). The phase-equilibrium measurements of Cirilli (1946) and the electrochemical measurements of Rezukhina et al. (1963) may, however, be partly due to the production of defect spinel generating apparent equilibrium for hercynite + corundum + Fe to higher f_{O_2} than the metastable extension of Equilibrium 1.

As noted above, high pressure phase-equilibrium experiments may be used independently to calculate the position of Equilibrium 1 with rather different results from ours. Reactions between hercynite, almandine, and sillimanite,
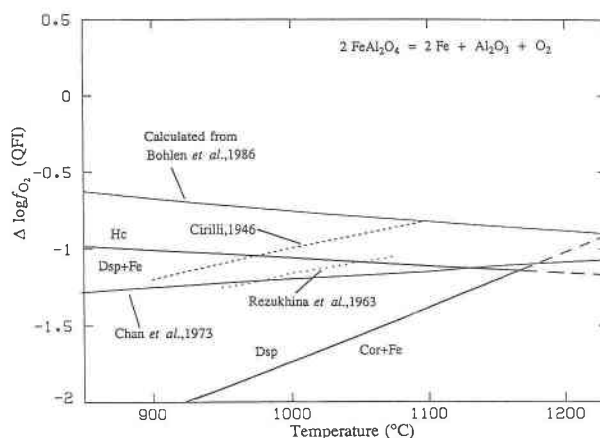

Fig. 4. Comparison of the experimentally determined position of Reaction 1, hercynite = Fe + corundum + O_2, from the experiments of Chan et al. (1973), Cirilli (1946), and Rezukhina et al. (1963). The position of Reaction 1 calculated from the high pressure phase-equilibrium experiments of Bohlen et al. (1986) is also shown. The positions of Reactions 2 and 4 obtained in this study are shown for reference. QFI is the quartz-iron-fayalite buffer.
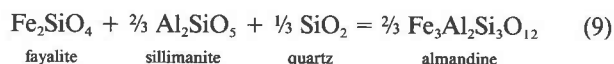
$$3 FeAl_2O_4 + 5 SiO_2 = Fe_3Al_2Si_3O_{12} + 2 Al_2SiO_5, \quad (7)$$
$$\text{hercynite} \quad \text{quartz} \quad \text{almandine} \quad \text{sillimanite}$$

$$3 FeAl_2O_4 + 3 Al_2SiO_5 = Fe_3Al_2Si_3O_{12} + 5 Al_2O_3, \quad (8)$$
$$\text{hercynite} \quad \text{sillimanite} \quad \text{almandine} \quad \text{corundum}$$

have been calibrated by Bohlen et al. (1986) (Equilibrium 7) and Shulters and Bohlen (1989) (Equilibrium 8) as functions of temperature and pressure. Using thermal expansions and compressibilities from Wood (1987), we obtain at 1 bar for Reactions 7 and 8:

$$\log K_7(\pm 0.03) = -2.63 + \frac{2460}{T} \quad (1153-1373 \text{ K}),$$

$$\log K_8(\pm 0.02) = -3.06 + \frac{2360}{T} \quad (1173-1373 \text{ K}).$$

These results may be combined with values of other equilibrium constants to obtain the difference in f_{O_2} between Equilibrium 1 and the QIF buffer. This is done in the following way. Woodland and Wood (1989) have measured the free energy of almandine electrochemically and give the values of log K for several equilibria involving this phase. For the reaction

$$Fe_2SiO_4 + \tfrac{2}{3} Al_2SiO_5 + \tfrac{1}{3} SiO_2 = \tfrac{2}{3} Fe_3Al_2Si_3O_{12} \quad (9)$$
$$\text{fayalite} \quad \text{sillimanite} \quad \text{quartz} \quad \text{almandine}$$

Woodland and Wood (1989) give

$$\log K_9(\pm 0.1) = -0.38 + \frac{520}{T} \quad (10)$$

By subtracting Equilibrium 6 from 5 (and dividing by 5) we obtain log K for the formation of sillimanite:

$$Al_2O_3 + SiO_2 = Al_2SiO_5 \quad (11)$$
$$\text{corundum} \quad \text{quartz} \quad \text{sillimanite}$$

$$\log K_{11}(\pm 0.01)$$
$$= 0.09 + 20/T \quad (1153-1373 \text{ K}). \quad (12)$$

Combining log K's for 7, 9, and 11 gives the following equilibrium, the equilibrium constant for which is equal to the f_{O_2} difference between Equilibrium 1 and QIF:

$$2 FeAl_2O_4 + SiO_2 = Fe_2SiO_4 + 2 Al_2O_3 \quad (13)$$
$$\text{hercynite} \quad \text{quartz} \quad \text{fayalite} \quad \text{corundum}$$

$$\log K_{13}(\pm 0.11) = \log K_1 - \log K^{QIF}$$

$$= -1.55 + \frac{1080}{T}.$$

This calculation indicates that Equilibrium 1 (hc = cor + Fe) should lie about 0.7 log units below QIF in the temperature range of our experiments (Fig. 4). Our measurements show, however, that hercynite is stable at f_{O_2} values as low as 1.1 log units below QIF at 1 atm, where it reacts by means of Reaction 2 rather than Reaction 1. The discrepancy suggests either that the defect spinel equilibria are metastable or that there is a free energy

difference between low pressure and high pressure hercynite.

Our electrochemical results on sintered mixtures of hercynite + corundum + Fe strongly suggest that, at 1 atm, Equilibrium 1 is not where it is predicted to be from the high pressure experiments. If it were, sintering of the stable assemblage could not produce a metastable hercynite that is more stable than stable hercynite. Therefore, we conclude that the defect spinel is stable and that hercynite is stabilized at low pressure by an unsuspected mechanism, probably solid solution of excess Al_2O_3 or FeO.

The experimental studies of Roy et al. (1953) and Viertel and Seifert (1980) on the system $MgAl_2O_4$-Al_2O_3 indicate that excess alumina can be accommodated in the magnesium aluminate at low pressure and high temperature. At 1100 °C the amount of alumina in solid solution is about 10 mol% at 1 bar but only about 1 mol% at 10 kbar. If we assume that analogous behavior occurs in iron spinels, solid solution with alumina would widen the stability field of hercynite at low pressure and cause a discrepancy between the actual stability field and that calculated from high pressure experiments. The cell edges of hercynites sintered together with corundum at 1200 °C do show small shifts to lower values, which is consistent with the presence of excess alumina, since γ-Al_2O_3 (7.905 Å, Navrotsky et al., 1986) has a smaller cell edge than hercynite [8.153(1), this study]. Furthermore, microprobe analysis of the sintered mixtures of hercynite + corundum + Fe indicates that the bulk of the spinels are stoichiometric $FeAl_2O_4$ but that they have thin alumina-rich reaction rims. In one sample we were able to obtain an analysis indicating a composition of $Fe_{0.87}Al_{2.09}O_4$, i.e., about 13% of excess γ-Al_2O_3. Since it was produced from stoichiometric hercynite plus corundum, it must be a stable solid solution, and it is sufficient to widen the hercynite stability field substantially. This solid solution is the probable reason for the discrepancy between the high pressure and low pressure measurements of the position of Equilibrium 1. However, the appearance of apparently stable $Fe_{0.5}Al_{2.33}O_4$ spinel indicates that solid solution is not complete on the $FeAl_2O_4$-Al_2O_3 join at 1 atm and 900–1100 °C.

CONCLUSIONS

At temperatures below 1175 °C hercynite, corundum, and Fe appear not to be stable together at 1 atm pressure, reacting to form a spinel phase of approximate stoichiometry $Fe_{0.5}Al_{2.33}O_4$. The stability of this phase explains the discrepancies between earlier low pressure measurements of the hercynite-corundum-Fe equilibrium. Some measurements referred to metastable hercynite-corundum-Fe equilibria whereas others measured equilibria involving hercynite, defect spinel, and Fe. The defect spinel is only produced from hercynite at very low f_{O_2} and over a narrow range in f_{O_2}, e.g., to 1.0 log units below QIF at 900 °C, decreasing to -1.1 to -1.4 log units below QIF at 1100 °C. A Schreinemakers analysis of phase relations

in the system $Fe-Fe_2O_3-Al_2O_3$ demonstrates that the hercynite-corundum-Fe reaction is stable above 1175 °C and that the defect spinel should be more stable relative to hercynite + corundum below 1175 °C. Since, however, hercynite$_{ss}$ occurs together with corundum in contact metamorphic aureoles (e.g., Tilley, 1924), we suggest that addition of Fe^{3+} at high f_{O_2} stabilizes hercynite$_{ss}$ + corundum assemblages in nature. Furthermore, hercynite + corundum is stabilized by increasing pressure, having for $Fe_{0.5}Al_{2.33}O_4$ stoichiometry a volume of 37.45 cc at 298 K, 1 atm, compared to 38.55 cc for the defect spinel.

Although our data resolve some of the discrepancy between the measurements of hercynite stability, they are still inconsistent with hercynite free energies derived from the high pressure experiments of Bohlen et al. (1986) and Shulters and Bohlen (1989). The experiments at 1 atm indicate a larger stability field for hercynite than do the high pressure experiments. We have found, however, that hercynite + corundum + Fe mixtures sintered at 1 atm produce alumina-rich reaction rims on the spinel. Nonstoichiometry of this type tends to stabilize hercynite and is probably the explanation for the difference between the low and high pressure experiments. At high pressure, solution of excess γ-Al_2O_3 would be inhibited because γ-Al_2O_3 has a high partial molar volume in spinel ($\sim$27.9 cc) compared to the volume of corundum (25.6 cc).

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