DER DATA FOR KINGITE

Calculated		Measured[a]	
hkl	d(Å)	I	d(Å)
122	2.529	3	2.529
32$\bar{1}$	2.480	7	2.476
0$\bar{4}$1	2.450	5	2.446
		1	2.404
11$\bar{3}$	2.353	1	2.365
		5	2.336
231	2.315	7	2.300
		2	2.292
		2	2.274
		3	2.269
		1	2.255
		3	2.248
3$\bar{3}$1	2.232	7	2.233
		4	2.216
		4	2.208
		3	2.196
		1	2.189
		1	2.182
$\bar{3}$31	2.163	2	2.159
		2	2.148
		3	2.127
$\bar{3}$22	2.116	14	2.112
		3	2.054
		1	2.041
$\bar{4}$21	2.035	6	2.026
		2	2.005
33$\bar{2}$	1.988	8	1.990
050	1.973	13	1.974
15$\bar{1}$	1.918	3	1.922
23$\bar{3}$	1.912	1	1.914
042	1.898	5	1.900
2$\bar{3}$3	1.882	1	1.882
412	1.875	1	1.875
340	1.856	3	1.858
051	1.831	13	1.835
$\bar{5}$10	1.814	1	1.814
1$\bar{1}$4	1.806	3	1.805
25$\bar{1}$	1.787	2	1.788
		4	1.722

Kαpha radiation, $ramda = 1.7889$ Å.

both crystal systems. The calcuation assuming monoclinic symmetry did not converge. The cell parameters obtained from the final least squares adjustment, assuming triclinic symmetry, are as follows: $a = 9.15 \pm 0.01$ Å, $b = 10.00 \pm 0.01$ Å, $c = 7.24 \pm 0.02$ Å, $\alpha = 98.6 \pm 0.1°$, $\beta = 93.6 \pm 0.1°$, $\gamma = 93.2 \pm 0.1°$, $V = 652 \pm 2$ Å³, $Z = 2$ (using above described chemical formula), $\rho_{calc} = 2.465$, $\rho_{meas} = 2.2–2.3$. (by Norrish et al.)

Meta-kingite, which is obtained by dehydrating kingite at 160°C and gives the same X-ray pattern as that reported by Norris et al., gives insufficient diffraction spots in the electron diffraction pattern to allow a similar calculation of unit-cell parameters.

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THE SYNTHESIS OF CHLORITOID AT LOW PRESSURES

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ABSTRACT

At oxygen fugacities along the Ni-NiO buffer, triclinic chloritoid has been synthesized from oxide mixes at water pressures between 8.7 kbar and 1 kbar and at temperatures between 650°C and 525°C respectively. The data indicates that the 7 Å chlorite assemblage, previously considered to be the low pressure metastable equivalent of chloritoid, is unstable with respect to chloritoid.

The mineral chloritoid, $FeAl_2SiO_5(OH)_2$, has been the subject of several experimental studies in recent years. (Halferdahl, 1961, Ganguly and Newton, 1968). Although it has been described from various apparently low-pressure geological environments, including contact metamorphic aureoles, chloritoid has never been successfully synthesized below pressures of the order of 10 kbar. The lowest pressure of synthesis reported is at 9.2 kbar and 650°C by Halferdahl (1961).

In previous low pressure studies on chloritoid by Halferdahl and on iron cordierite (composition: chloritoid+SiO_2, Fig. 1) by Schreyer
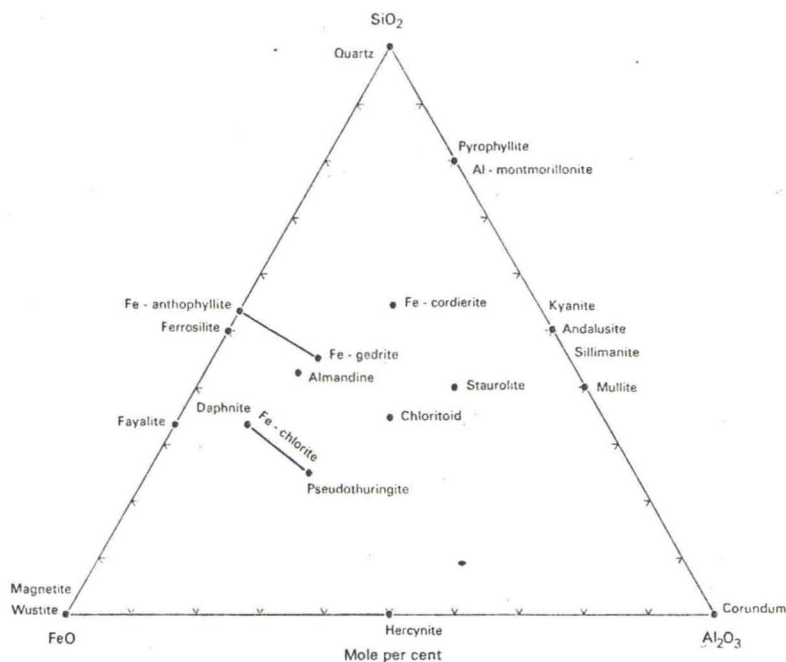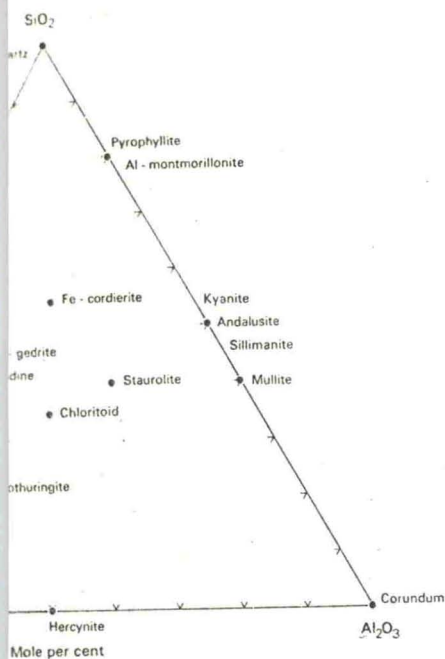
FIG. 1. Crystalline phases in the system FeO-Fe₂O₃-Al₂O₃-SiO₂-H₂O projected onto the FeO-Al₂O₃-SiO₂ plane.

(1965) the use of highly reactive oxide mixes resulted in the crystallization of relatively less reactive crystalline phases. At water pressure below 10 kbar, and within the apparent stability field of chloritoid, a 7 Å iron chlorite (chamosite) bearing assemblage was persistent and attempts to synthesize chloritoid failed. Both workers considered the chamosite assemblage to be metastable, but were unable to produce any conclusive data on the relative stabilities of chloritoid and the chamosite assemblage. In the present study it has been established that the chamosite assemblage is, in fact, unstable with respect to chloritoid at pressures from 1 to 10 kbar.

Standard hydrothermal techniques and equipment were used in the current study. All the experiments were carried out in cold seal bombs, with the oxygen fugacity controlled by the Ni-NiO buffer. The charge arrangement was similar to that of Eugster and Wones (1962) and the starting materials were either oxide mixtures or synthetic crystalline phases. Argon was used as the pressure medium at 5.5 kbar and above, and water at lower pressures.

Data from the present study is shown in Table 1. Identification of chloritoid was based primarily on X-ray diffraction patterns of the

SiO₂

Pyrophyllite
Al - montmorillonite

Fe - cordierite   Kyanite
                         Andalusite
                         Sillimanite
gedrite
dine   Staurolite   Mullite

Chloritoid

othuringite

                                    Corundum
Hercynite   Al₂O₃
Mole per cent

stem FeO-Fe₂O₃-Al₂O₃-SiO₂-H₂O projected onto
O-Al₂O₃-SiO₂ plane.

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TABLE 1. EXPERIMENTAL DATA, COMPOSITION FeOAl₂O₃SiO₂+EXCESS H₂O, ON THE SYNTHESIS OF CHLORITOID [$f(O_2)$ DEFINED BY THE Ni-NiO BUFFER]

Run	Starting material	P (kbar)	T (°C)	Time (hrs)	Products[b]
1	Ctd. qtz. her. minor cor.	8.7	675	229	Fe-anth. qtz. her. cor.
2	Oxides	8.7	650	242	Ctd.[a]
3	Oxides	8.7	625	185	Ctd. minor qtz. her. cor.
4	Oxides	8.7	600	139	Ctd. cham. qtz. her. cor.
5	Oxides	8.7	575	267	Cham. qtz. her. cor. minor ctd.
6	Cham. qtz. her. cor. minor ctd.	8.7	575	228	Ctd. minor qtz. her. cor.
7	Ctd. minor qtz. her. cor.	7	650	456	Fe-anth. qtz. her. cor.
8	Oxides	7	625	503	Ctd. minor qtz. her. cor.[a]
9	Oxides	7	600	200	Cham. qtz. her. cor.
10	Cham. qtz. her. cor.	7	600	600	Ctd. minor qtz. her. cor.
11	Oxides	5.5	600	400	Ctd. cham. qtz. her. cor.[a]
12	Ctd. cham. qtz. her. cor.	5.5	600	692	Ctd.
13	Oxides	1	525	2132	Cham. qtz. her. cor.
14	Cham. qtz. her. cor.	1	550	2489	Fe-Cord. her. qtz.
15	Fe-cord. her. qtz.	1	525	2132	Ctd. cham. qtz. her. cor.[a]

[a] Highest temperature of chloritoid synthesis.

[b] Abbreviations: cham—chamosite: cor—corundum: ctd—chloritoid: fe-anth-ferro—anthophyllite: Fe-cord—Fe cordierite: her—hercynite rich spinel: qtz—quartz.

reaction products. The d-spacings and unit cell constants for chloritoid synthesized at 8.7 kbar and 650°C and at 5.5 kbar and 600°C are listed in Table 2. The unit cell constants were refined on a triclinic cell using a least squares cell edge program written by Appleman, Handwerker and Evans (1963).

At water pressures between 8.7 and 5.5 kbar the energy barrier, which must exist between the "metastable" chamosite assemblage and the stable chloritoid was overcome by either increasing the temperature of the experiments (Runs 2, 3, 4) up to the upper temperature limit of chloritoid synthesis, or by increasing the duration of the experiments by re-running the initial products at the same temperature (Runs 5, 6, 9, 10, 11, 12). At 1 kbar water pressure and 525°C runs over 2000 hours duration failed to yield chloritoid from an oxide mix. Increasing the temperature from 525°C to 550°C (Runs 13, 14) was equally unsuccessful in producing chloritoid due to the appearance of the high temperature breakdown products iron cordierite, hercynite and quartz. The hercynite

TABLE 2. PARTIAL LISTING OF SPACINGS OF SYNTHETIC CHLORITOID

1			2		
d	*hkl*	*I*	*d*	*hkl*	*I*
4.472	$\bar{2}$01 002	10	4.468	$\bar{2}$01 002	10
3.254[a]	$\bar{1}$12 1$\bar{1}$2	2	3.253[a]	$\bar{1}$12 1$\bar{1}$2	2
2.970	003	8	2.970	003	8
—	—	—	2.925	112 202	1
2.776	$\bar{2}$03	2	2.775	$\bar{2}$03	2
2.698	0$\bar{2}$1 $\bar{3}$11	3	2.699	0$\bar{2}$1 $\bar{3}$11	4
2.462	$\bar{3}$12 0$\bar{2}$2	6	2.461	$\bar{3}$12 0$\bar{2}$2	6
2.400	311	1	2.400	311	1
2.372	$\bar{2}$21 $\bar{4}$01	1	—	—	—
2.302[a]	$\bar{2}$21 113 2$\bar{2}$1 203	1	2.302[a]	$\bar{1}$21 113 2$\bar{2}$1 203	1
2.140	221 $\bar{3}$13 $\bar{1}$23 401 0$\bar{2}$3	1	—	—	—
1.580	$\bar{3}$31 $\bar{2}$25 0$\bar{2}$5	1	1.580	$\bar{3}$31 0$\bar{2}$5 $\bar{2}$25	1

	1	2
a	9.502 ± 0.01 Å	9.483 ± 0.003
b	5.491 ± 0.005 Å	5.538 ± 0.005
c	9.185 ± 0.006 Å	9.174 ± 0.005
α	$96°37' \pm 4'$	$96°48' \pm 5'$
β	$101°56' \pm 6'$	$101°49' \pm 4'$
γ	$89°56' \pm 3'$	$89°59' \pm 3'$

1 Synthesized at 650°C and 8.7 kbar
2 Synthesized at 600°C and 5.5 kbar
[a] Listed by Halferdahl (1961) as unique to triclinic polymorph.

SPACINGS OF SYNTHETIC CHLORITOID

	2	
d	hkl	I
4.468	$\bar{2}01$ 002	10
3.253[a]	$\bar{1}12$ $1\bar{1}2$	2
2.970 2.925	003 112 202	8 1
2.775	$\bar{2}03$	2
2.699	$0\bar{2}1$ $\bar{3}11$	4
2.461	$\bar{3}12$ $0\bar{2}2$	6
2.400	311	1
—	—	—
2.302[a]	$\bar{1}21$ 113 $2\bar{2}1$ 203	1
—	—	—
1.580	$\bar{3}31$ $02\bar{5}$ $\bar{2}2\bar{5}$	1

9.483 ± 0.003
5.538 ± 0.005
9.174 ± 0.005
$96°48' \pm 5'$
$101°49' \pm 4'$
$89°59' \pm 3'$

bar
bar
unique to triclinic polymorph.

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and quartz are considered to be mutually unstable, the equilibrium high temperature breakdown assemblage being iron cordierite and hercynite. It was, however, possible to synthesize chloritoid, mixed with chamosite, quartz, hercynite and corundum, by taking this high temperature assemblage, iron cordierite, hercynite and quartz, and holding it at a temperature, within the chloritoid stability field (Run 15). The chloritoid, chamosite, quartz, hercynite and corundum assemblage is unstable and is an intermediate step in the reaction in which chloritoid is the final stable product. (Compare with Runs 11, 12).

These results at 1 kbar water pressure are most easily accounted for by assuming that, within the chloritoid stability field, both the iron cordierite and chamosite bearing assemblages have a lower Gibbs free energy than the oxide mix but higher than chloritoid. However, from an oxide mix chloritoid nucleates and grows much more slowly than the chamosite assemblage, requiring either a temperature close to the upper stability limit of chloritoid or long run duration or both to produce chloritoid. At 1 kbar water pressure the run times to produce chloritoid from an oxide mix, via the chamosite assemblage, are prohibitive, but are of reasonable length starting from the iron cordierite bearing assemblage.

The synthesis of chloritoid at water pressures as low as 1 kbar, in a hydrostatic environment, shows conclusively that stress is not a major factor affecting chloritoid stability, (Harker, 1932, pp. 147–151) and serves to emphasize the need for careful experimentation in iron-aluminum-silica systems, where reaction rates are slow and resultant "metastability" may be common.

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