Synthetic armalcolite and pseudobrookite

A. YA. MEDVEDEV

Institute of Geochemistry, PB. 4019, 664033 Irkutsk, Russia

Abstract

Armalcolite and pseudobrookite have been crystallized from synthetic melts of basaltic composition with variable amounts of added TiO_2. It was found that the composition of the armalcolite and pseudobrookite are dependent on the TiO_2 content of the melt and the conditions (particularly oxygen fugacity, but also temperature and quenching rate) of formation. The maximum Al_2O_3 content of pseudobrookite appears to be $\sim$14–15 wt.% Al_2O_3, a spinel-like phase being exsolved at higher Al_2O_3 concentrations. Generally armalcolite is formed at low pO_2 and pseudobrookite at higher oxygen fugacities.

KEYWORDS: armalcolite, pseudobrookite, synthetic melts.

Introduction

THE MgO–FeO–Fe_2O_3–TiO_2 system is geochemically significant as an indicator of oxygen fugacity and temperature and can be used for producing refractory ceramics and ferromagnetic materials. A summary of the natural phases, particularly pseudobrookite (Fe_2TiO_5) and armalcolite ($(Fe,Mg)Ti_2O_5$), was published by Bowles (1988). The system has not been extensively investigated experimentally. $MgTi_2O_5$ (Brown and Navrotsky, 1989; Wechsler and Navrotsky, 1984) and 'anosovite' Ti_3O_5 (Rusakov and Zhdanov, 1951) have been synthesized. The phases formed within the MgO–Fe_2O_3–TiO_2 and MgO–Al_2O_3–Fe_2O_3–TiO_2 systems have been little studied but the boundary series have received some attention. The $MgTi_2O_5$ to $FeTi_2O_5$ series has been examined by Moore and Sigurdson (1949) and by Lindsley *et al.* (1974) whilst Sigurdson and Cole (1949) have studied the $MgTi_2O_5$ to Al_2TiO_5 series. The Fe_2TiO_5 to $FeTi_2O_5$ series has been synthesized by Akimoto *et al.* (1957). The natural minerals armalcolite (Anderson *et al.*, 1970), pseudobrookite and 'kennedyite' ($Fe_2MgTi_3O_{10}$; von Knorring and Cox, 1961) fall within the MgO–FeO–Fe_2O_3–TiO_2 field and often contain Al_2O_3 and other oxides in addition. 'Anosovite' has been found in slag materials (Lapin *et al.*, 1956) and belongs to the MgO–FeO–TiO–TiO_2 field. Many examples of lunar armalcolite also fall within this field. 'Kennedyite' (ideally $Fe_2MgTi_3O_{10}$) was discovered in the olivine–augite–feldspar rocks of the Mateke Hills, Zimbabwe, by von Knorring and Cox (1961). They showed the structure of 'kennedyite' to be similar to pseudobrookite and determined the chemical composition suggesting that Cr_2O_3, Al_2O_3 and FeO are not involved in the structure but represent mechanical admixtures of other phases. Unfortunately the original definition did not set any boundaries to the composition of 'kennedyite' within this field and it has been found more convenient (Bowles, 1988) to abandon the name 'kennedyite' and to divide the Fe_2TiO_5–Ti_3O_5–Mg_2TiO_5 field into pseudobrookite, armalcolite and 'anosovite'. Data on synthetic armalcolite and pseudobrookite are sparse. Armalcolite has been synthesized from a mixture of oxides corresponding to the composition of a lunar rock (10017; Lind and Housley, 1972) and Akimoto *et al.* (1970) have obtained Cr_2O_3-bearing armalcolite by melting actual lunar rocks (10085 and 10017) at 1125 to 1225°C at 10^{-11} to 10^{-12} atm. ($\sim 10^{-7}$ to 10^{-8} MPa). Friel and Harker (1977) found armalcolite stable at 1200°C and $10^{-9.5}$ to $10^{-10.5}$ atm. ($10^{-5.5}$ to $10^{-6.5}$ MPa).

Experimental procedures

Synthetic armalcolite and pseudobrookite were obtained as quenched phases when studying the behaviour of titanium in basaltic melts. The minerals

Mineralogical Magazine, April 1996, Vol. 60, pp. 347–353
© *Copyright the Mineralogical Society*

FIG. 1. Microphotograph of synthetic pseudobrookite (sample 28). The pseudobrookite forms grey, tabular crystals with a prominent cleavage. White is plagioclase, black is residual glass.

were identified by X-ray powder diffraction. The experiments on quenching were carried out between 1200 and 1300°C, with a total pressure of 0.1 MPa and partial oxygen pressures from $10^{-11.2}$ to 2.1×10^{-2} MPa. During these experiments the material (TR-2 basalt with variable amounts of added TiO_2) was melted at an appropriate temperature and then quenched after 2 h in the furnace. A few experiments were performed on the behaviour of titanium involving crystallization of basaltic melts at different rates. These crystallized melts were obtained using a high-temperature furnace with a temperature controller.

The experiments consisted of several stages. At first crucibles containing the mixtures were heated to an initial temperature of 900°C. After 8–10 h the temperature was increased to 1300°C at the rate of 130°C per hour. The temperature was maintained at 1300°C for 2 h and then decreased to a 'working' temperature. The working temperatures were 1275, 1250, 1150, 1100, 1050, 1000, 950 and 900°C. After 3 h at the working temperature the mixture was quenched (Medvedev, 1989). Depending on the oxygen fugacity, the crucibles were either made of aluminium oxide (high pO_2) or metallic molybdenum (low pO_2). Armalcolite and pseudobrookite could not be derived from stoichiometric mixtures of oxides by melting because the oxide melt requires temperatures higher than 1500°C. It was found that the mineral assemblages in all experiments were fairly constant, even if the rate of cooling and the quenching temperatures varied. The mineral assemblages formed during the various experiments were armalcolite or pseudobrookite, plagioclase, residual glass and, occasionally, pyroxene and differ only in the proportion and size of the mineral phases. With a minimum quenching temperature and rate of cooling, the crystal size was maximized, whereas the proportion of residual glass decreased. This paper describes some chemical features of the armalcolite and pseudobrookite synthesized both by quenching and crystallization.

Results

The synthetic armalcolite and pseudobrookite minerals form tabular and spicular crystals (Fig. 1). The tetragonal cleavage of the mineral is observed when the long axis is cut perpendicularly by the thin section. The crystal size reaches 5 mm on the long axis. Stellate mineral accumulations are produced as a result of quenching at high temperatures. The armalcolite and pseudobrookite vary from dark brown to black in colour with an adamantine to metallic lustre. In thin section these minerals are often transparent and yellow to brownish red in colour. They are black where the long axis is cut perpendicularly by the thin section. No distinct relationship is apparent between the chemical composition and the refractive indices.

$$n_o = 2.35 - 2.40; \; n'_e = 2.28 - 2.38$$

The chemical composition of each mineral was determined using an electron microprobe (JEOL Superprobe 733). The procedure has been presented by Medvedev *et al.* (1987) and the compositions are given in Table 1. Scanning both along and across some crystals indicated that no inhomogeneity of individual crystals was apparent in any of the experiments. Table 1 demonstrates the wide compositional range of armalcolite and pseudobrookite, particularly as far as Ti is concerned (40 to 73 wt.% TiO_2).

The analytical data have been plotted in Fe_2TiO_5–$MgTi_2O_5$–Ti_3O_5 space according to the method proposed by Bowles (1988) and this is shown in Fig. 2. This illustrates the wide range of mineral compositions which have been obtained and establishes the fact that both armalcolite and pseudobrookite have been produced.

The concentration of Ti in these minerals is almost directly dependent on the Ti content of the melt

TABLE 1. Data on 46 synthetic and one natural examples of armalcolite and pseudobrookite. Microprobe analyses for Fe, Ti, Al and Mg are shown as the oxides with the total Fe presented as FeO. The distribution of Fe between FeO and Fe_2O_3 and the end-members have been calculated following Bowles (1988). The experimental conditions are also indicated for each sample.

	ΣFe as				Calculated			Calculated end-member compositions					Melting	Crystallization		TiO_2 content	
	FeO	TiO_2	Al_2O_3	MgO	FeO	Fe_2O_3	Total	$FeTi_2O_5$	Fe_2TiO_5	$MgTi_2O_5$	Al_2TiO_5	Ti_3O_5	point (°C)	rate (°C/hr)	pO_2 (Mpa)	of the melt (wt.%)	Crystallization range
1	27.89	60.33	2.15	6.45	10.53	19.29	98.75	32.69	26.94	35.67	4.70	0.00	natural			2.83	
2	24.56	58.00	5.22	8.68	3.50	23.40	98.80	10.56	31.73	46.62	11.09	0.00	1300	quenched	2.1×10^{-2}	26.14	
3	27.80	56.70	5.20	8.31	2.53	28.08	100.82	7.53	37.55	44.03	10.89	0.00	1300	quenched	2.1×10^{-2}	21.22	
4	28.13	55.90	5.02	8.02	2.72	28.24	99.90	8.17	38.21	42.98	10.64	0.00	1300	quenched	2.1×10^{-2}	20.23	
5	28.77	55.20	4.76	7.45	3.56	28.02	98.99	10.86	38.43	40.48	10.23	0.00	1300	quenched	2.1×10^{-2}	19.25	
6	34.34	51.90	4.27	6.32	2.64	35.23	100.36	8.06	48.38	34.38	9.18	0.00	1300	quenched	2.1×10^{-2}	13.34	
7	38.06	47.60	3.50	4.88	2.61	39.40	97.99	8.28	56.28	27.61	7.83	0.00	1300	quenched	2.1×10^{-2}	10.38	
8	34.81	50.10	2.60	7.02	0.53	38.10	98.35	1.65	53.55	39.08	5.72	0.00	1250	quenched	2.1×10^{-2}	8.41	
9	36.17	49.40	2.27	6.72	0.52	39.62	98.53	1.64	55.83	37.52	5.01	0.00	1250	quenched	2.1×10^{-2}	7.43	
10	39.46	46.70	3.25	5.38	0.53	43.26	99.12	1.67	61.06	30.08	7.19	0.00	1200	quenched	2.1×10^{-2}	7.43	
11	40.93	45.20	2.81	5.04	0.16	45.31	98.52	0.50	64.70	28.51	6.29	0.00	1200	quenched	2.1×10^{-2}	6.44	
12	45.74	41.90	2.72	3.59	0.06	50.76	99.03	0.20	73.16	20.50	6.14	0.00	1200	quenched	2.1×10^{-2}	5.46	
13	12.00	73.70	3.15	9.10	12.00	0.00	97.95	36.39	0.00	49.18	6.73	7.70	1300	quenched	$10^{-8.5}$	26.14	
14	12.22	71.90	3.19	9.13	12.22	0.00	96.44	37.55	0.00	49.99	6.91	5.55	1300	quenched	$10^{-8.5}$	21.22	
15	13.12	71.90	3.54	8.85	13.12	0.00	97.41	39.95	0.00	48.02	7.59	4.44	1300	quenched	$10^{-8.5}$	18.26	
16	14.40	70.60	2.50	9.27	14.32	0.09	96.78	43.87	0.12	50.61	5.40	0.00	1250	quenched	$10^{-9.0}$	17.26	
17	15.90	68.90	2.59	8.97	13.47	2.70	96.63	41.45	3.74	49.19	5.62	0.00	1250	quenched	$10^{-9.0}$	15.31	
18	16.62	67.60	2.58	8.77	12.93	4.10	95.98	40.13	5.72	48.51	5.64	0.00	1250	quenched	$10^{-9.0}$	11.37	
19	16.27	70.20	1.79	8.93	14.60	1.86	97.38	44.76	2.56	48.81	3.87	0.00	1200	quenched	$10^{-10.2}$	17.26	
20	16.37	69.60	2.16	8.94	14.01	2.63	97.34	42.91	3.62	48.81	4.66	0.00	1200	quenched	$10^{-10.2}$	16.29	
21	17.84	68.50	2.21	8.61	13.62	4.69	97.63	41.73	6.47	47.03	4.77	0.00	1200	quenched	$10^{-10.2}$	15.31	
22	21.03	64.60	2.59	7.93	11.66	10.42	97.20	36.08	14.51	43.76	5.65	0.00	1200	quenched	$10^{-10.2}$	8.41	
23	25.35	58.10	2.95	6.67	9.14	18.01	94.87	29.29	25.96	38.09	6.66	0.00	1200	quenched	$10^{-10.2}$	7.43	

Table 1 (*contd.*)

	ΣFe as				Calculated			Calculated end-member compositions					Melting point (°C)	Crystallization rate (°C/hr)	pO_2 (Mpa)	TiO_2 content of the melt (wt.%)	Crystallization range
	FeO	TiO_2	Al_2O_3	MgO	FeO	Fe_2O_3	Total	$FeTi_2O_5$	Fe_2TiO_5	$MgTi_2O_5$	Al_2TiO_5	Ti_3O_5					
24	44.20	41.82	4.88	3.10	0.68	48.37	98.85	2.16	69.30	17.59	10.95	0.00	1300	25	2.1×10^{-2}	6.44	1300–900
25	36.92	47.67	5.81	5.50	0.47	40.51	99.96	1.44	55.92	30.08	12.56	0.00	1300	25	2.1×10^{-2}	11.37	1300–900
26	44.70	40.90	4.91	3.06	0.04	49.63	98.54	0.13	71.38	17.43	11.06	0.00	1300	10	2.1×10^{-2}	6.44	1300–900
27	34.69	45.81	10.10	4.63	0.15	38.38	99.07	0.46	52.67	25.17	21.70	0.00	1300	10	2.1×10^{-2}	11.37	1300–900
28	44.48	39.77	6.35	2.87	0.00	49.43	98.42	0.00	69.87	16.07	14.06	0.00	1300	5	2.1×10^{-2}	6.44	1300–900
29	35.78	45.50	8.50	5.09	0.00	39.76	98.85	0.00	54.29	27.53	18.18	0.00	1300	5	2.1×10^{-2}	11.37	1300–900
30	32.78	43.41	13.97	4.25	0.00	36.43	98.06	0.00	48.48	22.40	29.12	0.00	1300	0.5	2.1×10^{-2}	11.37	1300–900
31	36.94	40.80	14.76	2.28	0.00	41.05	98.89	0.00	56.08	12.34	31.58	0.00	1300	0.5	2.1×10^{-2}	6.44	1300–900
32	44.29	41.29	5.43	3.08	0.12	49.09	99.01	0.38	70.07	17.41	12.14	0.00	1300	0.5	2.1×10^{-2}	6.44	1300–1200
33	42.73	43.78	5.04	3.91	0.34	47.11	100.18	1.07	66.11	21.74	11.08	0.00	1300	0.5	2.1×10^{-2}	10.38	1300–1200
34	38.11	42.25	9.80	3.40	0.00	42.35	97.80	0.00	59.51	18.92	21.57	0.00	1300	0.5	2.1×10^{-2}	6.44	1300–1250
35	27.45	52.32	7.18	7.80	0.31	30.17	97.78	0.93	41.33	42.33	15.41	0.00	1300	0.5	2.1×10^{-2}	11.37	1300–1250
36	40.17	45.52	6.62	4.11	1.02	43.51	100.78	3.14	60.07	22.48	14.31	0.00	1300	0.5	2.1×10^{-2}	6.44	1300–1275
37	28.88	53.59	7.76	7.42	1.22	30.74	100.73	3.62	40.98	39.19	16.21	0.00	1300	0.5	2.1×10^{-2}	11.37	1300–1275
38	40.01	45.22	6.54	4.34	0.39	44.04	100.53	1.19	60.88	23.77	14.16	0.00	1300	0.5	2.1×10^{-2}	6.44	1300–1150
39	29.69	51.88	7.71	7.53	0.00	33.00	100.12	0.00	44.05	39.83	16.12	0.00	1300	0.5	2.1×10^{-2}	11.37	1300–1150
40	40.86	42.44	7.39	3.75	0.00	45.41	98.99	0.00	63.21	20.68	16.11	0.00	1300	0.5	2.1×10^{-2}	6.44	1300–1100
41	30.22	51.04	7.86	6.30	1.86	31.52	98.58	5.67	43.22	34.23	16.88	0.00	1300	0.5	2.1×10^{-2}	11.37	1300–1100
42	49.50	42.41	9.96	2.66	1.26	42.50	98.79	3.91	59.50	14.75	21.84	0.00	1300	0.5	2.1×10^{-2}	6.44	1300–1050
43	31.22	50.81	8.44	5.08	4.02	30.23	98.58	12.31	41.70	27.76	18.23	0.00	1300	0.5	2.1×10^{-2}	11.37	1300–1050
44	39.23	42.15	10.07	2.70	1.05	42.44	98.41	3.26	59.58	15.02	22.14	0.00	1300	0.5	2.1×10^{-2}	6.44	1300–1000
45	30.62	49.53	9.97	5.03	2.85	30.86	98.24	8.71	42.43	27.39	21.47	0.00	1300	0.5	2.1×10^{-2}	11.37	1300–1000
46	38.27	42.51	10.65	2.38	2.07	40.23	97.84	6.48	56.72	13.29	23.51	0.00	1300	0.5	2.1×10^{-2}	6.44	1300–950
47	31.57	47.75	12.27	4.95	0.58	34.45	100.00	1.71	46.21	26.30	25.78	0.00	1300	0.5	2.1×10^{-2}	11.37	1300–950

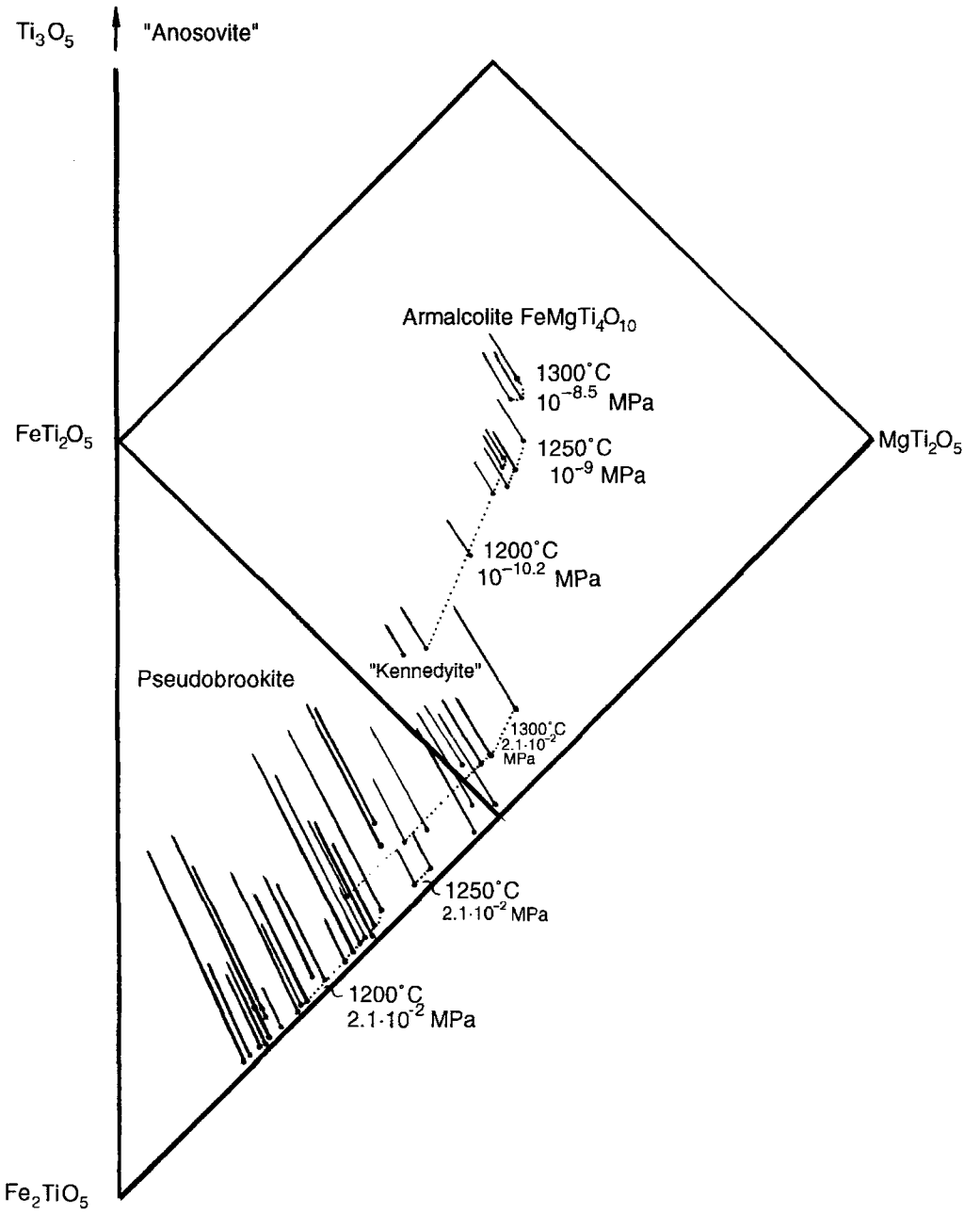

FIG. 2. Data from Table 1 plotted in the Fe_2TiO_5–$MgTi_2O_5$–Ti_3O_5 space according to the method proposed by Bowles (1988). Circles show the location of the mineral in terms of the Fe-Ti-Mg composition whilst the Al_2O_3 content is illustrated by the length of the oblique line. Examples of armalcolite composition were produced at 1200–1300°C. and $10^{-8.5}$ to $10^{-10.2}$ MPa while the pseudobrookites were formed at 2.1×10^{-2} MPa and 1200–1250°C by quenching or slower cooling. At 1300°C and 2.1×10^{-2} MPa armalcolite is formed when the amount of TiO_2 in the melt is high while pseudobrookite is produced from melts with a lower TiO_2 content.

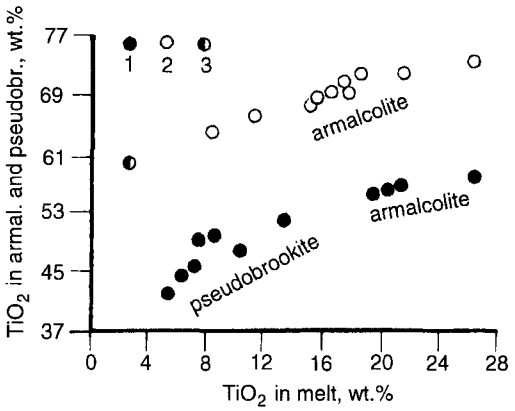

FIG. 3. Relationship of the TiO_2 content of armalcolite and pseudobrookite to that in the melt. 1 – air; 2 – oxygen fugacity corresponding to that of the wüstite–magnetite buffer; 3 – data from von Knorring and Cox (1961).

(Fig. 3). It is also evident that armalcolite synthesized at low oxygen fugacity contains more Ti than armalcolite and pseudobrookite obtained at high oxygen fugacity. In addition the Ti concentration in pseudobrookite is directly dependent on the rate of cooling from the melt, the Ti concentration being lower at lower cooling rates (Fig. 4). The separation of a spinel-like phase with 40–50 wt.% Al_2O_3 and TiO_2 <1 wt.% was observed in two samples numbers, 30 and 31; Fig. 5. In these examples the Al_2O_3 content of the host mineral amounts to 14–15 wt.% which appears to be the maximum permitted in armalcolite and pseudo-brookite. The limits of

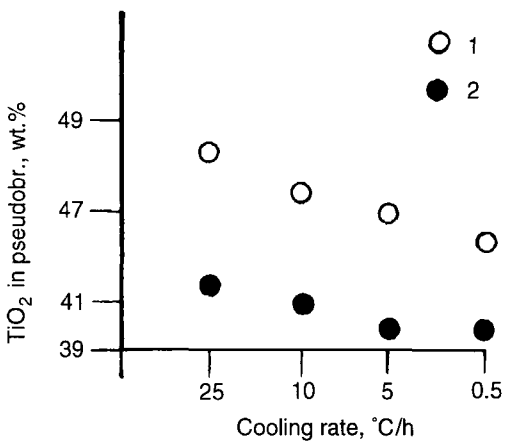

FIG. 4. Relationship of the TiO_2 content of pseudobrookite to the rate of cooling of the melt. 1 – TiO_2 = 6.44 wt.%; 2 – TiO_2 = 11.37 wt.% in the melt.

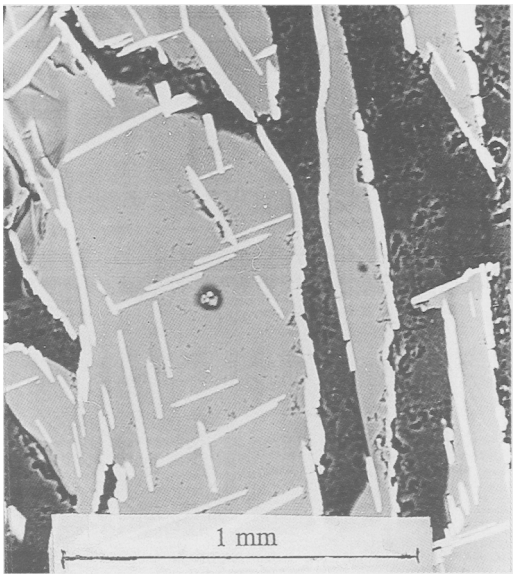

FIG. 5. Separation of a spinel-like phase (white) in pseudobrookite sample 31 (grey).

saturation for other elements have not been determined.

Conclusions

Armalcolite and pseudobrookite can be produced synthetically during crystallization from a melt of basaltic composition. The composition of the minerals produced is strongly dependent upon both the oxygen fugacity during the experiment and the amount of TiO_2 available. Temperature and the rate of crystallization appear to exert a smaller influence. The maximum capacity of pseudobrookite for Al_2O_3 is ~14–15 wt.%. At higher Al_2O_3 contents, a phase of spinel-like composition is exsolved.

The data provide excellent confirmation of the general supposition (e.g. Anderson *et al.*, 1970; Bowles, 1988) that minerals of armalcolite composition found in lunar, extraterrestrial and (occasionally) in terrestrial samples were generally formed under conditions of low oxygen fugacity whilst terrestrial minerals of pseudobrookite composition have been formed where more oxygen is available.

Acknowledgements

The author is indebted to L. Paradina and O. Belozerova for the determinations of the mineral compositions. Ms Tanya Bounaeva and J.F.W. Bowles are thanked for their help in preparation of the manuscript.

References

Akimoto, S., Nagata, T. and Katsura, T. (1957) The $TiFe_2O_5$–Ti_2FeO_5 solid solution series. *Nature*, **179**, 37–8.

Akimoto, S., Nishikawa, M., Nakamura, Y., Kushiro, I. and Katsura, T. (1970) Melting experiments of lunar crystalline rocks. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 1*, **1**, 129–33.

Anderson, A.T., Bunch, T.E., Cameron, E.N., Haggerty, S.E., Boyd, F.R., Finger, L.W., James, O.D., Keil, K., Printz, M., Ramdohr, P. and El Goresy, A. (1970) Armalcolite: A new mineral from the Apollo 11 samples. *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 1*, **1**, 55–63.

Bowles, J.F.W. (1988) Definition and range of compositions of naturally occurring minerals with the pseudobrookite structure. *Amer. Mineral.*, **73**, 1377–83.

Brown, N.E. and Navrotsky, A. (1989) Structural, thermodynamic, and kinematic aspects of disordering in the pseudobrookite-type compound karrooite, $MgTi_2O_5$. *Amer. Mineral.*, **74**, 902–12.

Friel, J.J. and Harker, R.I. (1977) Armalcolite stability as a function of pressure and oxygen fugacity. *Geochim. Cosmochim. Acta*, **41**, 403–10.

Lapin, V.V., Kurtzeva, N.N. and Ostrogorskaya, O.P. (1956) The composition of anosovite and of the titanium sesquioxide in titanium-rich slags. *Dokl. Akad. Nauk SSSR*, **109**, 824–7.

Lind, M.D. and Housley, R.M. (1972) Crystallization studies of lunar igneous rocks: Crystal structure of synthetic armalcolite. *Science*, **175**, 521–3.

Lindsley, D.H., Kesson, S.E., Hartzman, M.J. and Cushman, M.K. (1974) The stability of armalcolite: Experimental studies in the system MgO-Fe-Ti-O. *Proc. 5th Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 5*, **1**, 521–34.

Medvedev, A.Ya. (1989) Kennedyite synthesis in high-Ti melts. *Mineral. Zhurn.*, **11**, 67–74.

Medvedev, A.Ya, Almukhamedov, A.I. and Paradina, L.F. (1987) Titanium solubility in the basalt melt (experimental data). *Dokl. Akad. Nauk SSSR*, **293**, 1218–20.

Moore, C.H. Jr. and Sigurdson, H. (1949) Petrology of high titanium slags. *Trans. Amer. Inst. Min. Metall. Engs.*, **185**, 914–9.

Rusakov, A.A. and Zhdanov, G.S. (1951) Crystal structure and chemical formula of titanium oxide Ti_3O_5 (anosovite). *Dokl. Akad. Nauk SSSR*, **77**, 411–4.

Sigurdson, H. and Cole, S.S. (1949) Melting points in the system TiO_2–CaO–MgO–Al_2O_3. *Trans. Amer. Inst. Min. Metall. Engs.*, **185**, 905–8.

von Knorring, O. and Cox, K.G. (1961) Kennedyite, a new mineral of the pseudobrookite series. *Mineral. Mag.*, **32**, 676–82.

Wechsler, B.A. and Navrotsky, A. (1984) Thermodynamic and structural chemistry of compounds in the system MgO–TiO_2. *J. Solid State Chem.*, **55**, 165–80.

[Manuscript received 16 April 1993: revised 27 April 1995]