

Liquidus Equilibria in the System $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{F}_2\text{O}_{-1}-\text{H}_2\text{O}$ to 100 MPa: II. Differentiation Paths of Fluorosilicic Magmas in Hydrous Systems

DAVID DOLEJS* AND DON R. BAKER

DEPARTMENT OF EARTH AND PLANETARY SCIENCES, MCGILL UNIVERSITY, MONTREAL, QC H3A 2A7, CANADA

RECEIVED OCTOBER 7, 2005; ACCEPTED JANUARY 9, 2007;
ADVANCE ACCESS PUBLICATION MARCH 8, 2007

We investigated phase equilibria in the six-component system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{F}_2\text{O}_{-1}-\text{H}_2\text{O}$ at 100 MPa to characterize differentiation paths of natural fluorine-bearing granitic and rhyolitic magmas. Topaz and cryolite are stable saturating solid phases in calcium-poor systems. At 100 MPa the maximum solidus depression and fluorine solubility in evolving silicic melts are controlled by the eutectics haplogranite–cryolite– H_2O at 640°C and ~4 wt % F, and haplogranite–topaz– H_2O at 640°C and ~2 wt % F. Topaz and cryolite form a binary peralkaline eutectic at 660°C, 100 MPa and fluid saturation. The low-temperature nature of this invariant point causes displacement of multiphase eutectics with quartz and alkali feldspar towards the topaz–cryolite join and enables the silicate liquidus and cotectic surfaces to extend to very high fluorine concentrations (more than 30 wt % F) for weakly peraluminous and subaluminous compositions. The differentiation of fluorine-bearing magmas follows two distinct paths of fluorine behavior, depending on whether additional minerals buffer the alkali/alumina ratio in the melt. In systems with micas or aluminosilicates that buffer the activity of alumina, magmatic crystallization will reach either topaz or cryolite saturation and the system solidifies at low fluorine concentration. In leucogranitic suites precipitating quartz and feldspar only, the liquid line of descent will reach topaz or cryolite but fluorine will continue to increase until the quaternary eutectic with two fluorine-bearing solid phases is reached at 540°C, 100 MPa and aqueous-fluid saturation. The maximum water solubility in the haplogranitic melts increases with the fluorine content and reaches 12.5 ± 0.5 wt % H_2O at the quartz–cryolite–topaz eutectic composition. A continuous transition between hydrous fluorosilicate melts and solute-rich aqueous fluids is not documented by this study. Our experimental results are applicable to leucocratic

fluorosilicic magmas. In multicomponent systems, however, the presence of calcium may severely limit enrichment of fluorine by crystallization of fluorite.

KEY WORDS: granite; rhyolite; topaz; cryolite; magmatic differentiation

INTRODUCTION

In natural, fluorine-bearing silicic magmas, H_2O is an important volatile constituent (Thomas & Klemm, 1997; Thomas *et al.*, 2005). Fluorine and water in silicate melts exert similar effects, and (1) depress the melting temperature (Manning, 1981; Pichavant *et al.*, 1987; Webster *et al.*, 1987; Weidner & Martin, 1987), (2) decrease melt density (Dingwell *et al.*, 1993; Knoche *et al.*, 1995), (3) decrease melt viscosity (Dingwell *et al.*, 1985; Baker & Vaillancourt, 1995; Giordano *et al.*, 2004) and (4) increase element diffusivity (Baker & Bossanyi, 1994). These factors are capable of extending the differentiation of fluorine-bearing hydrous granites towards low-temperature mobile residual liquids whose petrogenetic significance is not yet known. To understand the liquid lines of descent, we need to know the stability of fluorine-bearing solid phases, the miscibility gaps between silicate and fluoride melts and the fluorine solubility in silicic melts.

Several unclear geochemical features of natural fluorine-bearing magmatic rocks require experimental investigation. The rock sequence granite/rhyolite–topaz granite/ongonite–quartz topazite is characterized by a

*Corresponding author. Present address: Bayerisches Geoinstitut, University of Bayreuth, 95440 Bayreuth, Germany. Telephone: +49-(0)921-553718. Fax: +49-(0)921-553769. E-mail: david.dolejs@uni-bayreuth.de

gentle decrease in SiO_2 concentrations as a result of the expansion of the quartz stability field (Korzhinskiy, 1959, 1960; Manning *et al.*, 1980; Kogarko & Krigman, 1981; Manning, 1981) and, in addition, by alkali depletion. Topaz rhyolites and ongonites become K-poor (less than 3.5 wt % K_2O), transitional topaz trondhjemites are K-depleted (~ 0.4 wt % K_2O , Kortemeier & Burt, 1988) and quartz topazites are alkali-free (0.1–0.5 wt % $\text{Na}_2\text{O} + \text{K}_2\text{O}$, e.g. Zhu & Liu, 1990; Johnston & Chappell, 1992). The alkali loss can be attributed to separation of an immiscible alkali–fluoride melt or exsolution of alkali–halide fluids (Kortemeier & Burt, 1988). The absence of alkali feldspars in quartz topazites has been explained by the existence of a peritectic transition albite + melt = quartz + topaz + cryolite/chiolite (Kovalenko & Kovalenko, 1976; Kogarko & Krigman, 1981). However, there is no alkali loss in this equilibrium and thus the origin of quartz topazites remains unexplained.

In a companion paper to this experimental study (Dolejš & Baker, 2007) we investigated melting equilibria in the quaternary system silica–albite–topaz–cryolite under anhydrous conditions. The silica–albite–topaz–cryolite system contains an extensive fluoride–silicate liquid miscibility gap that spans cryolite and silica liquidus volumes at temperatures above 960°C. Differentiation paths of natural fluorine-bearing magmas, however, do not reach liquid–liquid immiscibility but saturate with solid cryolite and/or topaz. Under anhydrous conditions levels of fluorine enrichment are strongly dependent on the melt alkali/aluminum ratio in the melt. In subaluminous compositions at 100 MPa and 740°C, fluorine concentration may be as high as 30 wt %.

Here we study melting equilibria in fluorosilicate systems under hydrous conditions. First we discuss the effect of H_2O on the sections cryolite–topaz and quartz–Cry₅₃Tp₄₇. We then show the effect of alkali/aluminum ratio on the maximum fluorine solubilities in quartz–albitic and granitic melts. Finally we discuss how the presence of micas or other phases that can buffer alumina activity has an effect on the fluorine content of granitic melts.

EXPERIMENTAL METHODS

All experiments were performed at 100 MPa in cold-seal pressure vessels (<850°C) or rapid-quench TZM pressure vessels (>850°C) using argon as pressure medium. Starting materials were synthetic glasses and natural mineral phases (Tables 1 and 2). Thirty-four base mixes in the albite–K-feldspar–quartz–topaz–cryolite system were prepared by careful weighing of constituents in the desired proportions and mixing in an agate mortar for 1 h (Table 3). Capsules were prepared from seamless gold or platinum tubing, distilled and deionized water was loaded with a microsyringe and covered with the starting powder. Loaded capsules were crimped and welded with an arc welder while partially

Table 1: List of phases, their abbreviations and compositions

Abbreviation	Phase	Chemical formula
ab	albite	$\text{NaAlSi}_3\text{O}_8$
and	andalusite	Al_2SiO_5
chi	chiolite	$\text{Na}_5\text{Al}_3\text{F}_{14}$
cry	cryolite	Na_3AlF_6
fsp	alkali feldspar	$(\text{Na}, \text{K})\text{AlSi}_3\text{O}_8$
G	haplogranite	$\text{Qz}_{38}\text{Ab}_{33}\text{Or}_{29}$
L	liquid (melt)	
L _{fl}	fluoride melt	
L _{sil}	silicate melt	
mal	malladrite	Na_2SiF_6
mu	muscovite	$\text{KAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$
ne	nepheline	NaAlSiO_4
qz	quartz	SiO_2
tp	fluortopaz	$\text{Al}_2\text{SiO}_4(\text{F}, \text{OH})_2$
V	aqueous vapor	
vil	villiaumite	NaF

Phase proportions associated with abbreviations (e.g. Cry₅₃Tp₄₇) are given in weight per cent.

submerged in a cold-water bath. Random checks of capsules by piercing and estimating water content by loss during heating revealed no H_2O loss during welding within weighing precision (0.02 mg); the total weight loss during welding is 0.04–0.08 mg in both anhydrous and hydrous runs and is attributed to metal loss. The weighed-in H_2O contents are accurate to 0.1 wt %. At the end of each experiment, the cold-seal vessel was placed in an air jet and quenched at 150°C/min whereas the runs in the TZM pressure vessels were quenched by free fall into the cooling collar at 100°C/s. Recovered capsules were weighed to check for leakage, opened immediately and studied by optical microscopy and electron microprobe.

Attainment of equilibrium is facilitated by the presence of H_2O and fluorine. No evidence for disequilibrium was encountered in experiments on the hydrous quartz–albite and haplogranite joins in 7 day runs. This is in agreement with attainment of equilibrium in the volatile-bearing systems after 4 days (Candela & Holland, 1984; Williams *et al.*, 1997; Frank *et al.*, 2003). For further details of experimental techniques and run-product descriptions, the reader is referred to the first part (Dolejš & Baker, 2007).

TERMINOLOGY

Abbreviations for all phases are summarized in Table 1. The terms liquid, fluid and vapor are used in accordance with Stalder *et al.* (2000) and Wyllie & Ryabchikov (2000): liquid represents silicate, fluorosilicate or fluoride melt

Table 2: Chemical composition of starting materials

Symbol	<i>n</i>	SiO ₂ (wt %)	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O	F	Total	A/NK molar	Notes
HPG-2		79.47	11.73		3.90	4.91			1.00	
	16	78.37(48)	11.53(34)	0.0041(53)	3.74(13)	4.979(94)		98.63(24)	0.999(36)	glass
AQ-1		81.56	11.47		6.97				1.00	
	10	82.10(69)	11.62(59)	0.0091(99)	6.53(35)	0.016(12)		100.32(54)	1.080(80)	glass
albite		68.74	19.44		11.82				1.00	
	18	67.91(34)	19.37(12)	0.078(57)	11.30(12)	0.146(21)		98.80(35)	1.033(13)	crystal
topaz		32.65	55.40				20.64			
	18	32.62(39)	54.64(28)	0.008(10)	0.049(79)	0.0071(84)	20.92(13)	99.44(52)		crystal
cryolite			24.28		44.28		54.30		0.3333	
	10	0.011(21)	25.65(53)	0.012(14)	45.67(12)	0.010(18)	57.29(89)	104.51(19)	0.3414(71)	crystal

For each substance, first row indicates theoretical amounts and second row gives analysis by electron microprobe. Analytical conditions: accelerating voltage 15 kV, beam current 5 nA, beam diameter 20 µm; *n*, number of analyzed points. Analytical totals are corrected for the fluorine-equivalent oxygen (the elevated total in the cryolite analysis is related to the correction procedure and has no effect on the element proportions). Standard deviations are reported as 1σ. A/NK = molar Al₂O₃/(Na₂O + K₂O).

Table 3: Modal and chemical composition of base mixes

Symbol	Constituents			SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	F ₂ O ₋₁	F	Al/(Na + K)
	(wt %)			(wt %)						molar
	<i>Silica</i>	<i>Topaz</i>	<i>Cryolite</i>							
TC-06		25.962	74.038	8.476	32.363	32.787		26.374	45.559	0.6
TC-08		38.029	61.971	12.416	36.118	27.443		24.024	41.498	0.8
TC-1		46.714	53.286	15.251	38.820	23.597		22.332	38.576	1.0
TC-12		53.264	46.737	17.389	40.858	20.697		21.056	36.372	1.2
TCQ-1	54.956	21.042	24.002	61.826	17.486	10.629		10.059	17.376	1.0
TCQ-2	28.925	11.075	60	32.541	20.706	26.570		20.183	34.864	0.474
TCQ-3	23.373	35.796	40.832	35.059	29.747	18.082		17.112	29.560	1.0
TCQ-5	10	42.043	47.958	23.726	34.938	21.238		20.099	34.718	1.0
	<i>Silica</i>	<i>Albite</i>	<i>Topaz</i>	<i>Cryolite</i>						
ATCQ-1	30.688	44.160	11.750	13.403	64.879	18.350	11.154	5.617	9.703	1.0
	<i>AQ-1</i>	<i>Topaz</i>	<i>Cryolite</i>							
AQTC-05	95	2.336	2.664	78.242	12.838	7.804		1.117	1.929	1.0
AQTC-10	90	4.671	5.329	74.926	14.206	8.635		2.233	3.858	1.0
AQTC-40	60	18.686	21.314	55.034	22.410	13.622		8.933	15.430	1.0
AQTC-60	40	28.028	31.972	41.773	27.880	16.945		13.399	23.146	1.0
AQTC-69	30.955	32.254	36.791	35.776	30.354	18.451		15.419	26.635	1.0
	<i>HPG-2</i>	<i>Topaz</i>	<i>Cryolite</i>							
GT-05	95	5		77.124	13.911	3.705	4.662	0.598	1.032	1.249
GT-10	90	10		74.784	16.095	3.510	4.416	1.195	2.064	1.525
GT-20	80	20		70.102	20.462	3.120	3.926	2.390	4.129	2.181
GT-30	70	30		65.420	24.830	2.730	3.435	3.585	6.193	3.025

(continued)

Table 3: Continued

Symbol	Constituents		SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	F ₂ O ₋₁	F	Al/(Na + K)
	(wt %)		(wt %)						molar
GC-05	95	5	75.492	12.355	5.919	4.662	1.572	2.715	0.836
GC-10	90	10	71.519	12.983	7.938	4.416	3.143	5.430	0.728
GC-20	80	20	63.572	14.239	11.977	3.926	6.286	10.859	0.594
GC-60	40	60	31.786	19.262	28.130	1.963	18.859	32.577	0.398
GTC-05	95	2.336 2.664	76.255	13.082	4.885	4.662	1.117	1.929	1.0
GTC-10	90	4.671 5.329	73.044	14.437	5.870	4.416	2.233	3.858	1.0
GTC-20	80	9.343 10.657	66.622	17.146	7.839	3.926	4.466	7.715	1.0
GTC-30	70	14.014 15.986	60.201	19.855	9.809	3.435	6.670	11.573	1.0
GTC-40	60	18.686 21.314	53.780	22.565	11.779	2.944	8.933	15.430	1.0
GTC-50	50	23.357 26.643	47.358	25.274	13.749	2.454	11.166	19.288	1.0
GTC-60	40	28.028 31.972	40.937	27.983	15.718	1.963	13.399	23.146	1.0
GTC-70	30	32.700 37.300	34.515	30.692	17.688	1.472	15.632	27.003	1.0
GTC5-30	70	5.393 24.607	57.386	17.173	13.627	3.435	8.379	14.474	0.657
GTC8-30	70	11.409 18.591	59.350	19.045	10.963	3.435	7.207	12.450	0.875
GTC12-30	70	15.979 14.021	60.842	20.467	8.939	3.435	6.317	10.912	1.111
GTC15-30	70	18.162 11.838	61.555	21.146	7.972	3.435	5.892	10.177	1.256

without or with a limited amount of dissolved H₂O (less than 15 wt % in this study); vapor is a low-density aqueous phase with a small amount of solutes (less than 20 wt %); fluid is a general term used for a H₂O-dominated phase with low to high solute concentration.

The term 'melt aluminosity' is a synonym for the aluminum/alkali cation ratio and is used to describe the relative variations of this ratio. The terms peralkaline, subaluminous and peraluminous are used as defined by Shand (1927) and Holtz *et al.* (1992); in the abbreviation Al/(Na + K) we use molar proportions.

For divariant fields and trivariant volumes, we use standard labeling (e.g. L + cry). For univariant curves and invariant points, we use the notation of Greig *et al.* (1955). For example, L (tp) indicates a phase boundary between L and L + tp fields. Similarly, L + V (cry + tp) is an invariant point between four fields: L + V, L + V + cry + tp, L + V + cry and L + V + tp. Phases reported in square brackets are present in all fields of the phase diagram; for example, [+V] indicates vapor-saturated conditions. The phase-diagram descriptions refer to the practical number of components (e.g. haplogranite–topaz binary, rather than haplogranite–topaz pseudobinary or quartz–albite–K-feldspar–topaz–H₂O quinary).

THE TOPAZ–CRYOLITE–H₂O SYSTEM

Peralkaline to peraluminous silicic magmas saturate with topaz and/or cryolite (Dolejš & Baker, 2004, 2007).

Therefore, we studied the topaz–cryolite binary system with 10 wt % H₂O (Table 4; Fig. 1). At 100 MPa, it is characterized by simple eutectic behavior with eutectic point cry + tp + L (V) at 660°C and cation Al/Na ~ 0.7. The eutectic temperature in fluid-saturated conditions is depressed by 110°C at 100 MPa relative to the anhydrous system and the cation Al/Na ratio decreases by at least 0.25 (Dolejš & Baker, 2007; Fig. 1). The occurrence of the three-phase field cry + tp + L (Fig. 1) confirms that the melt in the 10 wt % section is vapor-undersaturated (see Koster van Groos & Wyllie, 1968), and this implies that water solubility in the topaz–cryolite melt is greater than 10 wt % H₂O at 100 MPa.

The eutectic temperature of the cryolite–topaz–H₂O system is 60°C lower and the H₂O solubility is at least three times by weight higher than that of the haplogranite–H₂O system at 100 MPa (Tuttle & Bowen, 1958; Burnham, 1997; Holtz *et al.*, 2001). This suggests that the topaz–cryolite–haplogranite–H₂O eutectic may be displaced to very high fluorine concentrations near the topaz–cryolite side and water solubility may significantly increase in residual fluorogranitic melts.

THE QUARTZ–TOPAZ–CRYOLITE–H₂O SYSTEM

The liquidus relations in the quartz–topaz–cryolite system under hydrous conditions (Table 5) provide a general illustration of the liquid line of descent and describe variations

Table 4: Experimental results in the system cryolite–topaz– H_2O (100 MPa)

Run	Mix	H_2O (wt %)	Temperature (°C)	Duration (h)	Assemblage	Notes
608	TC-06	10	670	171.2	L + cry	
607	TC-06	10	650	166.2	subsolidus	no melting
459	TC-08	10	720	173.3	L + cry	quench crystals
482	TC-08	10	670	167.9	L + cry + tp	
606	TC-08	10	650	166.2	subsolidus	no melting
460	TC-1	10	720	173.3	L + tp	quench crystals
345	TC-1	10	700	327.6	L + tp	
481	TC-1	10	670	167.9	L + tp	
605	TC-1	10	650	166.2	subsolidus	no melting

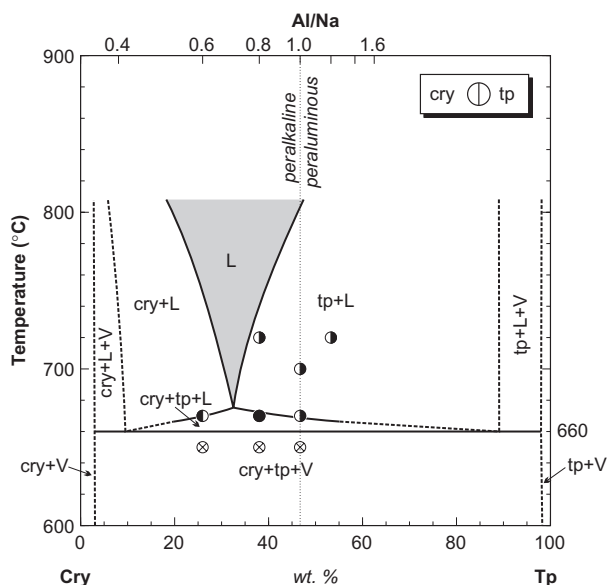


Fig. 1. Phase diagram of the cryolite–topaz system with 10 wt % H_2O at 100 MPa. The eutectic temperature decreases from an anhydrous eutectic at 770°C (Dolejš & Baker, 2007) through the L (cry + tp) piercing point at 670°C and 10 wt % H_2O to the H_2O -saturated eutectic 660°C (more than 10 wt % H_2O). Abbreviations are listed in Table 1.

in SiO_2 and F concentrations in residual fluorosilicate liquids. Figure 2 presents the isobaric section from SiO_2 to $Cry_{53}Tp_{47}$ at 10 wt % H_2O , which is the subaluminous section through the system. The pseudobinary solidus is a piercing point cry + V (qz + tp + L) and the sequence of liquidus fields indicates that the location of ternary eutectic departs from the join to weakly peraluminous conditions. This is in contrast to the weakly peralkaline composition

of the quartz–topaz–cryolite eutectic under anhydrous conditions (Dolejš & Baker, 2007). In addition, the eutectic composition is more SiO_2 -rich and F-poor than at anhydrous conditions (Fig. 2; Dolejš & Baker, 2007, fig. 14).

The residual liquids in the quartz–topaz–cryolite system have compositions close to nepheline with fluorine. The location of the nepheline– F_2O_{-1} join is marked by TCQ-3 (Fig. 2, Table 3), and we have determined H_2O solubility for this composition at 100 MPa. Melts of this composition cannot be quenched owing to their very high fluorine content (29.6 wt % F) and the water solubility must be estimated from the temperature– $X(H_2O)$ section (Fig. 3). The location of the vapor saturation, i.e. L (V) univariant curve, is given by the inflection on the topaz and topaz + cryolite liquidus curves. This defines maximum H_2O content in the melt 12.5 ± 0.5 wt % and this value represents a threefold increase by weight, in comparison with the fluorine-free haplogranitic minimum at the same pressure (Burnham, 1975; Holtz *et al.*, 2001). This measurement also agrees with the vapor undersaturation of the cryolite–topaz cotectic with 10 wt % H_2O (Fig. 1). These observations are in agreement with the increase in water solubility in granitic melts with increasing fluorine contents described by Holtz *et al.* (1993) and Webster & Rebert (1998). Those workers determined experimentally an increase by 0.5 and 0.8 wt % H_2O for each wt % F at 200 MPa, but only for fluorine concentrations less than 5 wt % in the melt.

Our experimental results suggest that the common presence of fluorine and H_2O in the melt does not result in F^- and OH^- site competition, which would lead to a decrease in water solubility with increasing fluorine concentration. Rather, additional fluorine in the melt promotes incorporation of hydroxyl species and/or molecular H_2O . This effect is possibly explained by decreasing ion polarizability when fluorine is added to silicate melts (Duffy, 1989) and this promotes hydroxylation of network modifiers and aluminosilicate tetrahedra. Increase in H_2O solubility in fluorosilicate melts can also be described by Lewis acid–base interactions (see London, 1987). Addition of F_2O_{-1} (strong Lewis acid; Duffy, 1989) leads to strong short-range order with low-field strength cations (Lewis bases) forming alkali–F and (alkali,Al)–F complexes. High-field strength cations and highly polarizable oxygen atoms remain associated (Si–O; Schaller *et al.*, 1992; Zeng & Stebbins, 2000). The added H_2O (a weak Lewis base) is expected to more extensively form alkali–OH bonds and replace bridging oxygens by hydroxyl groups than it does in fluorine-free compositions (Oglesby & Stebbins, 2000; Schmidt *et al.*, 2000). Such mechanism of increasing proportion of hydroxyl species in the melt can explain the increase in the H_2O solubility observed in experiments.

Table 5: *Experimental results in the system silica–cryolite–topaz–H₂O*

Run	Mix	H ₂ O (wt %)	Pressure (MPa)	Temperature (°C)	Duration (h)	Assemblage	Notes
182	TCQ-1	10	100	800	174.1	L + qz + V	
148	TCQ-1	10	100	700	169.3	L + qz + V	
269	TCQ-2	10	100	700	163.1	L + qz + cry	quench crystals
284	TCQ-2	10	100	650	165.5	L + qz + cry	quench crystals
637	TCQ-2	10	100	600	167.0	L + qz + cry	quench crystals
601	TCQ-2	10	100	580	171.6	subsolidus	no melting
277	TCQ-3	0	0.1	900	167.5	L	
412	TCQ-3	0	100	840	22.5	L	relics of crystals
273	TCQ-3	0	100	800	169.5	L	
492	TCQ-3	2	100	680	173.3	L (+qz) + tp + cry	quench crystals
491	TCQ-3	5	100	680	173.3	L + tp + cry	quench crystals
496	TCQ-3	7	100	700	171.8	L + tp	quench crystals
497	TCQ-3	8	100	700	171.8	L	quench crystals
498	TCQ-3	9	100	700	171.8	L	quench crystals
342	TCQ-3	10	100	700	327.6	L	quench cryolite
490	TCQ-3	10	100	680	173.3	L	quench crystals
483	TCQ-3	10	100	670	167.9	L + tp	quench crystals
477	TCQ-3	10	100	650	163.7	L + tp	quench crystals
421	TCQ-3	10	100	620	173.4	L + tp	quench crystals
636	TCQ-3	10	100	600	167.0	L + tp + cry + V	quench crystals
602	TCQ-3	10	100	580	171.6	subsolidus	no melting
515	TCQ-3	11	100	680	173.6	L	quench crystals
516	TCQ-3	12	100	680	173.6	L	quench crystals
603	TCQ-3	12	100	650	169.6	L	quench crystals
604	TCQ-3	13	100	650	169.6	L	quench crystals
635	TCQ-3	13	100	630	166.5	L + tp + cry	quench crystals
634	TCQ-3	15	100	630	166.5	L + tp + cry + V	quench crystals
343	TCQ-3	25	100	700	327.6	L + V	quench crystals
484	TCQ-5	10	100	670	167.9	L + tp	quench crystals
478	TCQ-5	10	100	650	163.7	L + tp + cry + V	quench crystals

THE ALBITE–QUARTZ–TOPAZ–CRYOLITE–H₂O SYSTEM

In the quinary albite–quartz–topaz–cryolite–H₂O system, we experimentally studied the pseudobinary join that connects the quartz–albite eutectic, Q_{Z41}Ab₅₉ (800°C, 100 MPa and H₂O saturation; Tuttle & Bowen, 1958) with the subaluminous topaz–cryolite composition, Cry₅₃Tp₄₇ (Table 6). The resulting temperature–composition section at 100 MPa is presented in Fig. 4.

Addition of topaz and cryolite causes depression of both quartz and albite liquidi, with quartz exhibiting a steeper dT/dx drop than albite (Fig. 4). This effect probably

stems from a decrease in the bulk SiO₂ content (by adding topaz and cryolite) and from NaAl–F short-range order in the melt structure (Manning *et al.*, 1980; Schaller *et al.*, 1992; Zeng & Stebbins, 2000). This depression of both quartz and albite liquidi is in contrast to the findings of Wyllie & Tuttle (1961) and Wyllie (1979), who observed decreasing liquidus temperature of albite and increasing liquidus temperature of quartz, with addition of fluorine. This difference is a result of adding fluorine in the form of HF, i.e. comparing two distinct phase diagram sections. Addition of hydrofluoric acid to the Q_{Z41}Ab₅₉ eutectic composition reaches composition Q_{Z73.4}Cry_{14.2}Tp_{12.4}, which has also been investigated in this study. It plots at

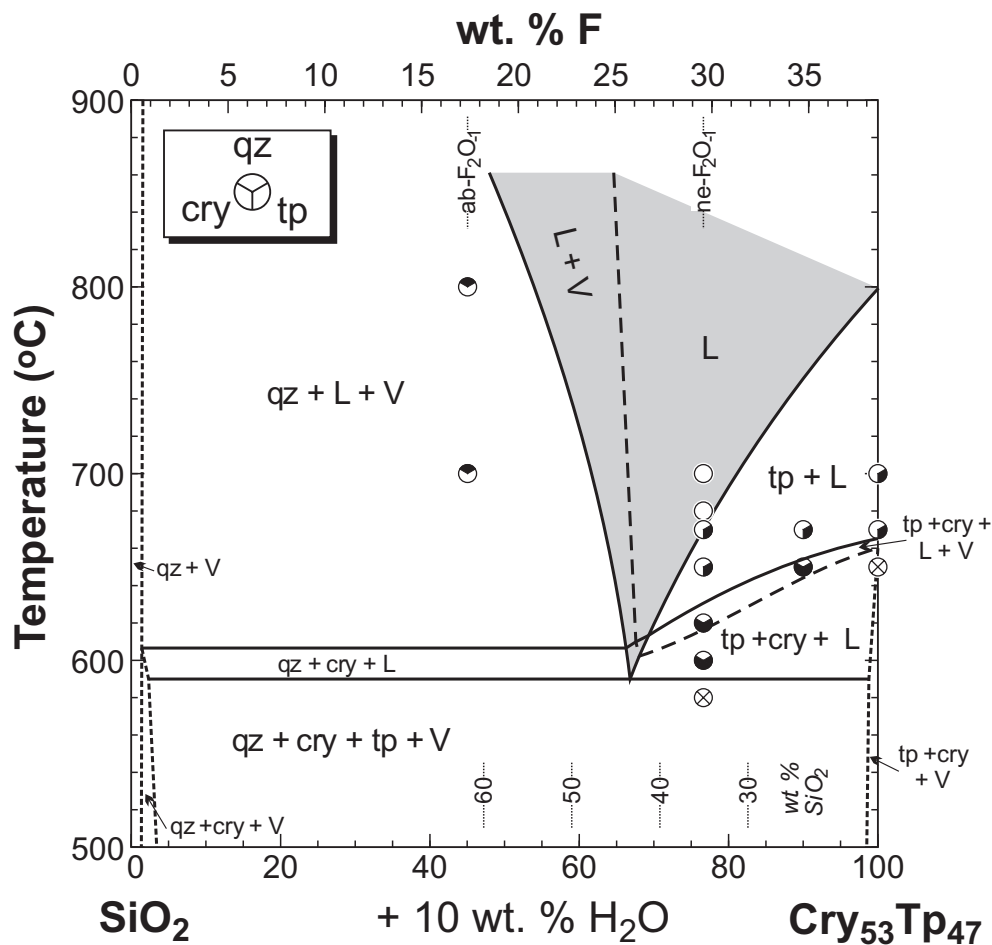


Fig. 2. Temperature–composition section SiO_2 – $\text{Cry}_{53}\text{Tp}_{47}$ with 10 wt % H_2O (100 MPa). This join represents a subaluminous isopleth through the quartz–topaz–cryolite ternary with added H_2O and intersects two joins: albite– F_2O_{-1} and nepheline– F_2O_{-1} . The quaternary quartz–topaz–cryolite– H_2O eutectic occurs at 590°C , close to the cry + V ($\text{qz} + \text{tp} + \text{L}$) piercing point (43 wt % SiO_2 , 26 wt % F); the position of the anhydrous eutectic can be compared with fig. 14 of Dolejš & Baker (2007). The H_2O -saturated tridymite melting occurs between 1190 and 1240°C (Kennedy *et al.*, 1962; Ostrovsky, 1966).

73.4 wt % SiO_2 and 26.6 wt % $\text{Cry}_{53}\text{Tp}_{47}$ (Fig. 2) and the quartz liquidus temperature has increased to approximately 1000°C . This is in agreement with the extended liquidus trend of Wyllie & Tuttle (1961) and Wyllie (1979).

The $\text{Ab}_{59}\text{Qz}_{41}$ – $\text{Cry}_{53}\text{Tp}_{47}$ section illustrates that crystallization temperatures are depressed from the fluid-saturated albite–quartz eutectic at 800°C (Tuttle & Bowen, 1958) through piercing points L + V ($\text{ab} + \text{cry}$) and L + V ($\text{cry} + \text{tp}$) at 600 – 610°C and to the quinary albite–quartz–topaz–cryolite eutectic at 580°C (100 MPa, H_2O saturation; Fig. 4). The cryolite and topaz liquidus curves intersect at the L + V ($\text{cry} + \text{tp}$) piercing point and the sequence of stability fields implies that the cryolite–topaz cotectic curve passes from peralkaline to peraluminous space. Below the L + V ($\text{ab} + \text{cry}$) and $\text{ab} + \text{L} + \text{V}$ ($\text{qz} + \text{cry}$) piercing points, residual melts have a peraluminous composition.

THE HAPLOGRANITE–TOPAZ–CRYOLITE– H_2O SYSTEM

Addition of K_2O to the previous system completes the senary composition space Na_2O – K_2O – Al_2O_3 – SiO_2 – F_2O_{-1} – H_2O necessary for the description of haplogranitic melts and full interpretation of the liquid lines of descent of natural silicic magmas. This system was studied in four temperature–composition sections and two isothermal sections through the haplogranite ($\text{Qz}_{38}\text{Ab}_{33}\text{Or}_{29}$)–topaz–cryolite– H_2O space. The compositions of the starting mixes are presented in Fig. 5, and experimental results are listed in Table 7.

The temperature–composition sections for the two limiting binaries: haplogranite–topaz and haplogranite–cryolite at 10 wt % H_2O , are shown in Fig. 6. The fluorine-free haplogranitic minimum occurs at 720°C ,

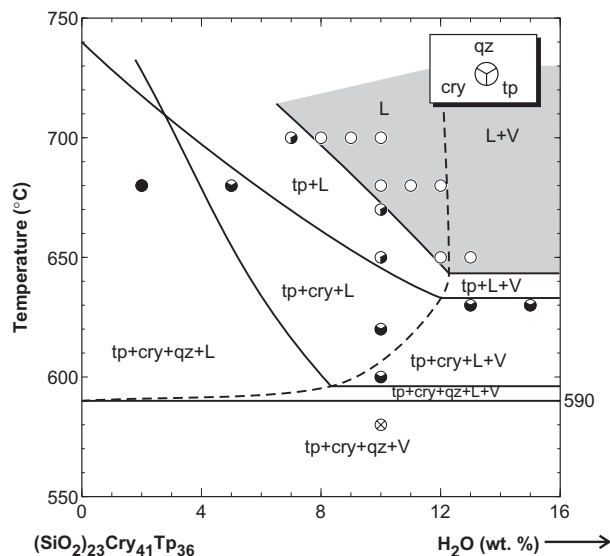


Fig. 3. Temperature– $X(\text{H}_2\text{O})$ section for the determination of water solubility in the TCQ-3 composition (100 MPa). The maximum H_2O solubility (12.5 ± 0.5 wt %) is defined by the L (V) univariant curve, located at the inflection of the topaz and cryolite liquidus curves.

100 MPa and H_2O saturation (Tuttle & Bowen, 1958). In the haplogranite–topaz pseudobinary, the solubility of topaz in the H_2O -saturated haplogranitic melt is low, corresponding to less than 2 wt % F below 700°C. In the haplogranite–cryolite pseudobinary, the solubility of cryolite is higher, about 4 wt % F. The pseudobinary eutectics are located at 640°C (100 MPa and H_2O saturation, Fig. 6), i.e. both fluorine-bearing minerals cause a solidus depression of 80°C, relative to the H_2O -saturated haplogranite minimum (Tuttle & Bowen, 1958). These eutectics and saturation limits represent limiting cases for strongly peralkaline or strongly peraluminous granitic melts, respectively.

Addition of either topaz or cryolite to the haplogranite system causes distinct depressions of quartz and feldspar liquidi, i.e. topaz and cryolite affect stabilities of quartz and feldspar differently (Fig. 6). In the haplogranite–cryolite pseudobinary, the alkali-feldspar liquidus is more depressed than that of quartz. Such increase in the activity of quartz compared with alkali feldspar is probably a result of strongly positive deviations from mixing in the silica–cryolite binary, manifested by liquid–liquid

Table 6: *Experimental results in the system silica–albite–cryolite–topaz– H_2O (100 MPa)*

Run	Mix	H_2O (wt %)	Temperature (°C)	Duration (h)	Assemblage	Notes
236	AQTC-05	10	700	172.4	L + ab + V	
237	AQTC-10	10	700	172.4	L + V	
246	AQTC-10	10	660	168.4	L + ab + V	
260	AQTC-10	10	620	171.3	L + ab + V	
329	AQTC-10	10	580	167.4	solidus	incipient melting
235	ATCQ-1	10	700	172.4	L + V	quench microlites
247	ATCQ-1	10	660	168.4	L + V	
256	ATCQ-1	10	620	171.3	L + ab + V	
325	ATCQ-1	10	580	167.4	solidus	incipient melting
544	AQTC-40	4	750	173.2	L	
545	AQTC-40	6	750	173.2	L	
566	AQTC-40	10	750	168.0	L + V	
238	AQTC-40	10	700	172.4	L + V	quench microlites
248	AQTC-40	10	660	168.4	L + V	quench microlites
259	AQTC-40	10	620	171.3	L	
327	AQTC-40	10	580	167.4	L + ab + cry (+tp)	
454	AQTC-50	10	800	163.5	L + V	
546	AQTC-60	4	750	173.2	L + tp (rare)	
547	AQTC-60	6	750	173.2	L	
567	AQTC-60	10	750	168.0	L + V	
267	AQTC-60	10	700	163.1	L + V	quench crystals
249	AQTC-60	10	660	168.4	L + tp + V	
261	AQTC-60	10	620	171.3	L + cry + tp + V	
330	AQTC-60	10	580	167.4	L + cry + tp + V	small amount of glass

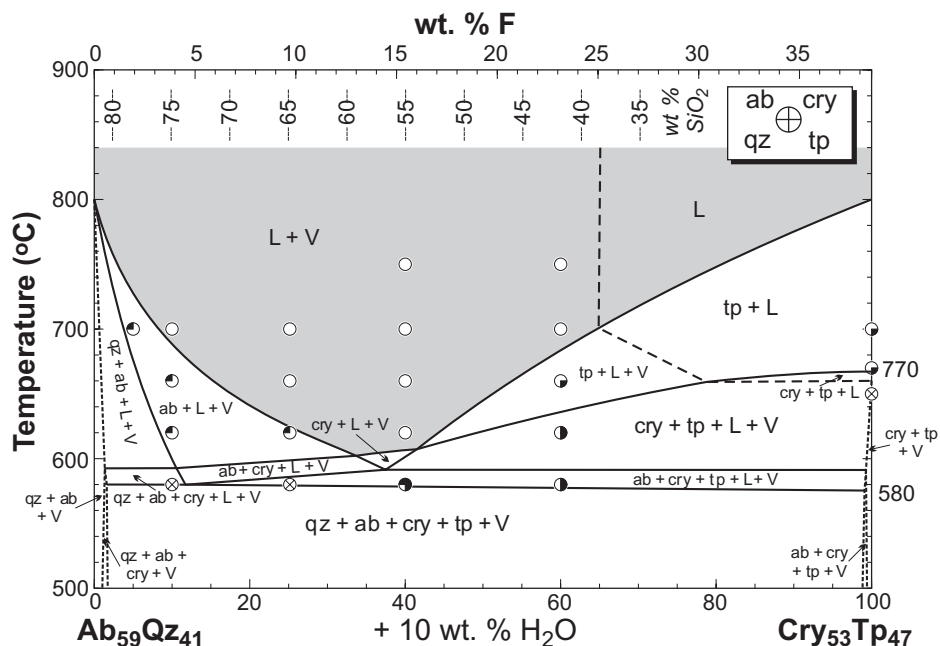


Fig. 4. Temperature–composition section $\text{Ab}_{59}\text{Qz}_{41}\text{--Cry}_{53}\text{Tp}_{47}$ ($\text{Al}/\text{Na}=1$) with 10 wt % H_2O (100 MPa). This join connects the quartz–albite eutectic composition (Tuttle & Bowen, 1958) with the subaluminous cryolite–topaz mixture. As a result of the increasing solubility of H_2O (see Fig. 19), the melt becomes vapor-undersaturated at high fluorine contents.

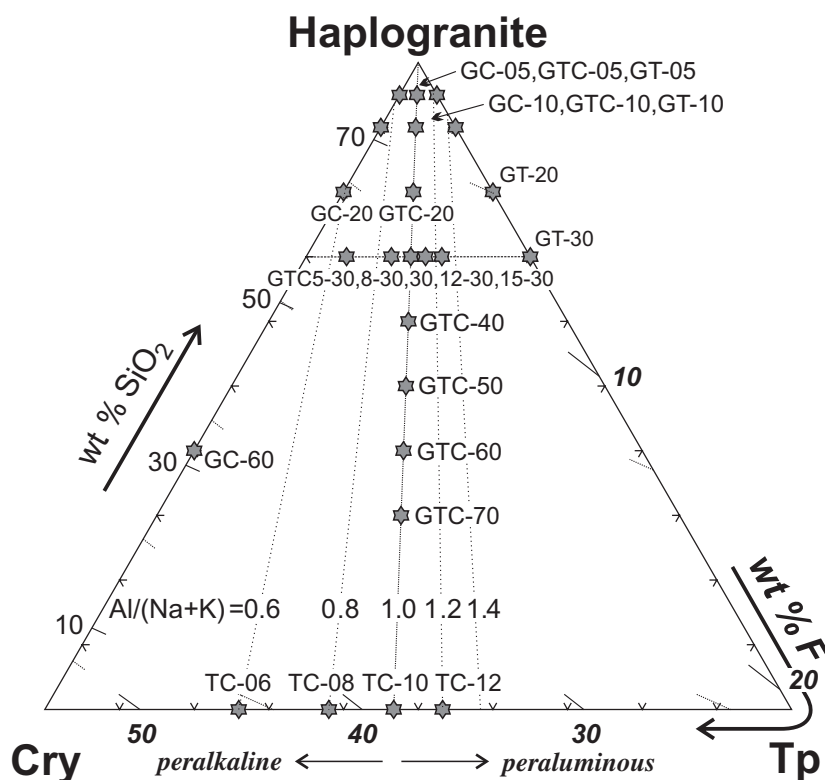


Fig. 5. Starting compositions in the ternary haplogranite–cryolite–topaz system. The following sections are illustrated in the subsequent figures: haplogranite–GT-30 (Fig. 6a), haplogranite–GC-30 (Fig. 6b), haplogranite–TC-10 = $\text{Cry}_{53}\text{Tp}_{47}$ (Fig. 7), isothermal ternary sections (Fig. 8a and b), GC-30–GT-30 (Fig. 9), and isothermal pseudoternary haplogranite–40% topaz–40% cryolite sections (Fig. 10).

Table 7: *Experimental results in the system haplogranite–cryolite–topaz–H₂O (100 MPa)*

Run	Mix	H ₂ O (wt %)	Temperature (°C)	Duration (h)	Assemblage	Notes
169	GT-05	10	660	166.9	L + fsp (+tp) + V	
191	GT-05	10	650	164.2	L + fsp + tp + V	small amount of glass
168	GT-05	10	630	166.0	subsolidus	no melting
463	GT-10	10	720	173.3	L + tp + V	
160	GT-10	10	660	187.9	L + fsp + tp + V	
192	GT-10	10	650	164.2	L + fsp + tp + V	
584	GT-20	0	800	169.4	L + tp	no equilibrium
613	GT-20	10	850	164.8	L + tp + V	
583	GT-20	10	800	169.4	L + tp + V	
138	GT-20	10	720	193.7	L + tp + V	
139	GT-30	10	720	193.7	L + tp + V	
167	GC-05	10	660	166.9	L + qz + V	
189	GC-05	10	650	164.2	L + qz + cry + V	
166	GC-05	10	630	166.0	subsolidus	no melting
89	GC-10	10	720	188.2	L + cry + V	
161	GC-10	10	660	187.9	L + qz + cry + V	
190	GC-10	10	650	164.2	L + qz + cry + V	
370	GC-20	0	800	167.2	L + cry	
609	GC-20	10	850	164.8	L + V	quench crystals
582	GC-20	10	800	169.4	L + cry + V	quench crystals
90	GC-20	10	720	188.2	L + cry + V	
592	GC-60	0	1040	2.8	L _{sil} + L _{fl}	
165	GTC-05	10	660	166.9	L + fsp + V	
164	GTC-05	10	630	166.9	L + fsp (+ qz) + V	
185	GTC-05	10	540	167.6	L + fsp + V	small amount of glass
371	GTC-10	0	800	167.2	L + ab	no equilibrium
455	GTC-10	10	800	166.0	L + V	
159	GTC-10	10	660	187.9	L + V	
179	GTC-10	10	600	169.2	L + fsp + V	
205	GTC-10	10	570	170.4	L + fsp + cry + V	
186	GTC-10	10	540	167.6	L + fsp + cry + V	small amount of glass
372	GTC-20	0	800	167.2	L (metastable)	no equilibrium
456	GTC-20	10	800	166.0	L + V	
177	GTC-20	10	630	169.6	L + V	
178	GTC-20	10	600	169.2	L + V	quench microlites
206	GTC-20	10	570	170.4	incipient melting	
187	GTC-20	10	540	167.6	subsolidus	no melting
209	GTC-20	10	520	171.2	subsolidus	no melting
466	GTC-30	0	850	145.3	L	
373	GTC-30	0	800	167.2	L	
457	GTC-30	10	800	166.0	L + V	quench crystals
207	GTC-30	10	570	170.4	L + fsp + cry + tp + V	
210	GTC-30	10	520	171.2	subsolidus	no melting
374	GTC-40	0	800	167.2	L	
181	GTC-40	10	800	174.1	L + V	quench microlites

(continued)

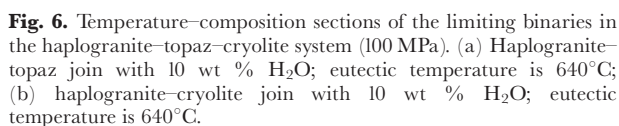
Table 7: Continued

Run	Mix	H ₂ O (wt %)	Temperature (°C)	Duration (h)	Assemblage	Notes
175	GTC-40	10	630	169.6	L + V	
174	GTC-40	10	600	169.2	L + cry (+ tp) + V	
208	GTC-40	10	570	170.4	L + fsp + cry + V	
188	GTC-40	10	540	167.6	L + fsp + tp + cry (+ qz)	
211	GTC-40	10	520	171.2	subsolidus	
439	GTC-50	0	800	175.2	L + tp	
458	GTC-50	10	800	166.0	L + V	quench crystals
467	GTC-60	0	850	145.3	L	
449	GTC-60	0	800	164.5	L + tp	
469	GTC-70	0	800	164.8	L	quench crystals
562	GTC-70	6	800	167.7	L	
563	GTC-70	10	800	167.7	L	
533	GTC5-30	0	800	166.2	L + cry	
532	GTC5-30	6	800	166.2	L + cry + V	
611	GTC5-30	10	850	164.8	L + cry + V	quench crystals
579	GTC5-30	10	800	169.4	L + cry + V	
577	GTC5-30	10	720	170.0	L + cry + V	
470	GTC8-30	0	800	164.8	L + cry	
520	GTC8-30	6	800	173.8	L + cry (very rare) + V	
521	GTC8-30	10	800	173.8	L + V	quench crystals
461	GTC8-30	10	720	173.3	L + cry + V	
471	GTC12-30	0	800	164.8	L + tp	
522	GTC12-30	6	800	173.8	L + tp + V	
523	GTC12-30	10	800	173.8	L + tp + V	
462	GTC12-30	10	720	173.3	L + cry + V	
534	GTC15-30	0	800	166.2	L + tp	
535	GTC15-30	6	800	166.2	L + tp + V	
612	GTC15-30	10	850	164.8	L + tp + V	
581	GTC15-30	10	800	169.4	L + tp + V	
580	GTC15-30	10	720	170.0	L + tp + V	

immiscibility (Dolejš & Baker, 2007). In the haplogranite–topaz pseudobinary, the effect is reversed, i.e. the quartz liquidus is more depressed than that of feldspar. This means that topaz does not cause, but rather suppresses positive deviations from ideal mixing in the melt. Such behavior is in agreement with the disappearance of liquid–liquid immiscibility in the silica–cryolite system and with the strong quartz liquidus depression when topaz is added (Dolejš & Baker, 2007). In addition, the greater depression of the quartz liquidus (Fig. 6a) is promoted by a decrease in bulk SiO₂ content upon addition of topaz.

The phase relations along the subaluminous haplogranite–Cry₅₃Tp₄₇ join at 10 wt % H₂O (Fig. 7) are very similar to those in the quartz–albite–cryolite–topaz

system (Fig. 4). Addition of topaz and cryolite causes a depression in granite crystallization temperatures to the quaternary eutectic at 540°C (100 MPa and H₂O saturation). Intersection of the topaz and cryolite liquidus curves defines the L + V (cry + tp) piercing point, whose presence indicates that melt compositions change from peralkaline to peraluminous along the topaz–cryolite cotectic. The L + V (cry + tp) piercing point is located at significantly higher fluorine concentration (11 wt % F) than individual solubilities of fluorine at topaz or cryolite saturation (Fig. 6). This means that fluorine solubility is much higher in subaluminous melts than in peralkaline or peraluminous systems. That is, the melt alkali/aluminum ratio has a significant effect on fluorine solubility.



Near-solidus crystallization of fluorine-rich granitic melts is illustrated in two isothermal-isobaric sections of the central portion of the haplogranite-cryolite-topaz-H₂O system. At 580°C, 100 MPa and 10 wt % H₂O (Fig. 10a) the presence of the L [+V] field indicates that the liquid compositions still remain within the ternary plane and exhibit no quartz or feldspar enrichment compared with the hydrous haplogranitic minimum. The liquid field is located between 6 and 10 wt % F and has a narrow span of aluminum/alkali cation ratios, 0.94-1.08. The L [+V] field closes at 550°C (Fig. 10b) and is replaced by the fsp + L [+V] field, indicating the departure of melt composition towards quartz-rich compositions. The eutectic melt composition is located in the quartz-feldspar-cryolite-topaz tetrahedron, more specifically in its quartz-haplogranite-cryolite-topaz subspace. The fsp + L [+V] field closes as an invariant point fsp + L (cry + qz + tp) [+V] at 3.6 wt % F and a weakly peraluminous composition (cation Al/(Na + K) = 1.05). This invariant point is a piercing point on the ternary plane of a tie-line connecting the eutectic melt composition in the quartz-feldspar-cryolite-topaz tetrahedron with the feldspar apex. By chemography, the eutectic melt composition is bracketed

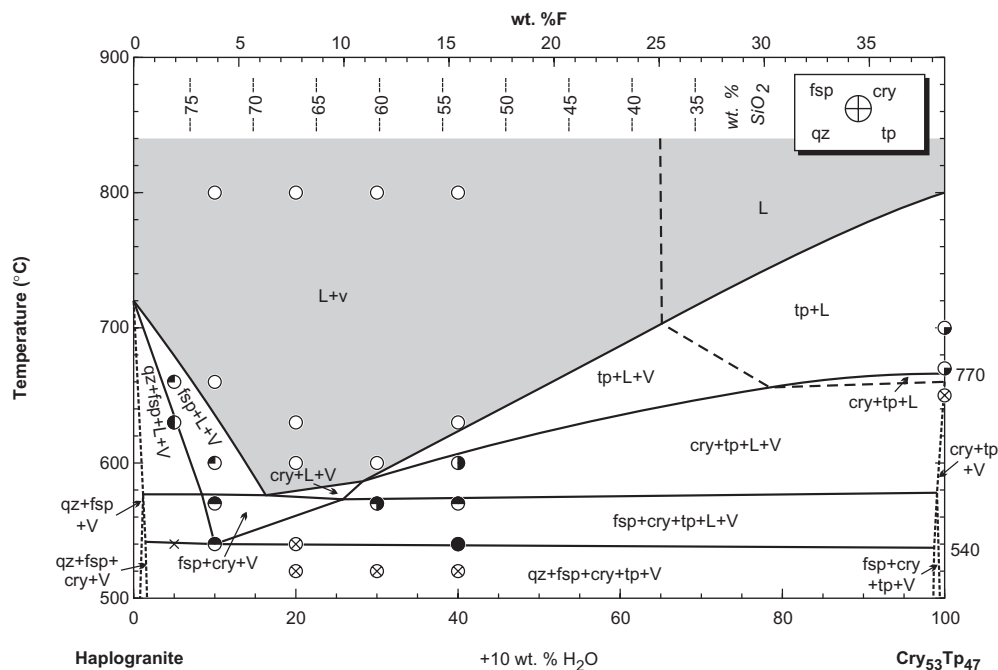


Fig. 7. Temperature–composition section haplogranite–Cry₅₃Tp₄₇, Al/(Na + K) = 1 with 10 wt % H₂O (100 MPa). The join connects the haplogranite minimum composition, Q_{Z38}Or₂₉Ab₃₃ (Tuttle & Bowen, 1958) with the subaluminous cryolite–topaz mixture.

between G₉₀Cry_{4.7}Tp_{5.3} [by weight, 3.6 wt % F, Al/(Na + K) = 1.05] and Q_{Z83.9}Cry_{7.6}Tp_{8.5} [5.9 wt % F, Al/(Na + K) = 1.18].

The experimental design imposes some constraints on interpretation of the results. As the amount of residual melt in the experimental charges decreases with decreasing temperature, the melt becomes fluid-saturated (the total H₂O content in the system is constant) and the fluid/melt ratio increases. As a result of incongruent dissolution of aluminosilicates in aqueous fluid (Manning, 1981; Dingwell, 1985; Webster, 1990), the composition of the near-eutectic melt departs from its projected position on the phase diagram. On the basis of our preliminary partitioning experiments and results of thermodynamic calculations, it is expected that the eutectic melt becomes slightly depleted in SiO₂ and F and that its aluminum/alkali ratio increases.

PETROLOGICAL IMPLICATIONS

The behavior of fluorine in silicate melts (see also Manning, 1981; Webster, 1990; Mysen *et al.*, 2004) stands in remarkable contrast to the effects of other volatile elements (Cl, S, B, P; Carroll & Webster, 1994). The very high solubility of fluorine in silicate melts (Koster van Groos & Wyllie, 1968; Webster, 1990; Carroll & Webster, 1994) is a consequence of fluorine–oxygen substitution in the melt structure (Mysen *et al.*, 2004) because of the similarity of ionic radii of fluorine (1.29 Å) and oxygen (1.35 Å;

Shannon, 1976). Formation of fluorosilicate and fluoroaluminates tetrahedral and octahedral complexes (Schaller *et al.*, 1992; Zeng & Stebbins, 2000; Mysen *et al.*, 2004) is responsible for a decrease in the activities of silicate melt components (Manning *et al.*, 1980; London, 1987). Therefore, liquidus and solidus temperatures are depressed and compositional shifts of haplogranite minima occur (Manning, 1981). Upon fluid saturation, incongruent fluid–melt partitioning is responsible for selectively sequestering elements from residual melts (Dingwell, 1985). In addition, the presence of rock-forming elements such as calcium or lithium may stabilize new fluorine-bearing phases, e.g. fluorite (Dolejš & Baker, 2006) or lithium micas.

Differentiation mechanisms of leucocratic silicic melts

The solidus temperatures of hydrous albitic and haplogranitic melts decrease with increasing fluorine contents to less than 600–630°C at 275 and 100 MPa, respectively (Wyllie & Tuttle, 1961; Koster van Groos & Wyllie, 1968; Manning, 1981). Experimental studies on natural fluorine-bearing silicic compositions with 0.9–1.2 wt % F demonstrate that solidus temperatures range between 675 and 500°C at 100–150 MPa and aqueous-fluid saturation (Webster *et al.*, 1987; Weidner & Martin, 1987; Xiong *et al.*, 2002). Our experimental determination of a solidus temperature of 540°C in the haplogranite–topaz–cryolite–H₂O system at 100 MPa falls

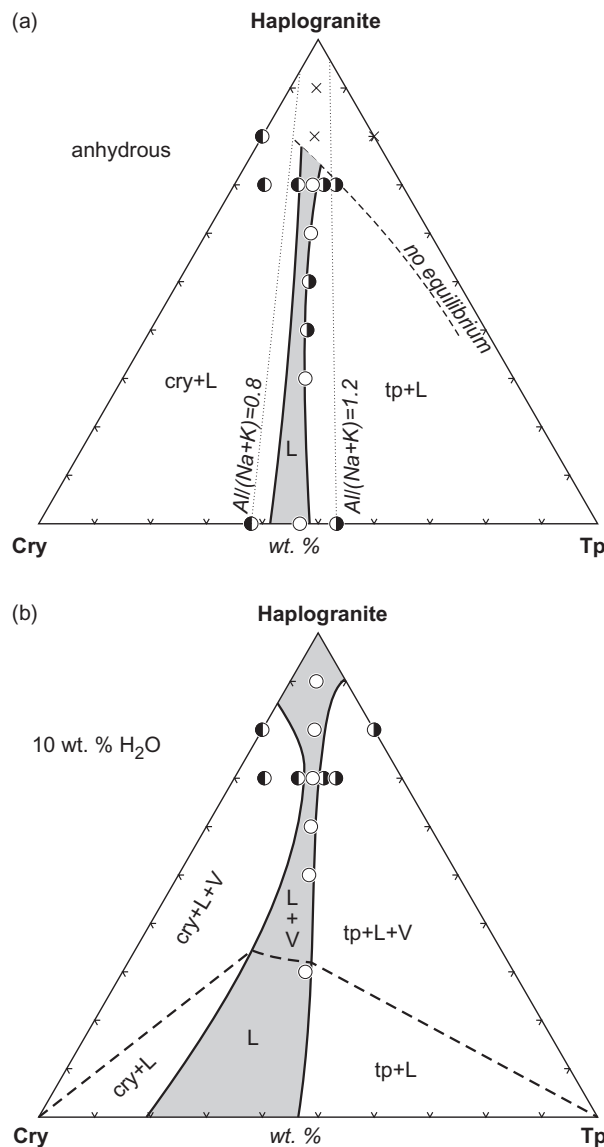


Fig. 8. Isothermal sections of the haplogranite–cryolite–topaz system at 800°C, 100 MPa at anhydrous conditions (a) and with 10 wt % H₂O (b). The liquid field, L [+V], is elongate because of the low melting temperatures of the haplogranite minimum and the cryolite–topaz eutectic (Dolejš & Baker, 2007). The cryolite and topaz saturation isotherms approach isopleths of the Al/(Na + K) ratio and intersect fluorine isopleths. As the alumina/alkali ratio changes in the ternary, the isothermal fluorine solubility increases from 4 wt % (haplogranite–cryolite join) to more than 39 wt % at the subaluminous composition and decreases to 2 wt % F (haplogranite–topaz join). ×, experiments with lack of equilibrium.

within this range of solidus temperatures. It is noteworthy that differences among previous studies must partly be due to variable fluorine concentrations in the system and in the residual melt.

Silicate–fluoride liquid–liquid immiscibility (Kogarko & Krigman, 1981; Veksler *et al.*, 2005; Dolejš & Baker, 2007) does not propagate to the low-temperature fluorosilicate

systems studied here. In fluorine-bearing hydrous silicic systems, cryolite and topaz are the saturating solid phases. The low eutectic temperature in the hydrous topaz–cryolite join (660°C) causes displacement of ternary and quaternary eutectics towards this join and thus enables the silicate-precipitating surfaces to extend to elevated concentrations of fluorine in residual melts. The relevant invariant points at 100 MPa and aqueous-fluid saturation are quartz–topaz–cryolite at 590°C, quartz–albite–topaz–cryolite quaternary eutectic at 580°C and quartz–alkali feldspar–topaz–cryolite quaternary eutectic at 540°C. Phase relations in these systems define differentiation paths of Li-, Ca- and Fe-poor fluorine-bearing granites, rhyolites, ongonites and their differentiates (quartz topazites, xianghualingites, elvans). We compare natural whole-rock compositions with experimental liquidus relations in the schematic Jänecke projection (Jänecke, 1906) on the quartz saturation surface (Fig. 11). Fluorine-bearing natural rocks are moderately to strongly peraluminous, whereas peralkaline types are nearly absent. Fluorine-bearing granites and ongonites cluster close to the feldspar–aluminosilicate (mica, andalusite)–topaz [+quartz] cotectic curves and represent magmatic liquids. The scatter most probably reflects effects of additional minor components on the phase relations and/or variable accumulation of crystallizing solids. On the other hand, compositions of quartz topazites and xianghualingites plot on the topaz [+quartz] surface, consistent with their biminerallitic assemblage; importantly, topazites do not appear to represent liquid compositions at reasonable temperatures. We propose that natural occurrences of fine-grained quartz topazites with magmatic flow banding and trapped xenoliths are crystal assemblages produced by alkali-bearing melts (see Kortemeier & Burt, 1988). Coarse-grained and miarolitic quartz topazites and topaz silexites can be interpreted as products of the disequilibrium crystallization of pegmatite-forming melts after volatile loss or were affected by hydrothermal alteration (Birch, 1984; Kleeman, 1985; Johnston & Chappell, 1992; see Hervig *et al.*, 1987) and are not comparable with experimental data. Importantly, the fluoride–silicate liquid–liquid immiscibility is located at very high fluorine contents, beyond the feldspar–topaz–cryolite [+quartz] eutectic, and is not approached by any whole-rock compositions (Fig. 11).

Effects of aluminum/alkali ratio

In the haplogranite–topaz–cryolite system with H₂O, the individual solubilities of topaz or cryolite in their pseudobinaries are very low, ~2 and 4 wt % F, respectively (Fig. 6). The solubilities of both phases, however, rapidly increase in the central subaluminous portion of the pseudoternary haplogranite–topaz–cryolite system (Fig. 8). When the isopleths of aluminum/alkali ratio and fluorine concentrations in the melt are imposed

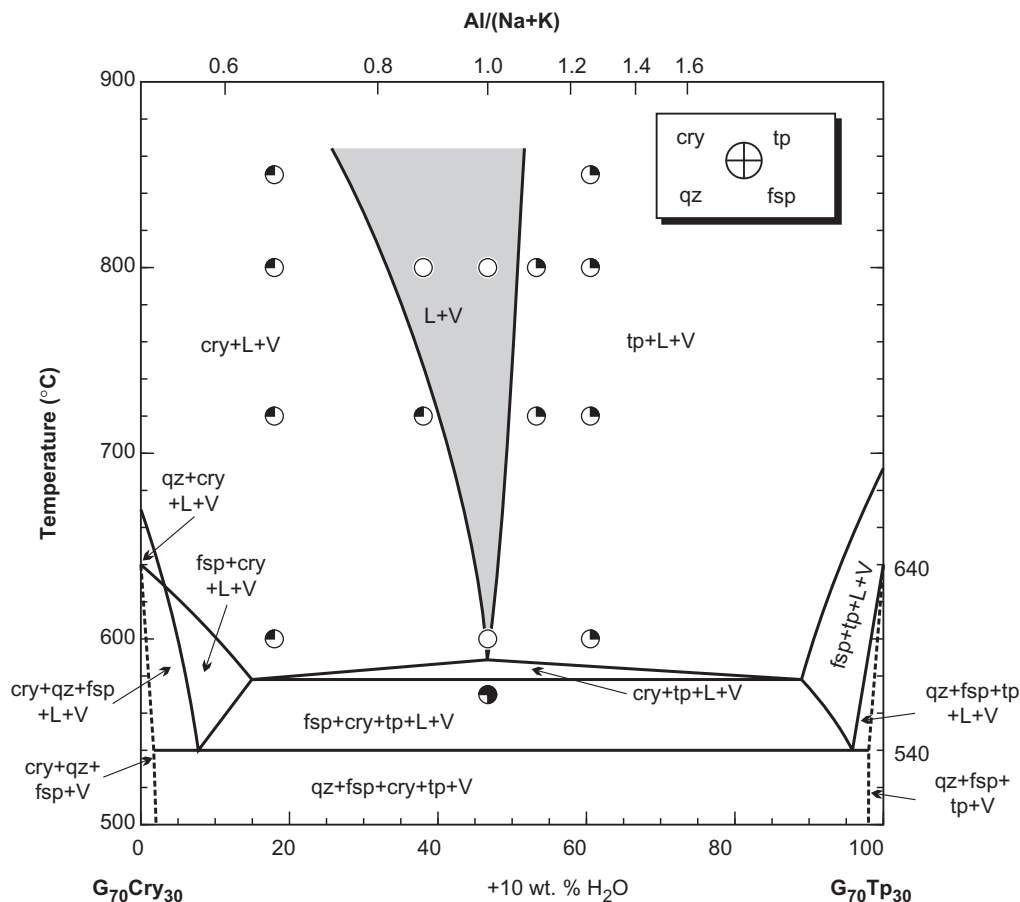


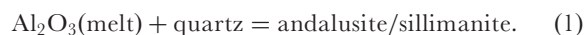
Fig. 9. Temperature–composition section through the system haplogranite–cryolite–topaz at 30 wt % cryolite + topaz, with 10 wt % H₂O (100 MPa). The L+V field is delimited by the cryolite and topaz surfaces and is constrained to a narrow range of alkali/aluminum ratios. Phase equilibria at end-member compositions are constrained by Fig. 6.

on this system (Fig. 5) these two variables are not independent in topaz- or cryolite-precipitating melts. That is, the fluorine concentration in the melt at topaz or cryolite saturation is not unique, but it strongly depends on the alumina/alkali ratio of the silicate melt.

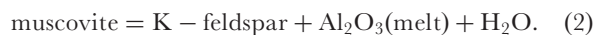
Granitic and rhyolitic magmas evolve by crystal fractionation along the quartz–feldspar cotectic surface and become enriched in fluorine. Once the melt is saturated in topaz or cryolite and, if $a(\text{Al}_2\text{O}_3)$ is not buffered by other solid phases, the residual melt will evolve to higher fluorine concentrations along the quartz–feldspar–topaz or quartz–feldspar–cryolite cotectic. These cotectics dictate the alkali/aluminum ratio of the melt, which will converge to a subaluminous value. All melts completely crystallize at the quaternary eutectic, where saturation with a second fluorine-bearing mineral occurs.

In multicomponent systems, the presence of other phases (micas, andalusite, cordierite, garnet, amphibole) buffers $a(\text{Al}_2\text{O}_3)$ in the melt. For example, an aluminosilicate mineral (andalusite, sillimanite) in the presence

of quartz determines $a(\text{Al}_2\text{O}_3)$ by the following equilibrium:



Similarly, the muscovite component in dioctahedral mica coexisting with quartz and alkali feldspar at fluid saturation dictates $a(\text{Al}_2\text{O}_3)$:



Numerous similar equilibria involving cordierite, garnet, amphibole and pyroxene and involving $a(\text{Al}_2\text{O}_3)$ were listed by Barton *et al.* (1991) and Barton (1996). Therefore, if $a(\text{Al}_2\text{O}_3)$ in the melt is buffered by additional precipitating mineral phases, the liquid line of descent on the quartz–feldspar cotectic surface will follow a specific isopleth of alkali/alumina ratio in the melt. When the cotectic curve with topaz or cryolite is reached, the assemblage becomes invariant. At this point, the melt completely crystallizes, without further evolving to high fluorine contents and without crystallization of a second fluorine-bearing phase.

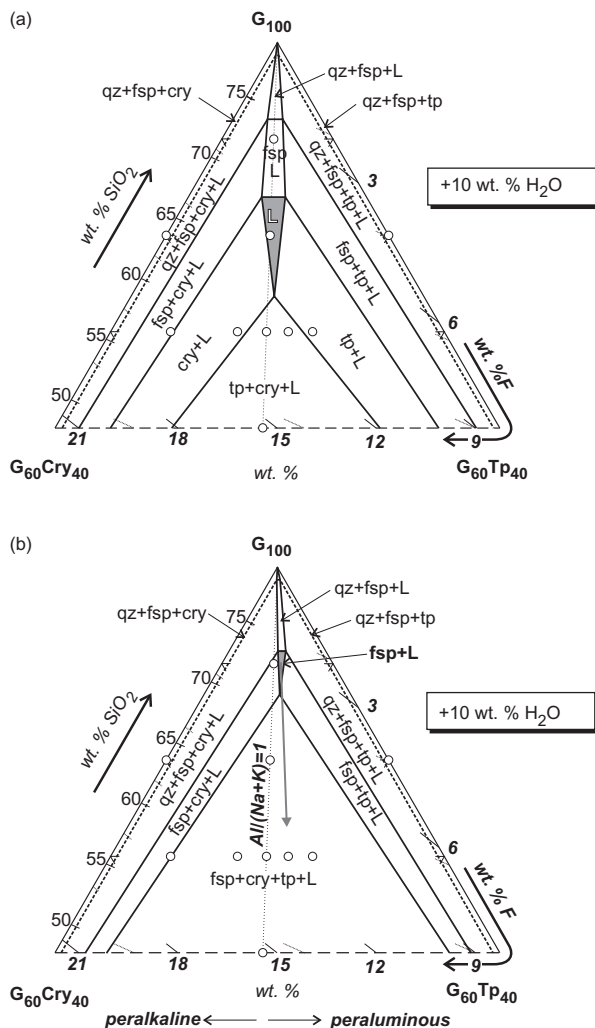


Fig. 10. Isothermal sections of a portion of the haplogranite (G)–cryolite–topaz system with 10 wt % H₂O (100 MPa): (a) 580°C, the composition of residual liquid remains ternary; (b) 550°C, gradual closing of the pseudoternary fsp + L field. This field will contract to the fsp + L tie-line connecting the pseudoternary eutectic melt composition with the feldspar composition. The gray arrow indicates the possible range of eutectic compositions, projected onto the haplogranite–cryolite–topaz plane (see text for discussion). ○, locations of starting compositions.

The first differentiation sequence with no external buffering is applicable to leucogranitic and leucorhyolitic magmas, comparable with highly evolved topaz rhyolites and ongonites, whereas biotite-bearing, two-mica or aluminosilicate-bearing granites will follow a buffered sequence.

Effects of additional components

Additional rock-forming elements (Ca, Mg, Fe, or Li) or volatile constituents (B, P) will affect the differentiation

model described above. The fluorine solubilities may be limited by saturation in new fluorine-bearing phases. These may include fluorine-bearing minerals (lithium fluoromicas, viliaumite, fluorite; Burt & London, 1982; Dolejš & Baker, 2004, 2006), immiscible fluoride liquids (Kogarko & Krigman, 1981; Veksler, 2004) or fluorine-rich aqueous fluids (Webster, 1990). In natural peralkaline and calc-alkaline magmas, fluorite becomes the stable solid phase (Hogan & Gilbert, 1995; Marshall *et al.*, 1998). Furthermore, Dolejš & Baker's (2006) thermodynamic calculations demonstrate that fluorite is also stable in Fe-, Mg- and Ti-bearing silicic rocks. Fluorite buffers fluorine concentrations to low levels, the values of which are determined by the calcium content in the melt (Price *et al.*, 1999; Scaillet & Macdonald, 2004; Dolejš & Baker, 2006). The widespread stability and low solubility of fluorite prevents melt enrichment in fluorine concentrations above 0.5–1 wt % F in most calcium-bearing igneous systems (see Price *et al.*, 1999; Dolejš & Baker, 2006).

Fluorine behavior in Li-, B- and P-rich granitic and pegmatitic melts remains, however, much less understood. These suites are Ca-poor (Černý, 1998; Stilling, 1998) and fluorite stability is suppressed to near-solidus conditions (Webster *et al.*, 1987; Weidner & Martin, 1987). The presence of lithium in many evolved granites (Cuney *et al.*, 1992; Charoy & Noronha, 1996; Förster *et al.*, 1999; Černý *et al.*, 2005) stabilizes lithium micas and amblygonite–montebrasite solid solutions that may act as sinks for fluorine during prolonged differentiation (London, 1997) because fluorine preferentially partitions into these mineral phases (Icenhower & London, 1995; London *et al.*, 2001). The amount of precipitating solids is limited by the low amounts of lithium and phosphorus available in the melt. Thus, these minerals are unlikely to inhibit the fluorine enrichment in residual melts. Another effect is the significant depression of crystallization temperatures by lithium. The solidus temperature in the system LiAlSiO₄–NaAlSi₃O₈–SiO₂–H₂O is lowered to 640°C at 200 MPa (Stewart, 1978), and with addition of Li₂B₄O₇ it further decreases to 500°C at 200 MPa (London, 1986). These depressions are 100 and 240°C relative to the NaAlSi₃O₈–SiO₂–H₂O ternary at the same pressure (Tuttle & Bowen, 1958). Similar solidus depressions occur in the feldspar-free but fluorine-bearing systems. In the quartz–trilithionite pseudobinary join, Munoz (1971) determined a solidus temperature of 600°C at 200 MPa and fluid saturation. These observations suggest that lithium, unlike calcium, significantly suppresses the crystallization temperatures in lithium-rich granitic and pegmatitic melts and that the occurrence of Li–F micas does not prevent high enrichment in fluorine in residual melts (Munoz, 1971).

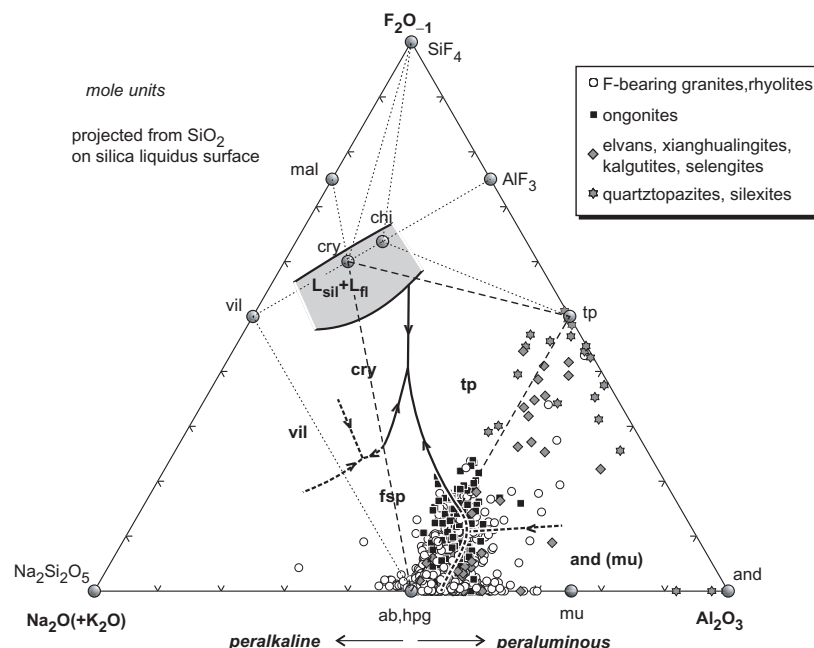


Fig. 11. Liquidus projection of the $(\text{Na}_2\text{O} + \text{K}_2\text{O})\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-F}_2\text{O}_{-1}$ from the SiO_2 apex onto the silica saturation surface; the Jänecke projection (Jänecke, 1906). The boundary curves and the liquid miscibility gap are from this study; the position of the haplogranite–aluminosilicate eutectic is based on Joyce & Voigt (1994). Sources of whole-rock data are listed in the Electronic Appendix of Dolejš & Baker (2004).

H₂O solubility and fluid saturation

Depolymerization of silicate melt by fluorine appears to promote water solubility (Holtz *et al.*, 1993; Webster & Rebbert, 1998). In contrast to the results of Dingwell (1985) and Webster (1990), who documented a decrease or minimal change of the H_2O solubility up to 8 wt % F, numerous other studies reported positive correlation between the fluorine content and the H_2O solubility in the melt. For example, Holtz *et al.* (1993) found that at 200 MPa addition of 4.5 wt % F to synthetic granitic melts increases H_2O solubility by 2.2 wt %. Similarly, Webster & Rebbert (1998) found that addition of 1.1 wt % F to a natural rhyolite increases water content by 0.9 wt %. These increases and the presence of melt inclusions in topaz-bearing granites that contain up to 10 wt % H_2O (Thomas & Klemm, 1997) are consistent with our experimental results.

The knowledge of H_2O solubility in silicate melts is critical for interpreting the timing of fluid saturation. An increase in H_2O solubility allows extensive magmatic fractionation, and suppresses saturation with aqueous fluid phase and dispersal of economically important elements. As a consequence, residual magmas attain high fluorine and H_2O concentrations and exhibit significant enrichments in lithophile elements (Li, Rb, Cs, Sn, Nb, Ta; Cuney *et al.*, 1992; Webster *et al.*, 1997, 2004). This enrichment is observed in topaz rhyolites and ongonites (Štemprok, 1991; Dergachev, 1992) but quartz

topazites are remarkably depleted in alkalis (<1 wt % $\text{Na}_2\text{O} + \text{K}_2\text{O}$), lithophile elements and ore metals (Kortemeir & Burt, 1988; Johnston & Chappell, 1992). This suggests that saturation in aqueous fluid and sequestration of incompatible elements occurs at the ongonite–topazite transition (see also Birch, 1984; Kortemeir & Burt, 1988; Johnston & Chappell, 1992).

Hydrothermal fluids in fluorosilicate systems

With increasing fluorine concentration in the melt, the coexisting aqueous fluid becomes rich in aluminosilicate solutes (Dingwell, 1985; Webster, 1990). The presence of SiO_2 -rich melt or gel inclusions in quartz topazites and greisens (Eadington & Nashar, 1978; Williamson *et al.*, 1997, 2002) is in agreement with very high solubility of quartz in fluorine-bearing aqueous fluids (Dolejš, 2006). Consequently, the solvus between hydrous fluorosilicate melts and solute-rich aqueous fluids contracts with increasing fluorine concentrations. Although a continuous magmatic–hydrothermal transition has been advocated by previous researchers (e.g. London, 1986), we found that fluorine-rich haplogranitic melts had a finite water content under the conditions we studied.

We can draw several important conclusions about fluid–melt partitioning at high fluorine concentrations from phase-diagram topology. Figure 12 is a schematic quaternary projection with the end-members aluminosilicates

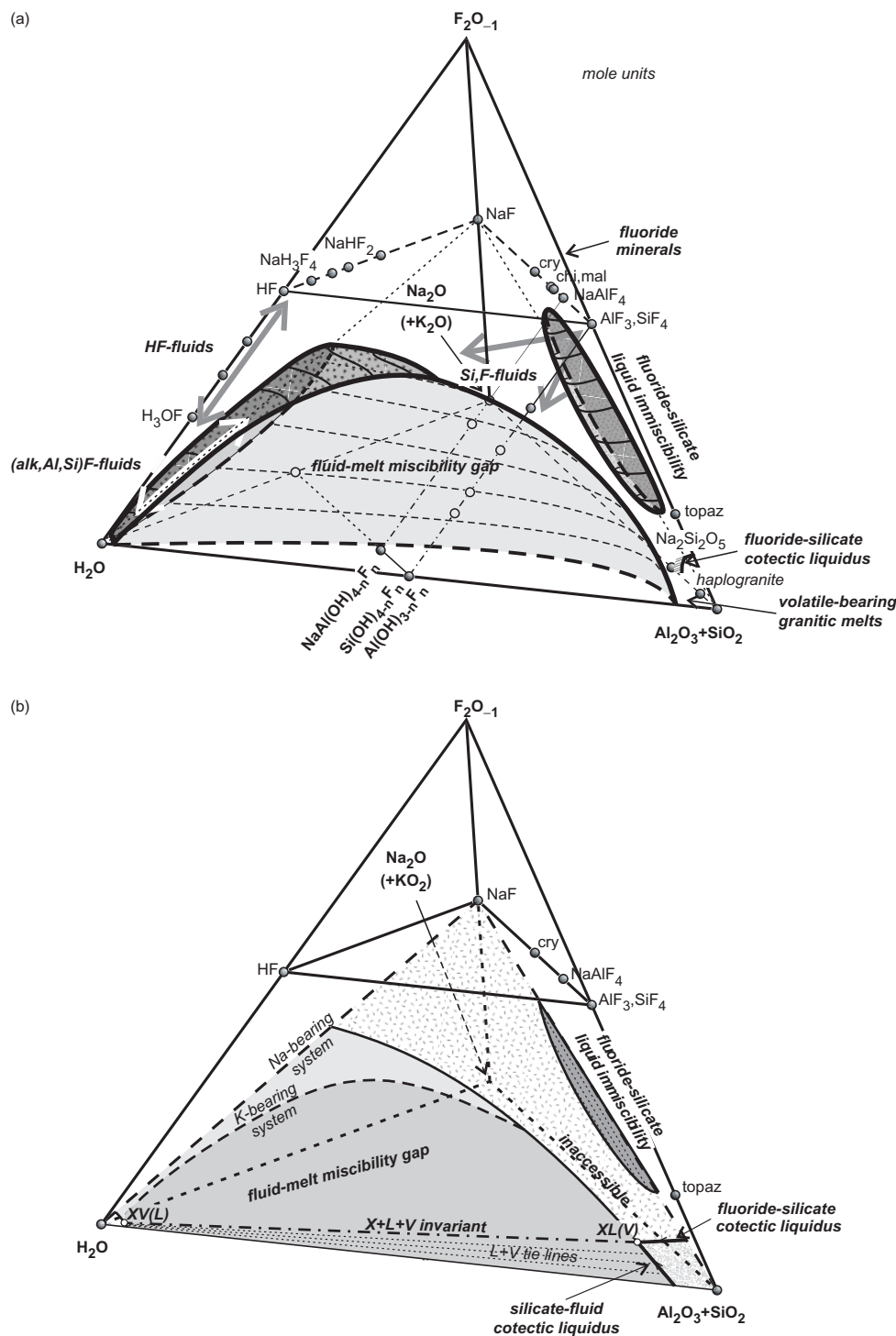


Fig. 12. Topology of the liquid-fluid and the fluoride-silicate liquid-liquid miscibility gaps in the system $(\text{Na}_2\text{O} + \text{K}_2\text{O})-(\text{Al}_2\text{O}_3 + \text{SiO}_2)-\text{H}_2\text{O}-\text{F}_2\text{O}_{-1}$ (mole units). (a) Three-dimensional projection with locations of stable compounds and aqueous complexes. Arrows indicate compositions of various types of fluids. The liquid-fluid miscibility gap originates at the haplogranite- H_2O join (front edge) and closes by the critical curve, which connects hydrous fluoride liquids (left face) and $\text{HF}-\text{SiF}_4$ vapors (front face). The silicate-fluoride cotectic surfaces schematically illustrate buffering effects on the fluorine concentrations in the melt and the composition of the coexisting fluid phase (see text for detailed discussion). (b) Section through the aluminosilicate- H_2O -(Na,K)F ternary. Additional data sources: haplogranite- H_2O , Luth & Tuttle (1969); albite- $\text{Na}_2\text{Si}_2\text{O}_5-\text{H}_2\text{O}$, Mustart (1972); $\text{NaF}-\text{H}_2\text{O}$, Ravich & Valyashko (1965); $\text{KF}-\text{H}_2\text{O}$, Urusova & Ravich (1966); $\text{HF}-\text{H}_2\text{O}$, Mootz *et al.* (1981); $\text{NaF}-\text{HF}$, Adamczak *et al.* (1959); $\text{KF}-\text{HF}$, Cady (1934); fluoride-silicate liquid-liquid immiscibility, Rutlin (1998); aqueous complexes, Tagirov & Schott (2001) and Tagirov *et al.* (2002).

($\text{Al}_2\text{O}_3 + \text{SiO}_2$), alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$), fluorine (F_2O_{-1}) and water (H_2O). Phase relations in the tetrahedron define the geometry and tie-line orientation of the liquid (melt)–vapor (fluid) solvus.

The front edge of the tetrahedron is the silicate– H_2O binary showing immiscibility between hydrous silicate melt (~ 4.2 wt % H_2O at 100 MPa; Burnham, 1997; Holtz *et al.*, 2001) and an aqueous vapor with very small fraction of aluminosilicate solutes (Eugster & Baumgartner, 1987; Paillat *et al.*, 1992). The miscibility gap between hydrous silicate melts and aqueous fluid shrinks as it propagates into the tetrahedron interior. In peralkaline systems, which plot at the tetrahedron base, the solubility of H_2O in the melt increases (Dingwell *et al.*, 1997) and alkali silicates are extensively soluble in the aqueous fluids (Luth & Tuttle, 1969). Complete miscibility between peralkaline silicate melts and aqueous fluids occurs at low pressures (Mustart, 1972); that is, the liquid–vapor solvus closes in the tetrahedron base. In systems containing fluorine, which plot on the front face of the tetrahedron, solubility of aluminosilicates in aqueous fluid increases as a result of the formation of aluminosilicofluoride complexes (Dingwell, 1985; Haselton *et al.*, 1988; Aksyuk & Zhukovskaya, 1998; Tagirov *et al.*, 2002). HF and SiF_4 , which plot in the central portion of the tetrahedron front face, are low-density fluids at high temperatures (Franck & Spalhoff, 1957; Devyatykh *et al.*, 1999) and form supercritical mixtures with H_2O . Therefore, the liquid–vapor gap in the front face has to close before reaching the H_2O –HF– SiF_4 tie-lines. An additional constraint on the extent of melt–fluid immiscibility arises from the phase equilibria along the alkali fluoride– H_2O binary. This join is represented by a line from the left front apex to the centre of the back edge (NaF). If the relationship between alkali fluoride and H_2O is supercritical, the melt–fluid gap must completely close within the tetrahedron body. On the other hand, if the alkali fluoride– H_2O join is subcritical, there is no continuous miscibility between hydrous fluorosilicate melts and aqueous fluids and the liquid–vapor solvus remains open. The NaF– H_2O system exhibits subcritical behavior at less than 400 MPa (Ravich & Valyashko, 1965; Koster van Groos & Wyllie, 1968; Kotelnikova & Kotelnikov, 2002), whereas the KF– H_2O system exhibits a continuous transition from molten salt to aqueous vapor with a maximum vapor pressure of 190 MPa (Urusova & Ravich, 1966). This observation implies that the supercritical transition from hydrous fluorosilicate melts to solute-rich aqueous fluids may occur in potassium-rich systems only.

We illustrate petrological applications of these features by projecting the melt–fluid miscibility gap on the silicate–(Na,K)F– H_2O plane (Fig. 12b). During magmatic differentiation volatile-bearing magmas will evolve from

the lower right apex along the silicate liquidus and eventually reach cotectic with a fluoride solid phase (for example, topaz or cryolite) or will exsolve aqueous fluid. The liquid line of descent depends on the initial F/ H_2O ratio in the melt. When the melt is fluid-saturated, the composition of the coexisting aqueous vapor is determined by L+V tie-lines between the vapor-saturated silicate liquidus and L+X-present vapors (Fig. 12b). On the vapor side, tie-lines project close to the H_2O apex, implying that the fluorine-bearing fluids are not acidic HF-rich or SiF_4 -dominated solutions, but rather contain alkali–aluminumfluoride and silicofluoride complexes. Because the stoichiometry of the predominant aqueous complexes differs from bulk composition of the melt, one can expect moderate departures from congruent partitioning of elements between melt and fluid. This is in agreement with results of previous fluid–melt partitioning and solubility studies (Dingwell, 1985; Haselton *et al.*, 1988; Tagirov *et al.*, 2002).

All crystallization paths converge to the vapor-saturated eutectic with silicate and fluorine-bearing minerals. This invariant point is labeled X+L (V) in Fig. 12b. The composition of the aqueous fluid coexisting with the eutectic hydrous fluorosilicate melts is located at the invariant point on the vapor surface labeled as X+V (L). The continuous transition from volatile-rich silicate melts to solute-rich fluids is expected to appear only at high alkali, high K/Na and/or fluorine concentrations. In natural conditions, formation of residual melts extremely rich in alkalis and fluorine will be inhibited by crystallization of fluoride minerals (topaz, cryolite and villiamite) and in these systems the continuous melt–fluid transition is unlikely to occur.

ACKNOWLEDGEMENTS

Both parts of this study represent a portion of the first author's Ph.D. thesis at McGill University, supported by the J. B. Lynch and Carl Reinhardt McGill Major fellowships. We gratefully acknowledge discussions with Miroslav Štemprok, John Longhi, Don Burt and Mark Barton. The Theriak-Domino software by Christian de Capitani (University of Basel) was helpful in verifying phase-diagram topologies and mineral–melt thermodynamics. Research costs were covered by the Natural Sciences and Engineering Research Council grants to D.R.B. and by the Geological Society of America and the Society of Economic Geologists student grants to D. D. Bob Loeffler provided topaz crystals from the Topaz Mountain, Utah. Critical reviews by Hanna Nekvasil, Bruno Scaillet, Ilya Veksler, Don Burt and Ron Frost helped to improve the manuscript and are gratefully acknowledged.

REFERENCES

- Adamczak, R. L., Mattern, J. A. & Tieckelmann, H. (1959). A partial phase study of the system NaF–HF. *Journal of Physical Chemistry* **63**, 2063–2065.
- Aksyuk, A. M. & Zhukovskaya, T. N. (1998). The solubility of quartz in aqueous solutions of hydrofluoric acid at temperatures 500–1000°C and pressures of 100–500 MPa. *Doklady Earth Sciences* **361**, 745–748.
- Baker, D. R. & Bossanyi, H. (1994). The combined effect of F and H₂O on interdiffusion between peralkaline dacitic and rhyolitic melts. *Contributions to Mineralogy and Petrology* **117**, 203–214.
- Baker, D. R. & Vaillancourt, J. (1995). The low viscosities of F + H₂O-bearing granitic melts and implications for melt extraction and transport. *Earth and Planetary Science Letters* **132**, 199–211.
- Barton, M. D. (1996). Granitic magmatism and metallogeny of southwestern North America. In: Brown, M., Candela, P. A., Peck, D. L., et al. (eds) *The third Hutton symposium on the Origin of granites and related rocks. Geological Society of America, Special Paper* **315**, 261–280.
- Barton, M. D., Ilchik, R. P. & Marikos, M. A. (1991). Metasomatism. In: Kerrick, D. M. (ed.) *Contact Metamorphism. Mineralogical Society of America, Reviews in Mineralogy* **26**, 321–350.
- Birch, W. D. (1984). Quartz–topaz–loellingite rocks near Eldorado, Victoria. *Australian Journal of Earth Sciences* **31**, 269–278.
- Burnham, C. W. (1975). Water and magmas; a mixing model. *Geochimica et Cosmochimica Acta* **39**, 1077–1084.
- Burnham, C. W. (1997). Magmas and hydrothermal fluids. In: Barnes, H. L. (ed.) *Geochemistry of Hydrothermal Ore Deposits*. Wiley, New York: John Wiley, pp. 63–123.
- Burt, D. M. & London, D. (1982). Subsolidus equilibria. In: Černý, P. (ed.) *Granitic Pegmatites in Science and Industry. Mineralogical Association of Canada, Short Courses* **8**, 329–346.
- Cady, G. H. (1934). Freezing points and vapor pressures of the system potassium fluoride–hydrogen fluoride. *Journal of the American Chemical Society* **56**, 1431–1434.
- Candela, P. A. & Holland, H. D. (1984). The partitioning of copper and molybdenum between silicate melts and aqueous fluids. *Geochimica et Cosmochimica Acta* **48**, 373–380.
- Carroll, M. R. & Webster, J. D. (1994). Solubilities of sulfur, noble gases, nitrogen, chlorine, and fluorine in magmas. In: Carroll, M. R. & Holloway, J. R. (eds) *Volatiles in Magmas. Mineralogical Society of America, Reviews in Mineralogy* **30**, 231–279.
- Černý, P. (1998). Magmatic vs. metamorphic derivations of rare-element granitic pegmatites. *Krystalinikum* **24**, 7–36.
- Černý, P., Masau, M., Goad, B. E. & Ferreira, K. (2005). The Greer lake leucogranite, Manitoba, and the origin of lepidolite-subtype granitic pegmatites. *Lithos* **80**, 305–321.
- Charoy, B. & Noronha, F. (1996). Multistage growth of a rare-element, volatile-rich microgranite at Argemela (Portugal). *Journal of Petrology* **37**, 73–94.
- Cuncy, M., Marignac, C. & Weisbrod, A. (1992). The Beauvoir topaz–lepidolite albite granite (Massif Central, France): the disseminated magmatic Sn–Li–Ta–Nb–Be mineralization. *Economic Geology* **87**, 1766–1794.
- Dergachev, V. B. (1992). Geochemical types of ongonites. *Geochemistry International* **29**, 37–47.
- Devatykh, G. G., Pryakhin, D. A., Bulanov, A. D. & Balabanov, V. V. (1999). Phase diagram of silicon tetrafluoride. *Doklady Chemistry* **364**, 4–5.
- Dingwell, D. B. (1985). The structure and properties of fluorine-rich silicate melts: implications for granite petrogenesis. In: Taylor, R. P. & Strong, D. F. (eds) *Granite-Related Mineral Deposits: Geology, Petrogenesis and Tectonic Setting*. Halifax, N.S.: Canadian Institute of Mining, Metallurgy and Petroleum, pp. 72–81.
- Dingwell, D. B., Scarfe, C. M. & Cronin, D. J. (1985). The effect of fluorine on viscosities of melts in the system Na₂O–Al₂O₃–SiO₂: implications for phonolites, trachytes and rhyolites. *American Mineralogist* **70**, 80–87.
- Dingwell, D. B., Knoche, R. & Webb, S. L. (1993). The effect of F on the density of haplogranite melt. *American Mineralogist* **78**, 325–330.
- Dingwell, D. B., Holtz, F. & Behrens, H. (1997). The solubility of H₂O in peralkaline and peraluminous granitic melts. *American Mineralogist* **82**, 434–437.
- Dolejš, D. (2006). Quartz solubility in fluorine-bearing aqueous fluids. *Annual Report, Bayerisches Forschungsinstitut für experimentelle Geochemie und Geophysik, Universität Bayreuth* 2005, 84–86.
- Dolejš, D. & Baker, D. R. (2004). Thermodynamic analysis of the system Na₂O–K₂O–CaO–Al₂O₃–SiO₂–H₂O–F₂O_{–1}: stability of fluorine-bearing minerals in felsic igneous suites. *Contributions to Mineralogy and Petrology* **146**, 762–778.
- Dolejš, D. & Baker, D. R. (2006). Fluorite solubility in hydrous haplogranitic melts at 100 MPa. *Chemical Geology* **225**, 40–60.
- Dolejš, D. & Baker, D. R. (2007). Liquidus equilibria in the system K₂O–Na₂O–Al₂O₃–SiO₂–F₂O_{–1}–H₂O to 100 MPa: I. Silicate–fluoride liquid immiscibility in anhydrous systems. *Journal of Petrology* **48**, 785–806.
- Duffy, J. A. (1989). A common optical basicity scale for oxide and fluoride glasses. *Journal of Non-Crystalline Solids* **109**, 35–39.
- Eadington, P. J. & Nashar, B. (1978). Evidence for the magmatic origin of quartz–topaz rocks from the New England batholith, Australia. *Contributions to Mineralogy and Petrology* **67**, 433–438.
- Eugster, H. P. & Baumgartner, L. (1987). Mineral solubilities and speciation in supercritical metamorphic fluids. In: Carmichael, I. S. E. & Eugster, H. P. (eds) *Thermodynamic Modeling of Geological Materials: Minerals, Fluids and Melts. Mineralogical Society of America, Reviews in Mineralogy* **17**, 367–404.
- Forster, H.-J., Tischendorf, G., Trumbull, R. B. & Gottesmann, B. (1999). Late-collisional granites in the Variscan Erzgebirge, Germany. *Journal of Petrology* **40**, 1613–1645.
- Franck, E. U. & Spalthoff, W. (1957). Hydrogen fluoride. I. Specific heat, vapor pressure, and density up to 300° and 300 atmospheres. *Zeitschrift für Elektrochemie* **61**, 348–357.
- Frank, M. R., Candela, P. A. & Piccoli, P. M. (2003). Alkali exchange equilibria between a silicate melt and coexisting magmatic volatile phase: an experimental study at 800°C and 100 MPa. *Geochimica et Cosmochimica Acta* **67**, 1415–1427.
- Giordano, D., Romano, C., Dingwell, D. B., Poe, B. & Behrens, H. (2004). The combined effects of water and fluorine on the viscosity of silicic magmas. *Geochimica et Cosmochimica Acta* **68**, 5159–5168.
- Greig, J. W., Jensen, E. & Merwin, H. E. (1955). The system Cu–Fe–S. *Carnegie Institution of Washington Yearbook* **54**, 129–134.
- Haselton, H. T., Jr, Cygan, G. L. & d'Angelo, W. M. (1988). Chemistry of aqueous solutions coexisting with fluoride buffers in the system K₂O–Al₂O₃–SiO₂–H₂O–F₂O_{–1} (1 kbar, 400°–700°C). *Economic Geology* **83**, 163–173.
- Hervig, R. L., Kortemeier, W. T. & Burt, D. M. (1987). Ion-microprobe analyses of Li and B in topaz from different environments. *American Mineralogist* **72**, 392–396.
- Hogan, J. P. & Gilbert, M. C. (1995). The A-type Mount Scott granite sheet: importance of crustal magma traps. *Journal of Geophysical Research* **100**, 15779–15792.
- Holtz, F., Johannes, W. & Pichavant, M. (1992). Effect of excess aluminium on phase relations in the system Qz–Ab–Or: experimental

- investigation at 2 kbar and reduced H_2O -activity. *European Journal of Mineralogy* **4**, 137–152.
- Holtz, F., Dingwell, D. B. & Behrens, H. (1993). Effects of F, B_2O_3 and P_2O_5 on the solubility of water in haplogranite melts compared to natural silicate melts. *Contributions to Mineralogy and Petrology* **113**, 492–501.
- Holtz, F., Johannes, W., Tamic, N. & Behrens, H. (2001). Maximum and minimum water contents of granitic melts generated in the crust: a reevaluation and implications. *Lithos* **56**, 1–14.
- Icenhower, J. P. & London, D. (1995). An experimental study of element partitioning among biotite, muscovite, and coexisting peraluminous silicic melt at 200 MPa (H_2O). *American Mineralogist* **80**, 1229–1251.
- Jänecke, E. (1906). Über eine neue Darstellungsform der wässerigen Lösungen zweier und dreier gleichioniger Salze, reziproker Salzpaare und der van't Hoff'schen Untersuchungen über ozeanische Salzablagerungen. *Zeitschrift für Anorganische Chemie* **51**, 132–157.
- Johnston, C. & Chappell, B. W. (1992). Topaz-bearing rocks from Mount Gibson, North Queensland, Australia. *American Mineralogist* **77**, 303–313.
- Joyce, D. B. & Voigt, D. E. (1994). A phase equilibrium study in the system $\text{KAlSi}_3\text{O}_8\text{--NaAlSi}_3\text{O}_8\text{--SiO}_2\text{--Al}_2\text{SiO}_5\text{--H}_2\text{O}$ and petrogenetic implications. *American Mineralogist* **79**, 504–512.
- Kennedy, G. C., Wasserburg, G. J., Heard, H. C. & Newton, R. C. (1962). The upper three-phase region in the system $\text{SiO}_2\text{--H}_2\text{O}$. *American Journal of Science* **260**, 501–521.
- Kleeman, J. D. (1985). Origin of disseminated wolframite-bearing quartz–topaz rock at Torrington, New South Wales, Australia. *High-Heat Production (HHP) Granites, Hydrothermal Circulation and Ore Genesis*. London: Institution of Mining and Metallurgy, pp. 197–201.
- Knoche, R., Dingwell, D. B. & Webb, S. L. (1995). Melt densities for leucogranites and granitic pegmatites: partial molar volumes for SiO_2 , Al_2O_3 , Na_2O , K_2O , Li_2O , Rb_2O , Cs_2O , MgO , CaO , SrO , BaO , B_2O_3 , P_2O_5 , $\text{F}_2\text{O}_{0.5}$, TiO_2 , Nb_2O_5 , Ta_2O_5 , and WO_3 . *Geochimica et Cosmochimica Acta* **59**, 4645–4652.
- Kogarko, L. N. & Krigman, L. D. (1981). *Fluorine in Silicate Melts and Magmas*. Moscow: Nauka, 124 pp. (in Russian).
- Kortemeier, W. T. & Burt, D. M. (1988). Ongonite and topazite dikes in the flying W ranch area, Tonto basin, Arizona. *American Mineralogist* **73**, 507–523.
- Korzinskiy, D. S. (1959). Acid–base interaction of the components in silicate melts and the direction of cotectic lines. *Doklady Akademii Nauk SSSR, Earth Science Sections* **128**, 821–823.
- Korzinskiy, D. S. (1960). Acidity–alkalinity in magmatic processes. *International Geological Congress, Report of the 21st session*, Copenhagen, pp. 160–170.
- Koster van Groos, A. F. & Wylle, P. J. (1968). Melting relationships in the system $\text{NaAlSi}_3\text{O}_8\text{--NaF--H}_2\text{O}$ to 4 kilobars pressure. *Journal of Geology* **76**, 50–70.
- Kotelnikova, Z. A. & Kotelnikov, A. R. (2002). Synthetic NaF-bearing fluid inclusions. *Geochemistry International* **40**, 594–600.
- Kovalenko, V. I. & Kovalenko, N. I. (1976). *Ongonites: Subvolcanic Analogues of Rare-Metal Li–F Granites*. Moscow: Nauka, 127 pp. (in Russian).
- London, D. (1986). Magmatic–hydrothermal transition in the Tanco rare-element pegmatite: evidence from fluid inclusions and phase-equilibrium experiments. *American Mineralogist* **71**, 376–395.
- London, D. (1987). Internal differentiation of rare-element pegmatites: effects of boron, phosphorus, and fluorine. *Geochimica et Cosmochimica Acta* **51**, 403–420.
- London, D. (1997). Estimating abundances of volatile and other mobile components in evolved silicic melts through mineral–melt equilibria. *Journal of Petrology* **38**, 1691–1706.
- London, D., Morgan, G. B., VI & Wolf, M. B. (2001). Amblygonite–montebasite solid solutions as monitors of fluorine in evolved granitic and pegmatitic melts. *American Mineralogist* **86**, 225–233.
- Luth, W. C. & Tuttle, O. F. (1969). The hydrous vapor phase in equilibrium with granite and granite magmas. In: *Igneous and metamorphic geology - A volume in honor of Arie Poldervaart*. Geological Society of America, Memoir **115**, 513–548.
- Manning, D. A. C. (1981). The effect of fluorine on liquidus phase relationships in the system Qz--Ab--Or with excess water at 1 kb. *Contributions to Mineralogy and Petrology* **76**, 206–215.
- Manning, D. A. C., Hamilton, D. L., Henderson, C. M. B. & Dempsey, M. J. (1980). The probable occurrence of interstitial Al in hydrous, F-bearing and F-free aluminosilicate melts. *Contributions to Mineralogy and Petrology* **75**, 257–262.
- Marshall, A. S., Hinton, R. W. & Macdonald, R. (1998). Phenocrystic fluorite in peralkaline rhyolites, Olkaria, Kenya Rift Valley. *Mineralogical Magazine* **62**, 477–486.
- Mootz, D., Ohms, U. & Poll, W. (1981). Schmelzdiagramm $\text{H}_2\text{O--HF}$ und Strukturen der 1:1- und einer 1:2-Phase. *Zeitschrift für Anorganische und Allgemeine Chemie* **479**, 75–83.
- Munoz, J. L. (1971). Hydrothermal stability relations of synthetic lepidolite. *American Mineralogist* **56**, 2069–2087.
- Mustart, D. A. (1972). Phase relations in the peralkaline portion of the system $\text{Na}_2\text{O--Al}_2\text{O}_3\text{--SiO}_2\text{--H}_2\text{O}$. Ph.D. thesis, Stanford University, 187 pp.
- Mysen, B. O., Cody, G. D. & Smith, A. (2004). Solubility mechanisms of fluorine in peralkaline and meta-aluminous silicate glasses and in melts to magmatic temperatures. *Geochimica et Cosmochimica Acta* **68**, 2745–2769.
- Oglesby, J. V. & Stebbins, J. F. (2000). ^{29}Si CPMAS NMR investigations of silanol-group minerals and hydrous aluminosilicate glasses. *American Mineralogist* **85**, 722–731.
- Ostrovsky, I. A. (1966). $P\text{--}T$ diagram of the system $\text{SiO}_2\text{--H}_2\text{O}$. *Geological Journal* **5**, 127–134.
- Paillat, O., Elphick, S. C. & Brown, W. L. (1992). The solubility of water in $\text{NaAlSi}_3\text{O}_8$ melts: a re-examination of $\text{Ab--H}_2\text{O}$ phase relationships and critical behavior at high pressures. *Contributions to Mineralogy and Petrology* **112**, 490–500.
- Pichavant, M., Boher, M., Stenger, J.-F., Aïssa, M. & Charoy, B. (1987). Relations de phase des granites de Beauvoir à 1 et 3 kbar en conditions de saturation en H_2O . *Géologie de la France* **2–3**, 77–86.
- Price, J. D., Hogan, J. P., Gilbert, M. C., London, D. & Morgan, G. B., VI (1999). Experimental study of titanite–fluorite equilibria in the A-type Mount Scott granite: implications for assessing F contents of felsic magma. *Geology* **27**, 951–954.
- Ravich, M. I. & Vályashko, V. M. (1965). Solubility of sodium fluoride at elevated temperatures. *Russian Journal of Inorganic Chemistry* **10**, 107–109.
- Rutlin, J. L. (1998). Chemical reactions and mineral formation during sodium aluminium fluoride attack on aluminosilicate and anorthite based refractories. Dr-Ing. thesis, Norwegian University of Science and Technology, Trondheim, 167 pp.
- Scailliet, B. & Macdonald, R. (2004). Fluorite stability in silicic magmas. *Contributions to Mineralogy and Petrology* **147**, 319–329.
- Schaller, T., Dingwell, D. B., Keppler, H., Knoeller, W., Merwin, L. & Sebal, A. (1992). Fluorine in silicate glasses: a multinuclear nuclear magnetic resonance study. *Geochimica et Cosmochimica Acta* **56**, 701–707.

- Schmidt, B. C., Riemer, T., Kohn, S. C., Behrens, H. & Dupree, R. (2000). Different water solubility mechanisms in hydrous glasses along the Qz–Ab join: evidence from NMR spectroscopy. *Geochimica et Cosmochimica Acta* **64**, 513–526.
- Shand, S. J. (1927). *Eruptive Rocks: Their Genesis, Composition, Classification, and Their Relation to Ore-Deposits, with a Chapter on Meteorites*. Wiley: New York, 360 pp.
- Shannon, R. D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica* **A32**, 751–767.
- Stalder, R., Ulmer, P., Thompson, A. B. & Günther, D. (2000). Experimental approach to constrain second critical end-points in fluid silicate systems: near-solidus fluids and melts in the system albite–H₂O. *American Mineralogist* **85**, 68–77.
- Štemprok, M. (1991). Ongonite from Ongon Khairkhan, Mongolia. *Mineralogy and Petrology* **43**, 255–273.
- Stewart, D. B. (1978). Petrogenesis of lithium-rich pegmatites. *American Mineralogist* **63**, 970–980.
- Stilling, A. B. (1998). Bulk composition of the Tanco pegmatite at Bernic Lake, Manitoba, Canada. M.Sc. thesis, University of Manitoba, Winnipeg, 76 pp.
- Tagirov, B. & Schott, J. (2001). Aluminum speciation in crustal fluids revisited. *Geochimica et Cosmochimica Acta* **65**, 3965–3992.
- Tagirov, B., Schott, J., Harrichourry, J.-C. & Salvi, S. (2002). Experimental study of aluminum speciation in fluoride-rich supercritical fluids. *Geochimica et Cosmochimica Acta* **66**, 2013–2024.
- Thomas, R. & Klemm, W. (1997). Microthermometric study of silicate melt inclusions in Variscan granites from SE Germany: volatile contents and entrapment conditions. *Journal of Petrology* **38**, 1753–1765.
- Thomas, R., Förster, H.-J., Rickers, K. & Webster, J. D. (2005). Formation of extremely F-rich hydrous melt fractions and hydrothermal fluids during differentiation of highly evolved tin–granite magmas: a melt/fluid-inclusion study. *Contributions to Mineralogy and Petrology* **148**, 582–601.
- Tuttle, O. F. & Bowen, N. L. (1958). *Origin of Granite in the Light of Experimental Studies in the System NaAlSi₃O₈–KAlSi₃O₈–SiO₂–H₂O*. Geological Society of America, Memoir **74**, 153 pp.
- Urusova, M. A. & Ravich, M. I. (1966). Phase equilibria in the potassium fluoride–water system at elevated temperatures. *Russian Journal of Inorganic Chemistry* **11**, 353–357.
- Veksler, I. V. (2004). Liquid immiscibility and its role at the magmatic–hydrothermal transition: a summary of experimental studies. *Chemical Geology* **210**, 7–31.
- Veksler, I. V., Dorfman, A. M., Kamenetsky, M., Dulski, P. & Dingwell, D. B. (2005). Partitioning of lanthanides and Y between immiscible silicate and fluoride melts, fluorite and cryolite and the origin of the lanthanide tetrad effect in igneous rocks. *Geochimica et Cosmochimica Acta* **69**, 2847–2860.
- Webster, J. D. (1990). Partitioning of F between H₂O and CO₂ fluids and topaz rhyolite melt. Implications for mineralizing magmatic–hydrothermal fluids in F-rich granitic systems. *Contributions to Mineralogy and Petrology* **104**, 424–438.
- Webster, J. D. & Rebbert, C. R. (1998). Experimental investigation of H₂O and Cl[–] solubilities in F-enriched silicate liquids; implications for volatile saturation of topaz rhyolite magmas. *Contributions to Mineralogy and Petrology* **132**, 198–207.
- Webster, J. D., Holloway, J. R. & Hervig, R. L. (1987). Phase equilibria of a Be, U and F-enriched vitrophyre from Spor Mountain, Utah. *Geochimica et Cosmochimica Acta* **51**, 389–402.
- Webster, J. D., Thomas, R., Rhede, D., Förster, H.-J. & Seltmann, R. (1997). Melt inclusions in quartz from an evolved peraluminous pegmatite: geochemical evidence for strong tin enrichment in fluorine-rich and phosphorus-rich residual liquids. *Geochimica et Cosmochimica Acta* **61**, 2589–2604.
- Webster, J. D., Thomas, R., Förster, H.-J., Seltmann, R. & Tappen, C. (2004). Geochemical evolution of halogen-enriched granite magmas and mineralizing fluids of the Zinnwald tin–tungsten mining district, Erzgebirge, Germany. *Mineralium Deposita* **39**, 452–472.
- Weidner, J. R. & Martin, R. F. (1987). Phase equilibria of a fluorine-rich leucogranite from the St. Austell pluton, Cornwall. *Geochimica et Cosmochimica Acta* **51**, 1591–1597.
- Williams, T. J., Candela, P. A. & Piccoli, P. M. (1997). Hydrogen–alkali exchange between silicate melts and two-phase aqueous mixtures: an experimental investigation. *Contributions to Mineralogy and Petrology* **128**, 114–126.
- Williamson, B. J., Stanley, C. J. & Wilkinson, J. J. (1997). Implications from inclusions in topaz for greisenisation and mineralisation in the hensbarrow topaz granite, Cornwall, England. *Contributions to Mineralogy and Petrology* **127**, 119–128.
- Williamson, B. J., Wilkinson, J. J., Luckham, P. F. & Stanley, C. J. (2002). Formation of coagulated colloidal silica in high-temperature mineralizing fluids. *Mineralogical Magazine* **64**, 547–553.
- Wyllie, P. J. (1979). Magmas and volatile components. *American Mineralogist* **64**, 469–500.
- Wyllie, P. J. & Ryabchikov, I. D. (2000). Volatile components, magmas, and critical fluids in upwelling mantle. *Journal of Petrology* **41**, 1195–1206.
- Wyllie, P. J. & Tuttle, O. F. (1961). Experimental investigation of silicate systems containing two volatile components. Part II. The effects of NH₃ and HF, in addition to H₂O on the melting temperatures of albite and granite. *American Journal of Science* **259**, 128–143.
- Xiong, X.-L., Rao, B., Chen, F.-R., Zhu, J.-C. & Zhao, Z.-H. (2002). Crystallization and melting experiments of a fluorine-rich leucogranite from the Xianghualing Pluton, South China, at 150 MPa and H₂O-saturated conditions. *Journal of the Asian Earth Sciences* **21**, 175–188.
- Zeng, Q. & Stebbins, J. F. (2000). Fluoride sites in aluminosilicate glasses: high-resolution ¹⁹F NMR results. *American Mineralogist* **85**, 863–867.
- Zhu, J.-C. & Liu, W. (1990). Topazite–ongonite relationships and its bearing on vertical zonation in rare-metal granites: evidence from Xianghualing district, Hunan Province, China. In: Maurice, Y. T. (ed) *Proceedings of the Eighth Quadrennial IAGOD Symposium*. Stuttgart: Schweitzerbart, pp. 303–313.