

## THE SILICA UNDER-SATURATED PART OF THE SYSTEM NaAlSiO<sub>4</sub>-KAlSiO<sub>4</sub>-SiO<sub>2</sub> AT 1 ATM. PRELIMINARY DATA ON THE EFFECTS OF FLUORINE.

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In the ongoing efforts to clarify the role of volatiles in magmatic processes, researchers have focused more and more on complex systems and examined not only the effects of H<sub>2</sub>O and CO<sub>2</sub>, which are undoubtedly the most abundant in magmas, but also of "minor" elements like Cl and F. In particular the study of the effects of F has been gradually extended from the field of late-stage granitic systems, where F plays an important role in controlling the distribution of economic metals, to the petrogenesis of mafic and potassic rocks (Dingwell et al., 1985) and to the genesis of carbonatites (Jago, Gittins, 1991). The effects of F on the properties of magmas, while intensively studied, are not fully understood. Previous studies have examined the effect of F in conjunction with H<sub>2</sub>O in silica rich systems (Manning, 1981), investigated systems at high pressure (Foley et al., 1986; Melzer, Foley, 1996) or focused on particular joints (Luth, 1988; Luth, Muncill, 1989), but there are still relevant systems (i.e. melt compositions) in which the effect of F remains poorly defined. In particular the understanding of volcanic processes and modeling of explosive eruptions can certainly benefit from an improved knowledge of the effects of F on magma properties, due to the fact that during magma ascent in volcanic conduits F content increases with differentiation and degassing. In particular melt inclusions analyses reveal that F content in magmas can be quite high (up to 1 %; Belkin et al., 1998). Therefore assessing the effects of fluorine can also improve our understanding of MI behavior during laboratory experiments, a factor of primary importance to increase the significance of melt inclusions data. Among the various

Table 1 – Starting glass compositions

Glass #	Glass Compositions			
	Nepheline	Kalsilite	Silica	F
1	50	15	35	1.5
2	50	19	31	1.5
3	40	40	20	1.5
4	55	20	25	1.5
5	40	30	30	1.5
6	45	20	35	1.5
7	47.5	22.5	30	1.5

magmas that can be found mainly in volcanic districts showing the characteristics of explosive volcanism, silica undersaturated, potassic (i.e. alkaline) magmas form a complex and interesting variety of "leucite-bearing" rocks which occur on all continents (Gupta, Yagi, 1980). Important examples are Southern Spain, China, West Germany, East Africa, Australia, USA and especially Italy, where a worldwide famous volcano (i.e. the Vesuvius) is not only of great interest for researchers, but also a great risk for the population. In order to investigate the role of F in alkaline, silica under-saturated liquids, we selected the system Nepheline-Albite-Orthoclase-Kalsilite (i.e. the phonolitic system [PRS]), the Si-poor part of the Petrogeny's Residua System [PRS] (Bowen, 1935, 1937). The PRS well represents Si-poor alkaline liquids in the late stages of their evolution and is then suitable to study the effects of F in shallow volcanic settings. Moreover the PRS is relatively simple, which potentially minimizes the uncertainty in the interpretation of the results, and the basic phase relations in the system are known under dry conditions and also under different P<sub>H<sub>2</sub>O</sub> (Bowen, 1935, 1937; Schairer, Bowen, 1935; Schairer, 1950; Hamilton, McKenzie, 1965; Morse, 1969). Seven anhydrous glasses (Table 1) were prepared using as starting material Kalsilite (KAlSiO<sub>4</sub>), Nepheline (NaAlSiO<sub>4</sub>) and aluminosilicate (Al<sub>2</sub>Si<sub>6</sub>O<sub>15</sub>) gels. These gels were prepared according to the method described by Hamilton and Henderson (1968), using TEOS (tetraethyl orthosilicate) as source of SiO<sub>2</sub>, pure metal as source of Al, K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> for Na and K. 1.5 % F was added by direct substitution of F for O (i.e. the substitution vector F<sub>2</sub>O<sub>1</sub>) as NaF in exchange for the appropriate amount of NaAlSiO<sub>4</sub> gel and balancing Al and Si with the Al<sub>2</sub>Si<sub>6</sub>O<sub>15</sub> gel. Glass was prepared crushing and mixing appropriate amounts of the starting materials in an agate mortar under acetone, and loading batches of 150, 200 and 250 mg in platinum capsules. After dehydration at 400 °C for ~ 12 hrs, capsules were welded and put in 1 atm furnaces at temperatures from 1250 to 1450 °C for 24 to 144 hrs. Experimental runs (Table 2) were conducted in a 1 atm furnace. The furnace was first brought at run temperature and then the experimental charge (from 30 to 50 mg of crushed glass contained in a welded platinum capsule) was introduced and kept at run temperature for 9 to 30 days. Selected glasses were analyzed with electron microprobe prior to runs, to check homogeneity and composition. Earlier test runs (not listed in Table 2) showed that, when adding F, the crystallization of mineral phases is dramatically hindered. Hence, to foster crystallization we added a 1:1:1 mixture (from 2 to 4 wt. %) of natural sanidine, leucite and nepheline to each charge, to function as seeds. After the experimental runs, all products (glass and mineral phases where possible) were analyzed

Table 2 – Run results

Run	Glass	T °C	Length	After Run
1JW	1	900	9 Days	Glass + Feld <sup>(2)</sup>
	2			Glass + Ne <sup>(2)</sup>
	3			Glass + Leuc <sup>(1)</sup>
	4			Glass + Neph <sup>(1)</sup>
	5			Glass + Leuc <sup>(1)</sup>
	6			Felds + Leuc <sup>(2)</sup>
	7			Glass
2JW	1	1000	30 Days	Glass
	2			Glass
	3			Glass + Leuc <sup>(1)</sup>
	4			Glass + Neph <sup>(2)</sup>
	5			Glass + Leuc <sup>(1)</sup>
	6			Glass
	7			Glass

(1) Crystal abundance suggests that run T was well below the liquidus; (2) Crystal abundance suggests that run T was near the liquidus.

30 to 50 mg of crushed glass contained in a welded platinum capsule) was introduced and kept at run temperature for 9 to 30 days. Selected glasses were analyzed with electron microprobe prior to runs, to check homogeneity and composition. Earlier test runs (not listed in Table 2) showed that, when adding F, the crystallization of mineral phases is dramatically hindered. Hence, to foster crystallization we added a 1:1:1 mixture (from 2 to 4 wt. %) of natural sanidine, leucite and nepheline to each charge, to function as seeds. After the experimental runs, all products (glass and mineral phases where possible) were analyzed



by microprobe. Criteria used to distinguish mineral phases were morphology (feldspars have a lath or needle shape in glass, while nepheline is hexagonal or rectangular) and chemical analysis. These preliminary runs suggest that adding fluorine to the PRS system seems to have two strong effects: 1) a very strong inhibition of crystallization for alkaline feldspars and leucite, which, to the best of our knowledge, seems not to be a problem in the F free system. In earlier test runs, without the use of nucleation seeds, the only phase that was possible to crystallize was nepheline. A possible explanation is that fluorine tends to bond preferentially with potassium (and possibly aluminum); 2) a great depression of liquidus temperature compared to the dry system (Schairer, 1950; Fig. 1). Hence fluorine can potentially affect last stages of magma crystallization in this system. Further experiments are in progress to determine changes in phase relationships and compositions of crystallized minerals and to confirm these results with reversal experiments.

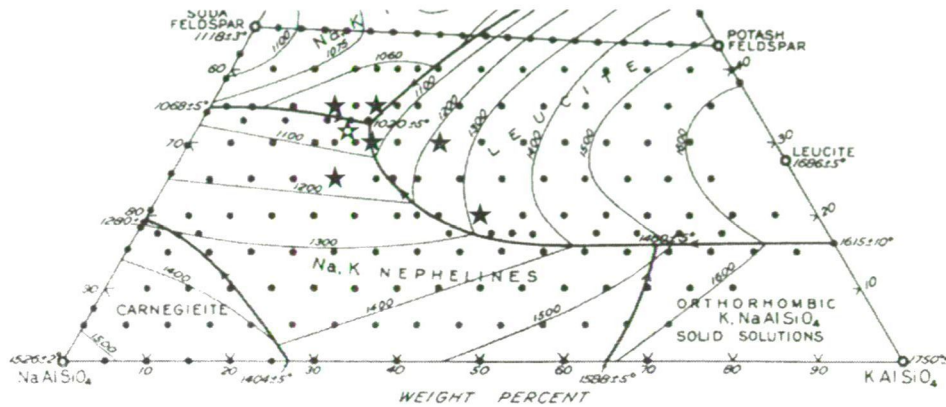


Fig. 1 – PRS system (after Schairer, 1950). Black dots are the original experiments by Schairer, Bowen, 1935. Stars are the compositions used in the present work.

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