Quantifying the effect of fluorine on the viscosity of silica undersaturated melts in the $NaAlSiO_4$-$KAlSiO_4$ system

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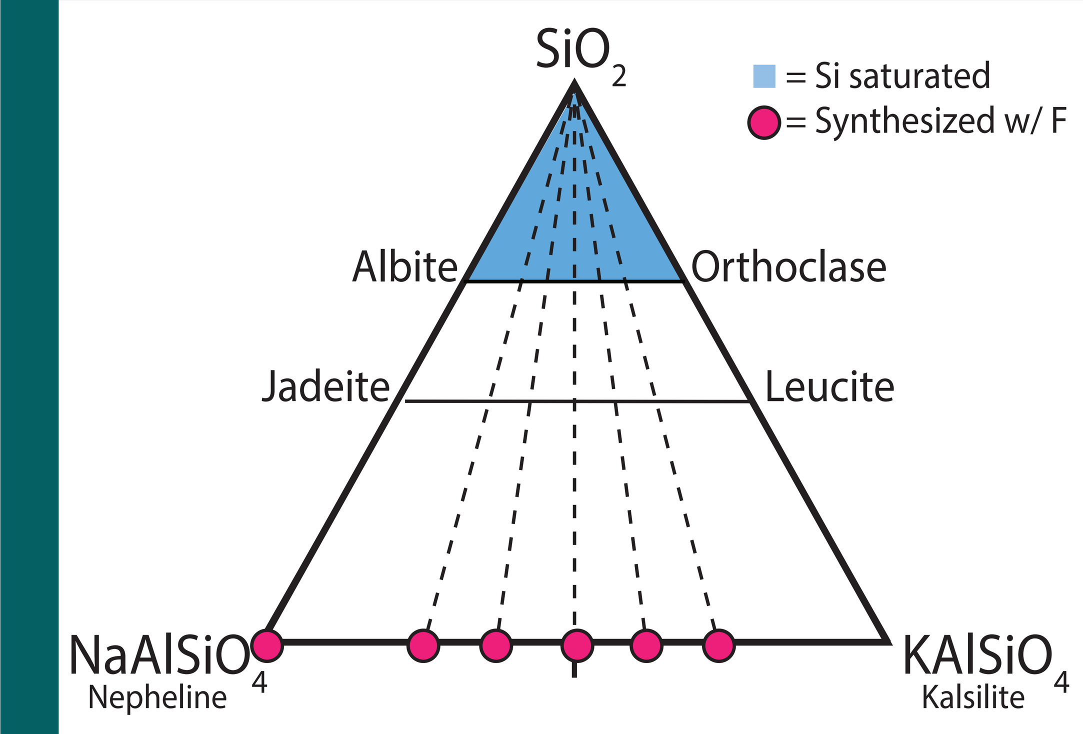
Introduction



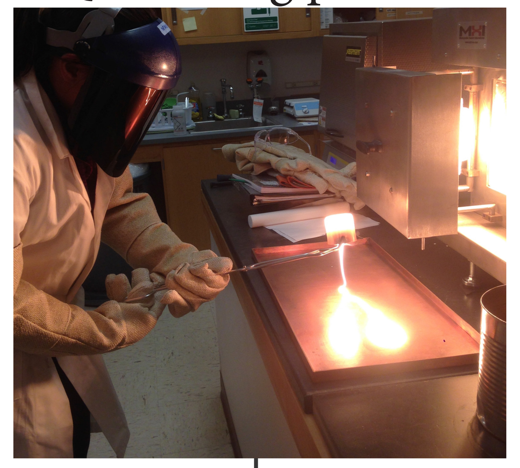
Melt viscosity directly influences the movement of magmas below and above the crust of the Earth. Physical properties like melt viscosity are dependent on the structure of a melt, which is in turn dependent on composition.

In magmatic systems, volatiles such as water, CO_2, and halogens have a large influence on viscosity. Fluorine, even in small amounts, has been shown to reduce the viscosity of most silicate melts (e.g. Dingwell et al. (1985), Dingwell (1987), Webb et al. (2004), Zimova and Webb (2006), Baasner et al. (2013) and others).

We quantify the effect of fluorine as a function of sodium-potassium mixing along the nepheline-kalsilite join. Le Losq and Neuville (2013) have shown that the structures created from this mixing are not random and directly influence viscosity.

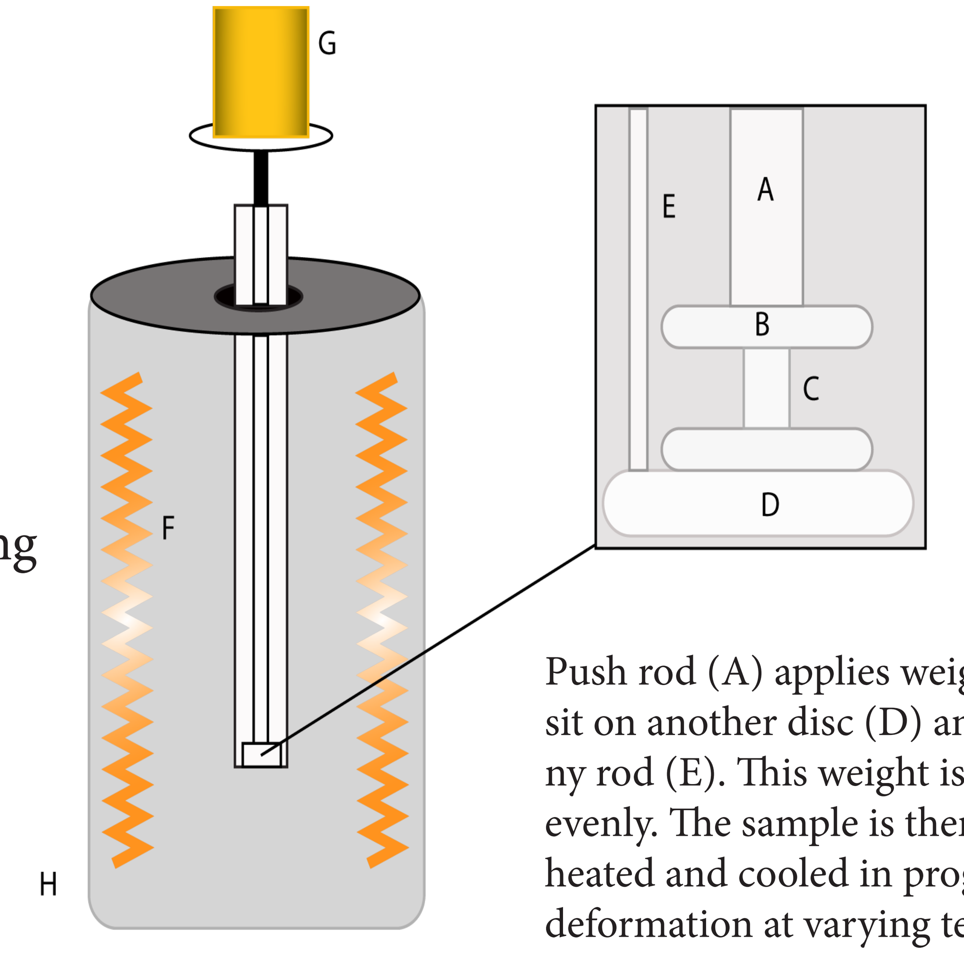
Methods

Quenching process



Sample cores after slab drilling

Parallel-plate viscometry



Viscosity is given by:

$$\left[\eta_s = \frac{mgh^2}{3V\,dh/dt}\right]$$

Where m is mass in kg, g is the force of gravity, h is sample height, $3v$ is volume and dh/dt is the change in height over time.

Push rod (A) applies weight (G) to silica discs (B), which sit on another disc (D) and are held in place using a skinny rod (E). This weight is distributed to the sample core (C) evenly. The sample is then lowered into the furnace and is heated and cooled in programmed steps to test the rate of deformation at varying temperatures.

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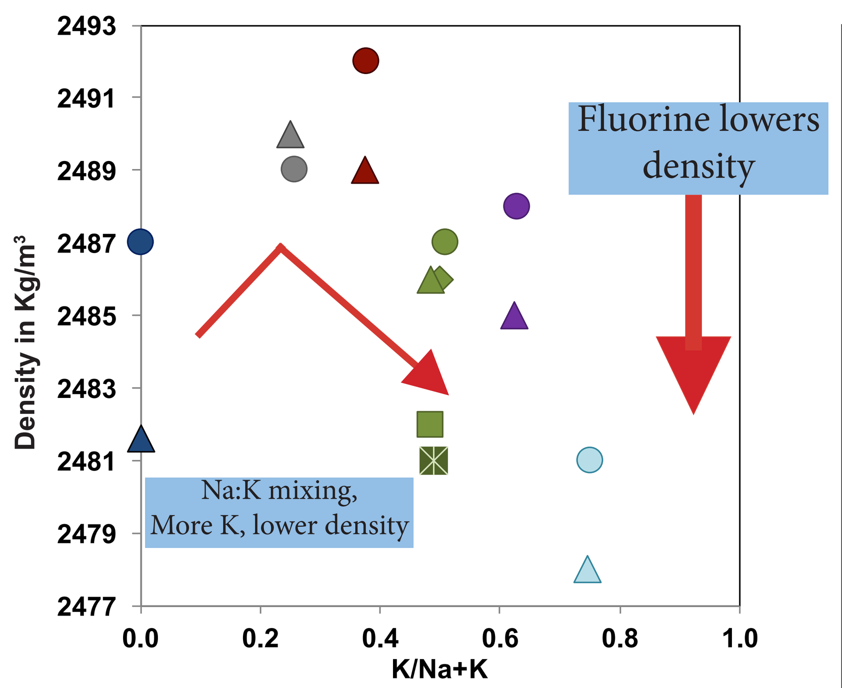
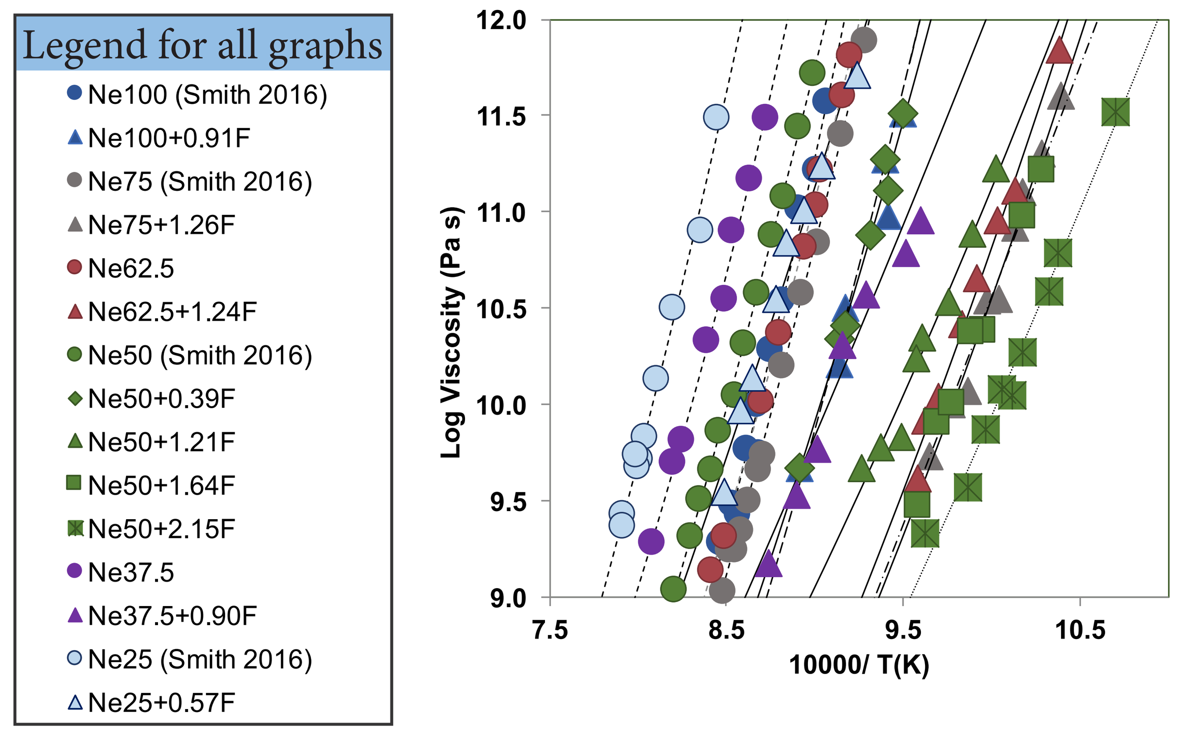
Sample Characterization

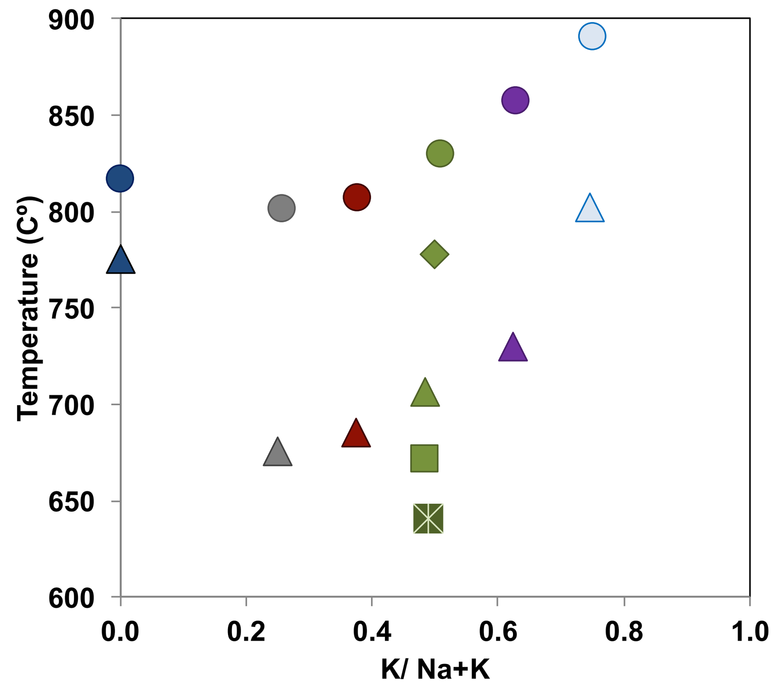


Microprobe composition results in mol.%

Composition	SiO_2	Al_2O_3	Na_2O	K_2O	F	NBO/T
Ne_{100}+0.91F	47.98	25.06	23.55	0.02	3.38	-0.01
$Ne_{75}Kls_{25}$+1.26F	47.36	24.21	17.34	5.88	4.70	-0.02
$Ne_{62.5}Kls_{37.5}$	49.38	25.26	15.77	9.58	0.01	0.00
$Ne_{62.5}Kls_{37.5}$+1.24F	47.69	24.18	1.68	8.82	4.66	-0.01
$Ne_{50}Kls_{50}$+0.39F	49.06	24.76	12.31	12.33	1.54	0.00
$Ne_{50}Kls_{50}$+1.21F	47.27	23.38	12.16	11.56	4.63	-0.01
$Ne_{50}Kls_{50}$+1.64F	46.56	23.98	11.92	11.34	6.19	-0.01
$Ne_{50}Kls_{50}$+2.15F	45.56	23.69	11.63	11.19	8.02	-0.01
$Ne_{37.5}Kls_{62.5}$	49.80	25.20	9.28	15.75	0.00	0.00
$Ne_{37.5}Kls_{62.5}$+ 0.90F	48.39	24.45	8.89	14.73	3.53	-0.01
$Ne_{25}Kls_{75}$+0.57F	48.78	24.96	6.11	17.90	2.26	-0.01

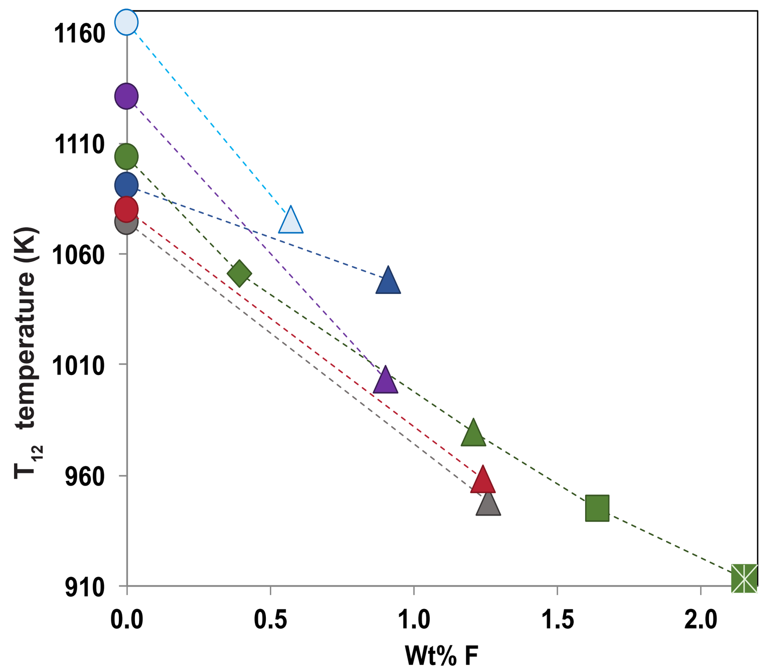
Viscosity Results





For our metaluminous or slightly peraluminous melts we observe that F reduces viscosity, which is also observed by Dingwell (1985), Zimova and Webb (2007), and others. The effect of F is greater at higher potassium concentrations. Compositions $Ne_{37.5}Kls_{62.5}$ (ΔT^{12}=127 °C) and $Ne_{25}Kls_{37.5}$ (ΔT^{12}=88 °C) saw the greatest reduction.

Viscosity is not a linear function of fluorine content, as can be seen in our $Ne_{50}Kls_{50}$+F compositions.

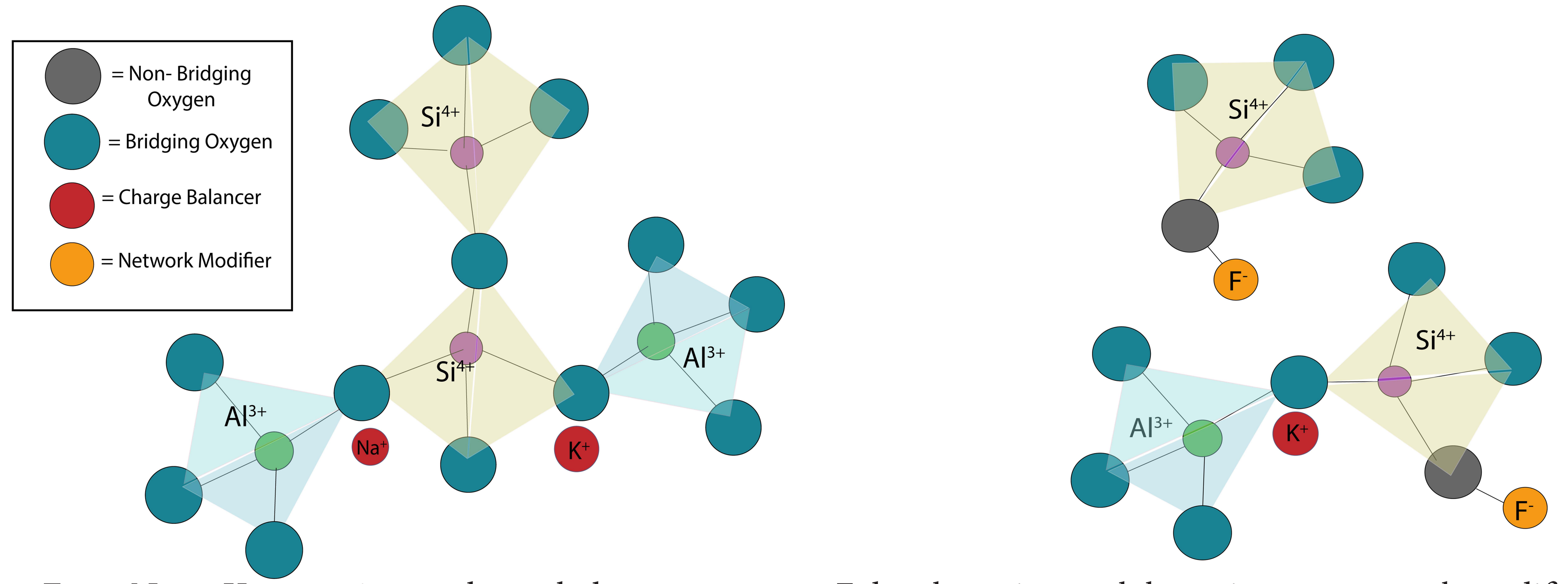


Implications

Structure of F-bearing aluminosilicate melts

F-free (Na,K)$AlSiO_4$ melt

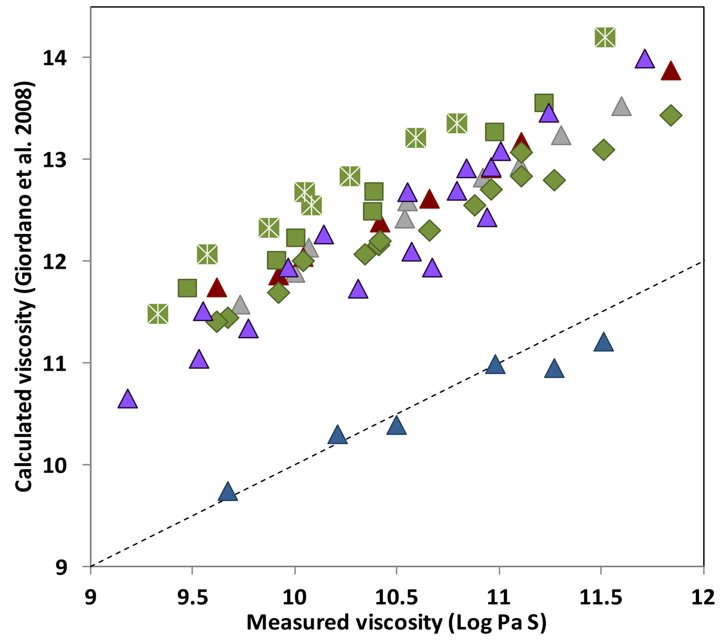
$NaAlSiO_4$ + F melt



Extra Na or K not acting as charge balancer can bond with O, terminating network. Hypothetical NBO/T~ 0 overall.

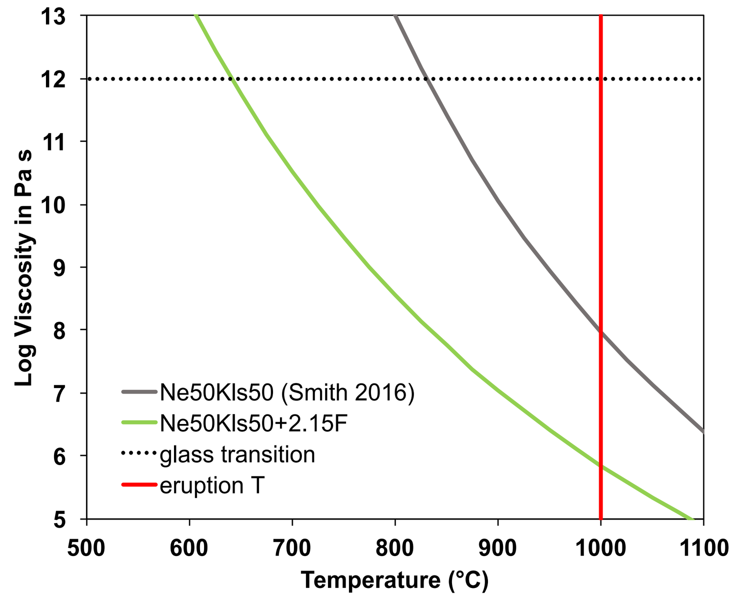
F depolymerizes melt by acting as a network modifier. Once F bonds to a corner oxygen, the tetrahedra can no longer form strong silicate bonds at that site. F is also thought to exist in other structures within melts, including AlF_3 or existing in close proximity to positive Na cations.

Comparison to Existing Viscosity Models



Empirical models (Giordano et al. 2008) calculate the chemical dependence of viscosity. This model overestimates the influence of fluorine on the viscosity of Ne-Kls melt compositions, except for Ne_{100}. However, the model correctly predicts that fluorine lowers viscosity of the melts.

Application to Volcanic Processes



If a feldspathoid melt containing dissolved fluorine were to erupt at the surface of the earth, it would be able to flow longer than a F-free lava at the same cooling rate. The F-free melt would reach the glass transition, where movement stops and glass is formed (~12 log Pa s), far before the F-bearing melt.