

Alkali zirconosilicate speciation in halogen-rich, felsic, peralkaline magmas

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Introduction

Alkali zirconosilicate minerals are frequent accessory phases in peralkaline nepheline syenites and granites. The wide variety of these minerals may be useful in constraining the physical and chemical conditions of late-stage crystallization of peralkaline rocks. However, little experimental work has been done with these minerals to date. Zirconium solubility studies by Watson (1979) at 2 kbar between 700°C and 800°C at water-saturated conditions yielded only zircon. However, these experiments were done exclusively with silica-saturated compositions and with H₂O as the sole volatile component. This study seeks to investigate the role of halogens in the saturation of alkali zirconosilicate minerals and the speciation of alkali zirconosilicate melt complexes in felsic peralkaline magmas.

Experimental method

Experiments were performed in the K₂O–Na₂O–Al₂O₃–SiO₂–ZrO₂–H₂O/Cl system. Starting materials were glasses with compositions of leucitite, alkali feldspar syenite and alkali feldspar granite (based on CIPW norms) with an agpaitic index of 1.3 to 1.4 and a Na/K ratio of 1.3. In addition to the halogen-free compositions, glasses were prepared with 0.3 wt.% F using the same base compositions. Finally, glasses of leucitite and alkali feldspar syenite composition with a Na/K ratio of 1.1 and agpaitic indices of 1.2 and 1.1 respectively were prepared containing 0.8 wt.% Cl. All glasses contained 1.0 wt.% ZrO₂.

The experiments were performed in cold-seal vessels utilizing an Ar pressure medium. In each experiment, 0.01 g of sample was sealed in a gold capsule with 0.002 mL of distilled water. Runs were done at 600°C and 700°C at 1 kbar confining pressure under water-saturated conditions. Although fO₂ was not controlled directly, it is believed to be within two log units of the Ni/NiO boundary due to the buffering effects of the vessel which is constructed of a Ni-bearing alloy (Chou, 1987). The run duration for all experiments was

one week. Run products were analyzed by electron microprobe analysis.

Results

Wadeite (K₂ZrSi₃O₉) was observed in the run products of the halogen-free experiments for both the leucitite and the alkali feldspar syenite compositions. The observed assemblages were glass + wadeite + nepheline ± leucite ± K-rich alkali feldspar and glass + wadeite + K-rich alkali feldspar + nepheline, respectively. The glass pools were generally too small to obtain reliable analyses. The granitic composition yielded glass ± alkali feldspar ± quartz, but no zirconium-bearing mineral phases, except for small aggregates of ZrO₂ grains, which are believed to be undissolved starting material.

Feldspar compositions were controlled by the presence or absence of nepheline. In the run products of the leucitite and the syenite experiments, the presence of nepheline served to greatly reduce the Na-content in the feldspars. Feldspar compositions were all near Or₉₅. In the granitic run products, however, feldspar compositions were approximately Or₇₅. Leucite compositions were very nearly ideal and nepheline in all experiments had a stoichiometry close to (Na_{0.75},K_{0.25})AlSiO₄.

The addition of fluorine to the glasses resulted in the appearance of parakeldyshite (Na₂ZrSi₂O₇) instead of wadeite in the syenite, although wadeite remained the stable zirconosilicate in the leucitite. Furthermore, nepheline was not observed in the run products of the alkali feldspar syenite experiments, resulting in a more sodic feldspar (Or₆₅), although the presence of nepheline in the leucitite experiments resulted in highly potassic feldspar compositions. Zircon was not observed in either the halogen-free or fluorine-bearing run products.

Experiments for chlorine-bearing starting materials were performed only at 700°C, since the run products at lower temperatures were almost completely devoid of glass and difficult to prepare for microprobe analysis. Owing to the low

solubility of Zr in the high-silica glass, chlorine-bearing experiments were not done. The run products from the silica-undersaturated experiments yielded wadeite + nepheline + leucite + glass, while the alkali feldspar syenite composition yielded zircon + alkali feldspar + glass. The alkali feldspar from these experiments was much more sodic than using halogen-free or fluorine-bearing glass, having a composition of about Or₅₅.

Discussion

The speciation of alkali zirconosilicate complexes in silica-saturated melts is clearly influenced by the presence of halogens. However, the fact that in all the silica-undersaturated experiments, wadeite was the only zirconosilicate to appear, suggests that halogens do not exert a strong influence on alkali zirconosilicate complexation in silica-undersaturated melts. Mysen and Virgo (1985) determined by Raman spectroscopic analysis that lower Al/(Al + Si) (i.e. higher SiO₂ activity) favours the formation of Na-aluminofluoride complexes in sodic aluminosilicate glasses. Conversely, AlF₃ becomes the predominant fluoride complex with decreasing silica activity. The implications of these findings for the speciation of alkali zirconosilicates are important. Based on zircon solubility studies, Watson (1979) noted a 2:1 ratio of excess alkali oxide to ZrO₂ in peralkaline melts. Excess alkali oxide refers to any alkali content above that required to charge balance Al. From this observation, Watson concluded that Zr forms complexes of the form M₄Zr(SiO₄)₂, in which M represents an alkali metal. In melts with relatively low silica activity where fluorine does not greatly affect the alkali activity, it also does not effect speciation of zirconosilicate complexes. This is supported by the results of this study. On the other hand, alkali activity is more strongly affected by

the addition of fluorine in higher-silica melts and, therefore, crystallization of a different zirconosilicate phase would be likely. The fact that a K-zirconosilicate appears in the F-free experiments, while a Na-zirconosilicate appears in the F-bearing experiments suggests that not only does fluorine form complexes with alkalis, but that it does so preferentially with K over Na.

The presence of Cl in the melt, like F, appears to disrupt the formation of alkali zirconosilicate complexes and this behaviour is, again, affected by silica activity. The appearance of zircon in the syenite experiments indicates that not only does Cl suppress the formation of alkali zirconosilicate complexes, but that it does so without discriminating between different alkalis.

Conclusion

The results of this experimental study indicate that the presence of halogens in the magma during late-stage crystallization of felsic, peralkaline rocks can greatly affect zirconosilicate mineralogy. The presence of fluorine suppresses the formation of K-zirconosilicate complexes, particularly in silica-saturated melts, favouring the crystallization of the sodic zirconosilicate, parakeldyshite. Chlorine, on the other hand, serves to suppress the formation of all alkali zirconosilicate complexes, stabilizing zircon in mildly peralkaline magmas.

References

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