

**Phase equilibria in NaAlSiO<sub>4</sub>–KAlSiO<sub>4</sub>–SiO<sub>2</sub>–H<sub>2</sub>O at 100 MPa pressure: equilibrium leucite composition and the enigma of primary analcime in blairmorites revisited.**

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**Electronic appendix and Table 3**

Bulk compositions on the join Anl–Lc were prepared as gels using the method of Hamilton and Henderson (1968); care was taken to ensure that no crystalline material was present in the starting materials. Experiments were carried out in cold-seal reaction vessels at 100 MPa pressure with some experiments lasting 3–4 months. Nimonic alloy bombs (32mm O.D., 7mm I.D.) were used at and below 700°C and an M22 vessel (50mm O.D., 7mm I.D) was employed at higher temperatures. Chromel–alumel thermocouples inserted into a small hole at the end of the bomb were used to monitor temperatures. About 30–40 mg powder starting material for each run was sealed in a gold tube (2 mm diameter × 2 cm long) together with 5–25 wt.% distilled water. K-rich starting materials had 5–10% water added and Na-rich samples had larger amounts to ensure an excess over that required to form analcime (~9%). Temperature control was ±5°C, and pressure to within ~5% (*cf.* James and Hamilton, 1969). Experiments with larger amounts of excess water were used to assess whether reactions between the primary silicates and hydrothermal fluid occurred during quenching. Most experiments were quenched by placing the bomb in a blast of compressed air with pressure controlled at 100 MPa; the outer surface of the nimonic bomb cooled to 400°C in ~5 min but some experiments were then allowed to cool more slowly over a period of 30 to 60 min. Cooling of the larger M22 bomb was slower, *i.e.* cooling to 400°C in ~10 min and to <100°C in 1½ to 2 h. Capsules did not change weight during the experiment and always ‘hissed’ when opened showing that they had not leaked.

Experiment products were inspected initially using a petrological microscope; subsolidus experiments produced very fine-grained assemblages of crystalline phases, generally in the range 2–10 µm so that powder X-ray diffraction was used routinely to identify the phases (*cf.* Saha, 1961; Liou, 1971; Barker, 1976; Gupta *et al.*, 2010). For K-rich experiments above 750°C (particularly above the solidus), larger leucites ~100 µm which contained fine lamellae (< 1 µm wide) of analcime were observed (*cf.* Fudali, 1963; Taylor and MacKenzie, 1975; Roux and MacKenzie, 1978). X-ray diffraction powder patterns were obtained with a Philips PW1050 vertical goniometer (Ni-filtered Cu K $\alpha$  radiation) and a paper chart recorder. Proportions of crystalline phases were obtained by comparison with scans obtained for two sets of standard mixtures: (1) set T1–T6, synthetic alkali feldspar (Or<sub>10</sub> in the modal proportions from 47.5–5 wt.%) + synthetic nepheline (Ks<sub>10</sub>, 47.5–5 wt.%) + natural analcime (10–90 wt.%); (2) set S1–S6, synthetic alkali feldspar (Or<sub>80</sub> in the range 47.5– 5 wt.%) + synthetic nepheline (Ks<sub>20</sub>, 47.5–5 wt.%) + natural leucite (10–90 wt.%). Results are summarized in Table 1 and errors are ~20% relative.

It is notoriously difficult to analyse analcime (in particular) and leucite with the electron microprobe and large spot sizes (10–20µm) are required to obtain reliable Na and K values. Unfortunately, only finely ground powders are available for the samples so unit cell parameters have been used to characterize the compositions of run products. Higher resolution XRD scans of the experimental samples were recently obtained with a Bruker D8ADVANCE powder diffractometer; data analysis was carried out with Bruker Diffraction EVA14.0 software. The alignment of the goniometer was calibrated against powdered Si (NIST standard reference material 640a). The diffraction peaks were well enough resolved to obtain quantitative peak positions for coexisting leucite, alkali feldspar, nepheline, and analcime. Peak widths of 0.2–0.25° 2θ (at half height) are consistent with the phases being well crystalline and essentially unzoned (range <3 wt.% Or and Ks). Unit cell parameters were calculated using the program ‘Unit Cell’ (Holland and Redfern, 1997). Cell parameters (1σ errors in brackets) and derived solid solution compositions are given in Table 2. The numbers of peaks used to calculate cell parameters are quite variable: alkali feldspar 6–18; nepheline 4–14; leucite 6–23; analcime 3–12. The errors for Or and Ks estimates are ± ~1–1.5 wt.%.

In some of our experiments there were too few peaks to obtain full unit cell parameters. In these cases published unit cell data for ‘standard samples’ were used to calculate *d* values for single peaks that could then be used to calibrate the compositions for our samples. The general equation for triclinic symmetry is given here where the superscript stars define reciprocal cell parameters:

$$\frac{1}{d_{hkl}^2} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2(klb^* c^* \cos \alpha^* + hla^* c^* \cos \beta^* + hka^* b^* \cos \gamma^*)$$

$$a^* = \frac{bc \sin \alpha}{V}, b^* = \frac{ac \sin \beta}{V}, c^* = \frac{ab \sin \gamma}{V} \quad \dots\dots\dots (1).$$

$$\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma}, \cos \beta^* = \frac{\cos \alpha \cos \gamma - \cos \beta}{\sin \alpha \sin \gamma}, \cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta}$$

$$V = abc \sqrt{(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)}$$

Working curves to obtain phase compositions for our samples using published data for ‘standard samples’ were obtained as follows.

*Alkali feldspars:* Source data for disordered alkali feldspar solid solutions are from Orville (1967), Donnay and Donnay (1952) and Wright and Stewart (1968). For most samples full unit cells could be obtained but where fewer peaks were available (-2 0 1) was used and where that was not resolved from interfering peaks either (1 3 0) or (1 1 1) feldspar peaks were used to calibrate the data.

From  $a$ : 
$$\text{Or (wt.\%)} = 211.4 \times a - 1722 \quad [R^2 = 0.997] \dots (2)$$

From (-2 0 1): 
$$\text{Or (wt.\%)} = -90.7 \times 2\theta(-201) + 1997 \quad [R^2 = 0.998] \dots (3)$$

From (1 3 0) Or 0-43: 
$$\text{Or (wt.\%)} = -22.2 \times 2\theta(130)^2 + 1012 \times 2\theta(130) + 11493 \quad [R^2 = 0.998] \dots (4)$$

(1 3 0) Or 43-100: 
$$\text{Or (wt.\%)} = 230 \times 2\theta(130)^2 + 11070 \times 2\theta(130) + 133362 \quad [R^2 = 0.994] \dots (5)$$

From (1 1 1): 
$$\text{Or (wt.\%)} = 54.8 \times 2\theta(111)^2 + 2603 \times 2\theta(111) + 30923 \quad [R^2 = 0.967] \dots (6)$$

*Nepheline/kalsilite*: Sources of data were Smith and Tuttle (1957), Hamilton and MacKenzie (1960; their  $2\theta$  values for (20.2) and (21.0) peaks were used to calculate 'model' unit cell parameters), Henderson and Roux (1977), and Hovis et al. (1992, 2003).

From  $V$ , Ks 0–25: 
$$\text{Ks (wt.\%)} = 2.56 \times V - 1836 \quad [R^2 = 0.851] \dots (7)$$

25–100: 
$$\text{Ks (wt.\%)} = 0.934 \times V - 651.2 \quad [R^2 = 0.995] \dots (8)$$

Equation 7 is not reliable for nepheline close to the Na endmember because of the variability in cell parameters reported for nominally pure-Na nephelines (Donnay et al., 1959; Henderson and Roux, 1977). Hamilton and MacKenzie (1960) showed tie-lines joining the same  $2\theta$  values for stoichiometric Ne–Ks compositions and for those with excess  $\text{SiO}_2$  (their Fig. 4A). By chance these appear to radiate from the likely compositions of coexisting alkali feldspars so we quote the equivalent Ks (wt.%) composition on the Ne–Ks join and plot the determined compositions at the intersection of the binary nepheline-feldspar tie line with the isothermal limits of excess  $\text{SiO}_2$  in nepheline solid solutions deduced from Hamilton (1961).

*Analcime.*

The cell edge data from Saha (1961) and Liou (1971) were used to estimate the Si/Al ratio of our analcime samples.

From  $a$ : 
$$\text{moles of SiO}_2 = -35.161 \times a + 486.35 \quad [R^2 = 0.994] \dots (9)$$

No reliable unit cell calibrations are available for determining the Na content of leucite and the K content for analcime but semi-quantitative data for  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  were obtained from Energy Dispersive spectra (ED) on the Scanning Electron Microscope (SEM).

*ED analyses with the SEM.*

We have already pointed out that sample powders are too fine grained to obtain reliable electron microprobe analyses for analcime and leucite. However, we have obtained semi-quantitative data for the  $\text{Na}_2\text{O}$  in leucite and  $\text{K}_2\text{O}$  in analcime using a Jeol JSM 6400 scanning electron

microscope. Powders were mounted on double-sided tape and thinly coated with carbon. Standard scanning mode was used to collect ED spectra using the cross-hair technique to place the sub-micron beam (1.5 nA specimen current; counting time 50 seconds). The sample mounts showed significant charging effects for many grains.

Grains (usually 5–20  $\mu\text{m}$ ) with clean, smooth surfaces were chosen where possible but many analyses were obtained on grains with irregular surfaces. Alkali feldspar grains were identified by having Si/Al peak ratios of  $\sim 3$ , analcime and leucite having Si/Al  $\sim 2$  and nepheline with Si/Al  $\sim 1.1$ – $1.2$ ). Many grains had variable Si/Al ratios reflecting analyses of composite grains. Nepheline and alkali feldspar frequently showed fine intergrowths on a length scale of a few microns. For grains with irregular surfaces, variable scattering and absorption of secondary X-rays must be a problem, particularly for Na. In addition the emission efficiency varied from grain to grain. To minimise such effects compositions were obtained using Na/K or K/Na ratios rather than absolute element peak heights but only semi-quantitative analyses for Na were obtained ( $\pm 10$ – $20\%$  relative). Grains of natural nepheline (Na<sub>2</sub>O 15.9, K<sub>2</sub>O 5.3 wt.%; Si/Al 1.13; Ne<sub>77.2</sub>Ks<sub>16.9</sub>Qz<sub>2.8</sub>), sanidine (Na<sub>2</sub>O 2.3, K<sub>2</sub>O 12.0 wt.%; Or<sub>71</sub>), and analcime (Na<sub>2</sub>O 12.5, K<sub>2</sub>O 0.1 wt.%; Lc<sub>0.5</sub>) of known composition were used as primary standards. Most of the synthetic sample grains were intergrowths of fine-grained phases but where possible at least 5 analyses of single-phase grains were averaged to define their compositions.

Equations for deducing alkali ratios were obtained for the three natural mineral standards and synthetic K-free analcime (LA18) (with zero intercept) are:

*Wide range Na/K.*

$$\text{Na}_2\text{O}/\text{K}_2\text{O} \text{ (wt ratio in standards)} = \text{Na}/\text{K} \text{ (SEM peak height ratio)} \times 1.081 \quad [\text{R}^2 \text{ 0.996}] \quad \dots(10)$$

(standards Na<sub>2</sub>O/K<sub>2</sub>O ratio range 0.2–150)

*Wide range K/Na.*

$$\text{K}_2\text{O}/\text{Na}_2\text{O}_{\text{wt}} = \text{K}/\text{Na}_{\text{pk}} \times 0.411 \text{ (standards K}_2\text{O}/\text{Na}_2\text{O ratio range 0.01–5.2)} \quad [\text{R}^2 \text{ 0.999}] \quad \dots(11)$$

*Narrow range Na/K.*

$$\text{Na}_2\text{O}/\text{K}_2\text{O}_{\text{wt}} = \text{Na}/\text{K}_{\text{pk}} \times 1.50 \text{ (standards Na}_2\text{O}/\text{K}_2\text{O ratio range 0.2–3.5)} \quad [\text{R}^2 \text{ 0.999}] \quad \dots (12)$$

*Narrow range K/Na*

$$\text{K}_2\text{O}/\text{Na}_2\text{O}_{\text{wt}} = \text{K}/\text{Na}_{\text{pk}} \times 0.668 \text{ (standards K}_2\text{O}/\text{Na}_2\text{O ratio range 0.01–0.5)} \quad [\text{R}^2 \text{ 1.000}] \quad \dots (13)$$

The narrow range standard fits provide the most reliable data for all the phases encountered in the experimental samples. The alkali ratios provide model proportions for Ab:Or, Ne:Ks, and An:Lc for alkali feldspars, nephelines and the analcime-leucite join; results are summarised in Table 3 in this appendix. Although the deduced compositions are only claimed to be semi-quantitative, analyses for nepheline and alkali feldspar in LA10, and for sanidine in LA20, are within 5–10% (relative) of the

XRD compositions. Also the average of the nepheline/alkali feldspar intergrowths in LA10 gives  $\sim\text{Lc}_{25\pm 10}$  compared to the nominal bulk composition of Lc20. The analysis referred to as Mixture LA20 in Table 3 has an average composition of  $\text{Lc}_{80\pm 10}$  and a Si/Al ratio of 2.03; this is clearly a fine-grained intergrowth of sanidine and nepheline and has the same alkali and Si/Al ratio as the bulk composition (Lc80). We conclude that the ED/SEM data provide reliable information on the Na-K contents of analysed phases, particularly for primary leucite.

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Table 3. Partial analyses of samples by energy-dispersive microprobe analyses with the SEM.

| Sample<br>(number of<br>analyses)  | Na peak<br>height<br>(error)* | K peak<br>height<br>(error)* | Na/K     | Si/Al<br>(error)* | Na <sub>2</sub> O<br>/K <sub>2</sub> O<br>(by wt.)<br>Eq. 12 | Na-phase wt.%<br>(error on lower<br>component) | K <sub>2</sub> O/<br>Na <sub>2</sub> O<br>(by wt.)<br>Eq. 13 | K-phase wt.%<br>(error on lower<br>component) |
|------------------------------------|-------------------------------|------------------------------|----------|-------------------|--|--|--|---|
| <i>Standards</i>                   | 1.4                           | 17                           | 0.079    | 2.9               |  |  |  |   |
| Sanidine (6) <sub>2</sub>          | (0.5)                         | (3)                          | (~0.03)  | (0.2)             |  |  |  |   |
| Crowsnest 15898 <sub>2</sub>       |                               |                              |          |                   |  |  |  |   |
| Analcime (4) <sub>2</sub>          | 12 (3)                        | 0.1                          | 122      | 2.03              |  |  |  |   |
| Crowsnest 15897 <sub>2</sub>       |                               | (0.03)                       | (~30)    | (0.06)            |  |  |  |   |
| Nepheline (6) <sub>2</sub>         | 27 (12)                       | 12.2                         | 2.24     | 1.12              |  |  |  |   |
| Marangudzi A20 <sub>2</sub>        |                               | (0.3)                        | (~0.3)   | (0.04)            |  |  |  |   |
| Analcime (6) <sub>2</sub>          | 13.7                          | ~0.1                         | 137      | 2.07              | 205  | Anl 99.5                                       | 0.005  | Lc 0.5  |
| LA18, this work <sub>2</sub>       | (2.5)                         |                              | (~40)    | (0.07)            |  |  |  | (0.2)   |
| <i>Samples</i>                     |                               |                              |          |                   |  |  |  |   |
| Leucite (5) <sub>2</sub>           | 1.15                          | 70 (7)                       | 0.017    | 2.01              | 0.025  | Anl 2.4  | 40.6   | Lc 97.6                                       |
| LA20                               | (0.6)                         |                              | (~0.008) | (0.05)            |  | (1.1)  |  |   |
| Sanidine (2) <sub>2</sub>          | 1.5                           | 20.0                         | 0.08     | 2.83              | 0.113  | Ab 10.0  | 8.9  | Or 90.0                                       |
| LA20                               | (0.3)                         | (1.4)                        | (~0.02)  | (0.12)            |  | (2.5)  |  |   |
| Mixture (6) <sub>2</sub>           | 4 (2)                         | 24 (6)                       | 0.17     | 2.03              | 0.26   | Anl 20   | 4.0  | Lc 80   |
| LA20                               |                               |                              | (~0.09)  | (0.17)            |  | (10)   |  |   |
| Nepheline (4) <sub>2</sub>         | 25.1                          | 5.0                          | 5.02     | 1.3               | 7.53   | Ne 88  | 0.13   | Ks 12   |
| LA10 <sub>2</sub>                  | (2.1)                         | (0.6)                        | (~0.8)   | (0.1)             |  |  |  | (2)   |
| Alkali feld (2) <sub>2</sub>       | 12                            | 5.8                          | 2.09     | 2.8               | 3.13   | Ab 76  | 0.32   | Or 24   |
| LA10 <sub>2</sub>                  | (1)                           | (0.4)                        | (~0.3)   | (0.2)             |  |  |  | (5)   |
| Mixture (5) <sub>2</sub>           | 12.9                          | 8.3                          | 1.55     | 2.0               | 2.96   | Anl 75   | 0.34   | Lc 25   |
| LA10                               | (2.7)                         | (3.0)                        | (~0.6)   | (0.2)             |  |  |  | (10)  |
| Leucite (5) <sub>2</sub>           | 1.5                           | 38.8                         | 0.039    | 2.02              | 0.058  | Anl 5.5  | 17.3   | Lc 94.5                                       |
| LA23                               | (0.4)                         | (6.4)                        | (~0.012) | (0.02)            |  | (2)  |  |   |
| Lc/Anl Mixture                     | 4.5                           | 25.0                         | 0.18     | 2.04              | 0.27   | Anl 21   | 3.71   | Lc 79   |
| (7) <sub>2</sub> LA23 <sub>2</sub> | (1.5)                         | (6.0)                        | (~0.1)   | (0.03)            |  | (10)   |  |   |
| Glass? (2) LA23                    | 6.8                           | 16.5                         | 0.41     | 2.01              | 0.61   | Anl 38   | 1.63   | Lc 62   |
|                                    | (1.0)                         | (1.0)                        | (0.05)   | (0.06)            |  | (6)  |  |   |
| Analcime (2) <sub>2</sub>          | 15                            | 1.2                          | 12.5     | 2.05              | 18.8   | Anl 95   | 0.053  | Lc 5.0  |
| LA17 <sub>2</sub>                  | (5)                           | (0.4)                        | (4)      | (0.02)            |  |  |  | (3)   |

\* error estimate

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