

# Plagioclase-alkali-feldspar geothermometry revisited

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**SUMMARY.** The plagioclase-alkali-feldspar geothermometer formulated by Stormer (1975) does not take into account the effect of small amounts of calcium in the alkali feldspar. This geothermometer has been reformulated using ternary regular solution model equations, and it is shown that as the Ca content of the alkali feldspar increases the temperature calculated using the Stormer geothermometer will be increasingly too high.

VARIOUS attempts have been made to formulate the distribution of sodium between high-temperature alkali feldspar and plagioclase as a geothermometer (Barth, 1951; Stormer, 1975). Stormer presents a thermodynamic treatment of the equilibrium relation for the reaction



as a geothermometer. He assumes that small amounts of Ca in the alkali feldspar and small amounts of K in the plagioclase have no effect on the equilibrium and models the activity-composition relations of the coexisting phases with the subregular solution model parameters for the binary systems, albite-anorthite for plagioclase and albite-orthoclase for alkali feldspar. It will be shown below that there is a significant correction to Stormer's geothermometer when small amounts of calcium occur in the alkali feldspar. The geothermometer has been reformulated to incorporate this correction using ternary subregular solution model equations for the activity coefficients. The subregular solution model is retained so that the geothermometer equation is comparable with that of Stormer (cf. Powell, 1974).

*Theory.* The equilibrium relation is:

$$-\Delta G_1^0 = RT \ln a_{\text{NaAlSi}_3\text{O}_8, \text{PL}} / a_{\text{NaAlSi}_3\text{O}_8, \text{AF}} \quad (2)$$

Assuming that the standard chemical potential of the albite component is the same in both plagioclase and alkali feldspar, then  $\Delta G_1^0 = 0$ , and  $a_{\text{NaAlSi}_3\text{O}_8, \text{PL}} = a_{\text{NaAlSi}_3\text{O}_8, \text{AF}}$ . In terms of activity coefficients and mole fractions:

$$K_D = x_{\text{Na}, \text{AF}} / x_{\text{Na}, \text{PL}} = \gamma_{\text{Na}, \text{PL}} / \gamma_{\text{Na}, \text{AF}},$$

where AF refers to alkali feldspar and PL to plagioclase.

This assumes that there are no contributions from Al-Si mixing in the alkali feldspar, and should therefore apply only to essentially disordered alkali feldspars. No contribution from Al-Si mixing in the plagioclase should appear because of short range order effects in the tetrahedral sites (Kerrick and Darken, 1975).

For ternary feldspars in the system  $\text{NaAlSi}_3\text{O}_8$ - $\text{KAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$  the subregular solution model expression for the activity coefficient of Na is (Wohl, 1946):

$$\begin{aligned} RT \ln \gamma_{\text{Na}} = & x_{\text{K}}^2 (w_{\text{NaK}} + 2x_{\text{Na}}(w_{\text{KNa}} - w_{\text{NaK}})) + x_{\text{Ca}}^2 (w_{\text{NaCa}} + 2x_{\text{Na}}(w_{\text{CaNa}} - w_{\text{NaCa}})) + \\ & + x_{\text{K}} x_{\text{Ca}} [\frac{1}{2}(w_{\text{NaK}} + w_{\text{KNa}} + w_{\text{NaCa}} + w_{\text{CaNa}} - w_{\text{CaK}} - w_{\text{KCa}}) + \\ & + x_{\text{Na}}(w_{\text{KNa}} - w_{\text{NaK}} + w_{\text{CaNa}} - w_{\text{NaCa}}) + (x_{\text{K}} - x_{\text{Ca}})(w_{\text{KCa}} - w_{\text{CaK}})]. \end{aligned}$$

For plagioclase,  $x_{\text{K}}$  is small and therefore terms in  $x_{\text{K}}^2$  and  $x_{\text{K}} x_{\text{Ca}}$  will also be small. If it is assumed that plagioclases are more or less ideal in the binary system  $\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$  (at least at 700 °C and 2000 bars,  $\gamma_{\text{Na}, \text{PL}} \approx 1$  for  $x_{\text{Na}, \text{AF}} = 1.0$  to 0.5, see Orville, 1972), then  $w_{\text{NaCa}} \approx w_{\text{CaNa}} \approx 0$ , and thus  $RT \ln \gamma_{\text{Na}, \text{PL}} \approx 0$ .

For alkali feldspar,  $x_{Ca}$  is small and therefore terms in  $x_{Ca}^2$  and  $x_{Ca}x_K$  will also be small. Thus  $RT \ln \gamma_{Na, AF} \approx x_K^2(w_{NaK} + 2x_{Na, AF}(w_{KNa} - w_{NaK}))$ .

Combining these results:

$$\ln K_D = -x_{K, AF}^2(w_{NaK} + 2x_{Na, AF}(w_{KNa} - w_{NaK}))/RT \quad (3)$$

The only difference between this and the comparable equation in Stormer (1975, (17), with the misprinted sign corrected) is the replacement of  $(1 - x_{Na, AF})^2$  by  $x_{K, AF}^2$ . The two equations

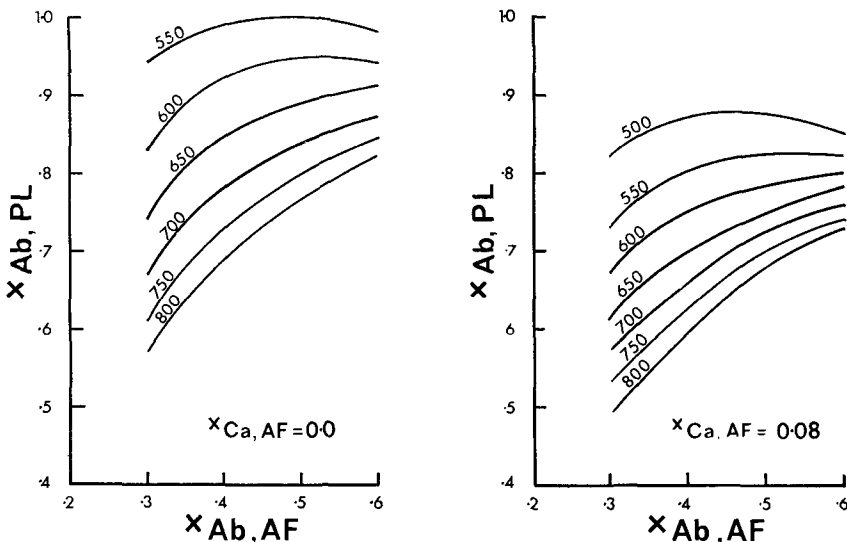


FIG. 1. Geothermometer diagrams for  $x_{Ca, AF} = 0.0$  and  $0.08$  at  $P = 1000$  bar. Temperature contours are in  $^{\circ}C$ .

are exactly equivalent for binary alkali feldspars with no Ca. Using  $W_{NaK} = 6330 + 0.093P - 4.63T$  and  $w_{KNa} = 7670 + 0.112P - 3.86T$  ( $T$  in K,  $P$  in bars) (Thompson and Waldbaum, 1969), and substituting into (3) gives:

$$T = \frac{-x_{K, AF}^2[6330 + 0.093P + 2x_{Na, AF}(1340 + 0.019P)]}{R \ln K_D + x_{K, AF}^2(-4.63 + 1.54 x_{Na, AF})} \quad (4)$$

Two graphs of  $x_{Na, PL}$  versus  $x_{Na, AF}$  contoured for temperature are shown in fig. 1 for  $P = 1000$  bars and  $x_{Ca, AF} = 0.0$  and  $0.08$ . The graph for  $x_{Ca} = 0.0$  is identical to that in Stormer (1975, Fig. 3). Fig. 1 shows that as the Ca content of the alkali feldspar increases the temperature calculated using Stormer's geothermometer will be increasingly too high. The drastic effect of replacing  $(1 - x_{Na, AF})^2$  by  $x_{K, AF}^2$  in the geotherm equation is because this term is squared in (4), so that for example there is a 40% difference between  $(1 - x_{Na, AF})^2$  and  $x_{K, AF}^2$  for  $x_{Na, AF} = 0.5$  and  $x_{Ca, AF} = 0.08$ .

*Application.* Equilibration temperatures for exsolution lamellae in perthites from augite syenites from the Igdlertgssalik centre, Igaliiko complex, SW. Greenland (Emeleus and Harry, 1970) calculated using (4) are compared with those calculated using the Stormer geothermometer in Table I. Temperatures from (4) fall in the range  $550^{\circ}$  to  $650^{\circ}C$  while the Stormer geothermometer gives temperatures in the range  $690^{\circ}$  to  $810^{\circ}C$ . The syenites contain nepheline coexisting with the perthitic alkali feldspar for which a nepheline-alkali-feldspar geothermometer (Powell and Powell, in press) gives equilibration temperatures in the range  $660^{\circ}$  to

TABLE I. Compositions of lamellae in perthites from the Igdlarfígssalik syenites and of coexisting feldspars from three trachytes, together with a comparison of temperatures calculated from equation 4 and from the Stormer geothermometer, for a pressure of 1000 bar.

Rock*	xCa	xNa	xK	$T_1$	$T_2$	Specs. from Carmichael (1965)	xCa	xNa	xK	$T_1$	$T_2$
58162	0.168 0.041	0.853 0.491	0.017 0.473	600	690	Cristobalite trachyte, Jan Mayen	0.070 0.272	0.595 0.656	0.335 0.072	1200	1370
63822	0.114 0.041	0.814 0.504	0.094 0.469	650	740	Biotite trachyte, Gough Island	0.054 0.314	0.456 0.546	0.491 0.140	1140	1220
63783	0.117 0.068	0.842 0.499	0.042 0.406	550	700	Biotite trachyte, Tristan da Cunha	0.023 0.363	0.489 0.572	0.488 0.065	1220	1255
58214	0.141 0.083	0.798 0.583	0.070 0.340	600	810	$T_1$ calculated from equation 7, $T_2$ from the Stormer geothermometer, both for a pressure of 1000 bar.					
63829	0.127 0.086	0.808 0.596	0.041 0.304	550	810	* GGU specimen numbers					
87112	0.144 0.056	0.830 0.468	0.038 0.493	575	700						

Erratum: For  $T_1$  calculated from equation 7, read  $T_1$  calculated from equation 4.

710 °C. Inter-grain migration of Na and K must effectively cease before the onset of perthite formation and therefore the equilibration temperature recorded by coexisting nepheline and alkali feldspar should be higher than that indicated by the lamellae in the perthites. While temperatures calculated using (4) are consistent with this, temperatures from the Stormer geothermometer are *higher* than those for nepheline-alkali-feldspar equilibration. Therefore it is suggested that equation (4) should be used as a replacement for the geothermometer equation given in Stormer (1975).

There is a dearth of published compositional data on coexisting plagioclase and alkali feldspar for comparing temperatures generated by (4) and by Stormer's equation. The data presented by Whitney and Stormer (1976) are not useful in this respect because the calcium contents of their alkali feldspars are very low,  $x_{\text{Ca, AF}}$  lies between 0.01 and 0.02. In Table I a comparison of calculated temperatures using (4) and the Stormer geothermometer is made for coexisting feldspar phenocrysts from three trachyte specimens from Carmichael (1965). Equation (4) gives lower temperatures than Stormer but nevertheless the calculated temperatures still seem too high. This may reflect uncertainties in the formulation of the geothermometer presented here (for example the temperature dependence of  $w_{\text{NaK}}$  and  $w_{\text{KNa}}$  was calculated from two-phase data below 800 °C) but also the possibility of disequilibrium between the alkali feldspar and the plagioclase in the trachyte cannot be ruled out (Carmichael, 1965).

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