MINERALOGICAL AND THERMODYNAMIC CONSTRAINTS ON THE METASOMATIC ORIGIN OF THE YORK RIVER NEPHELINE GNEISSES, BANCROFT, ONTARIO

GREGOR M. ANDERSON AND CLAUDIO CERMIGNANI

Department of Geology, Earth Sciences Centre, University of Toronto,
22 Russell Street, Toronto, Ontario M5S 3B1

ABSTRACT

The York River nepheline gneisses, exposed near Bancroft, Ontario, have often been interpreted over the last 100 years as the products of Na-metasomatism and "nephelinization" of metasedimentary or metavolcanic precursors. Only recently have sufficient data on minerals and fluids become available that models of such processes can be tested. One such model calls upon NaCl brines from evaporite units previously associated with the intercalated marbles to alter the anorthite component of plagioclase to nepheline according to the reaction $CaAl_2Si_2O_8 + 2Na^+ = 2NaAlSiO_4 + Ca^{2+}$. Rare fluid inclusions containing NaCl daughter crystals have been found, supporting the existence of strong brines at some time in the history of the rocks. Using log ($a^2_{Na^+}/a_{Ca^{2+}}$) *versus* log $a(SiO_2)$ as axes and estimated activities of the mineral components, we have used the program PTA to produce diagrams for 600°C, 2 kbar for the York River rocks. Such diagrams show that in most of the nepheline field wollastonite coexists, severely restricting the conditions for the possible formation of nepheline alone. On these diagrams are superimposed ($a^2_{Na^+}/a_{Ca^{2+}}$) contours calculated for NaCl brines in equilibrium with calcite, from the data of Fein & Walther (1989). These calculations make use of maximum and minimum values of $X(CO_2)$ estimated using program PTX from reactions involving grossular, calcite, plagioclase (present), and corundum and wollastonite (absent). This superposition shows that because of the restricted size of the nepheline field, only solutions having concentrations from about 0.3 to 1 molal in NaCl could produce nepheline from plagioclase, without at the same time producing wollastonite or sodalite. Subject to the various assumptions and approximations made, it appears that "nephelinization" by the exchange of sodium for calcium in plagioclase is unlikely to have produced much nepheline in these rocks.

Keywords: nepheline, metasomatism, thermodynamics, York River, Bancroft, Ontario.

SOMMAIRE

Au cours des cent dernières années, les gneiss néphéliniques de la rivière York, dans le district de Bancroft, en Ontario, ont souvent été interprétés comme produits d'une métasomatose sodique et d'une "néphéli-nisation" de précurseurs métasédimentaires ou métavol-caniques. Nous avons maintenant en main les données nécessaires sur les minéraux et la phase fluide impliqués pour évaluer rigoureusement cette hypothèse. Une telle hypothèse prévoit un rôle pour des saumures riches en NaCl dérivées d'une séquence évaporitique associée à des marbres, afin de transformer la composante anorthite du plagioclase en néphéline selon la réaction $CaAl_2Si_2O_8 + 2Na^+ = 2 NaAlSiO_4 + Ca^{2+}$. Nous avons trouvé de rares inclusions fluides qui contiennent des cristaux de NaCl, ce qui concorde avec la présence de saumures concentrées à un certain temps au cours de l'évolution de ces roches. En termes des axes log ($a^2_{Na^+}/a_{Ca^{2+}}$) *versus* log $a(SiO2)$, et avec des activités approximatives des composantes minérales, nous nous sommes servis du logiciel PTA pour produire des diagrammes pour 600°C, 2 kbar appropriés aux roches en question. Ces résultats montrent que la wollastonite coexiste avec la néphéline sur la plupart de son champ de stabilité, ce qui limite sévèrement les conditions de formation de la néphéline seule. Nous superposons sur ces diagrammes des contours de ($a^2_{Na^+}/a_{Ca^{2+}}$) calculés pour des saumures à NaCl en équilibre avec calcite, d'après les données de Fein et Walther (1989). Ces calculs utilisent les valeurs maximale et minimale de $X(CO_2)$ que donne le logiciel PTX pour les réactions impliquant grossulaire, calcite, plagioclase (présents), et corindon et wollastonite (absents). Cette superposition montre qu'à cause des limites sur le champ de stabilité de la néphéline, seules les solutions possédant une molalité entre environ 0.3 et 1 en NaCl pourraient être responsables de la production de néphéline aux dépens de plagioclase sans co-production de wollastonite ou de sodalite. Avec les suppositions et les approximations faites ici, il semble peu probable qu'une "néphélinisation" par échange du sodium pour le calcium dans le plagioclase soit responsable d'une fraction importante de la néphéline présente dans ces roches.

(Traduit par la Rédaction)

Mots-clés: néphéline, métasomatose, thermodynamique, rivière York, district de Bancroft, Ontario.

INTRODUCTION

The alkaline rocks of the York River area, near Bancroft, Ontario, are part of a discontinuous, 130-km-long belt of closely associated syenitic and nepheline-bearing gneisses (Fig. 1). The belt extends
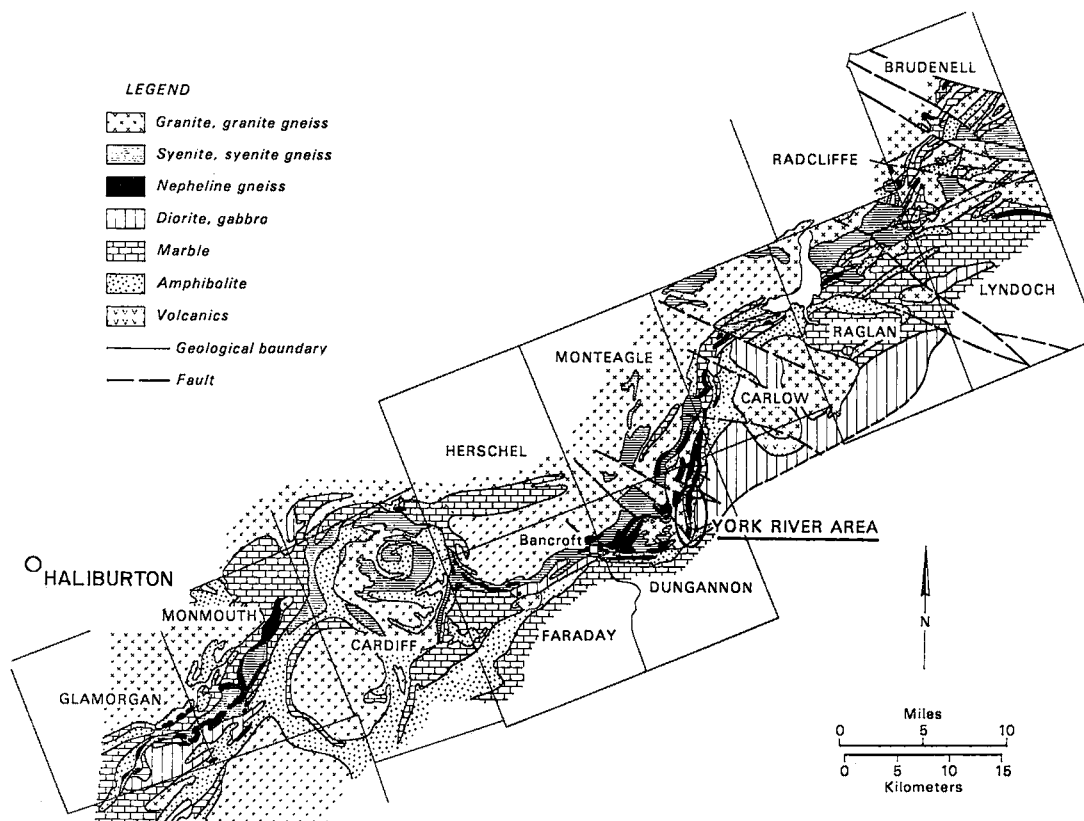
FIG. 1. Geological map of the Haliburton – Bancroft area, generalized from Hewitt (1954) and ODM Map No. 1957b.

through Haliburton, Hastings and Renfrew counties within the Grenville tectonic province of eastern Ontario. The alkaline rocks are associated with more abundant "Grenville-type" metasediments (dominantly marbles, amphibolites and paragneisses) and with intrusive rocks (mostly gabbros and granites).

The nepheline-bearing gneisses were first described by Adams (1894) in the Haliburton–Bancroft area, and have since received a great deal of attention (see references in Reeve & Anderson 1976). The rocks have been subjected to more than one episode of metamorphism, intrusion and deformation, and this complex history has made geological interpretation difficult.

The calculations and conclusions presented here apply to many rocks throughout the area, but we have in mind particularly the York River area (Fig. 2), as most of our data come from previous studies in this area. This area has been discussed several times in the literature, most notably by Tilley (1957), and was recently mapped in detail by Miller (1985).

Historically, the most commonly held interpretation has been that the alkaline character of the gneisses was developed as a result of extensive Na-metasomatism of metasedimentary or volcanic precursors, which resulted in the development of nepheline ("nephelinization"). In the most detailed model of nephelinization proposed to date, the metasomatic agent has been identified as "Cl-rich ...... strong brines" (Appleyard & Williams 1981) formed "by a process of anatexis of metasediments, through the fluxing action of evaporitic halite beds" (Appleyard & Stott 1975). No such rocks now occur in the area, of course, although there is an anhydrite zone reported at the Madawaska mine near Bancroft, which may witness the former occurrence of more extensive evaporitic rocks. Based on new data on bulk chemistry, a different interpretation was put forward by Miller (1985), who suggested that the alkaline character of the gneisses is essentially inherited from igneous nepheline-bearing precursors and that metasomatic phenomena are relatively minor.
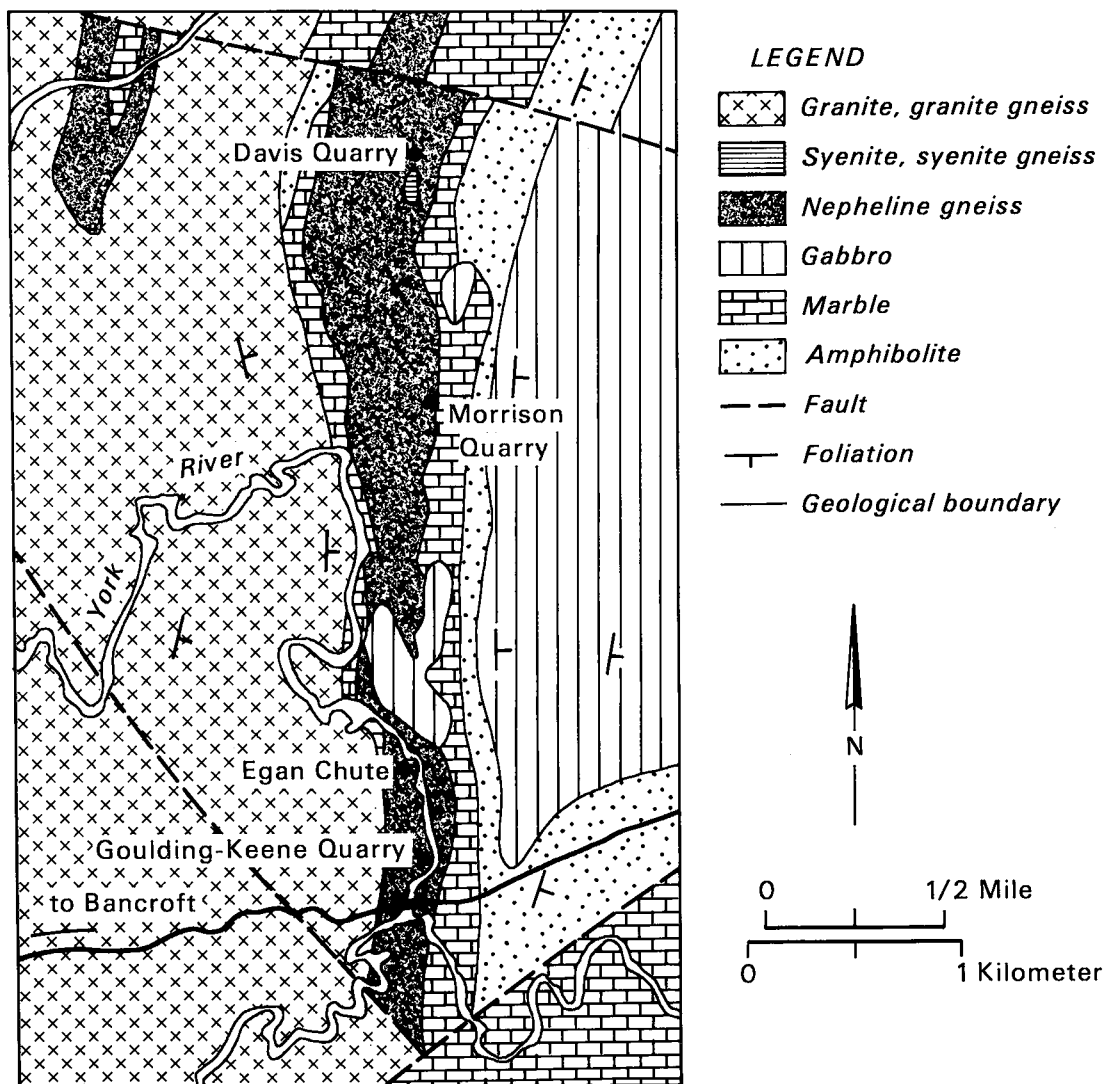
The association of evaporitic rocks with car-

FIG. 2. Map of the southern portion of the York River nepheline gneiss belt, generalized from Hewitt & James (1956).

bonate sequences is of course well known, and recent work (Trommsdorff & Skippen 1986) has provided evidence for the former existence of strong brines in marbles, so that the hypothesis that the evolution of the nepheline gneiss – marble sequences in the Haliburton – Bancroft area was accompanied by the presence of brines is certainly reasonable. This possibility can be investigated in at least two ways, with fluid inclusions, and by thermodynamic modeling, *i.e.*, by calculation of the composition of solutions in equilibrium with mineral assemblages observed in the gneisses. These fluids can then be considered in connection with various possible nepheline-forming reactions.

THE MODELING APPROACH

In this approach, reactions that might lead to the formation of nepheline are modeled thermodynamically. Subsolidus nepheline-forming reactions that have been proposed are desilication by an aqueous flux (Currie 1970), and Na-for-Ca exchange involving the anorthite component of plagioclase. We consider here only the second of these.

Pressure and temperature of metamorphism

The regional metamorphic grade in the York

River area is upper amphibolite, but there have been no determinations of pressure or temperature on the nepheline gneisses themselves. Appleyard & Williams (1981) concluded that metasomatism in the area probably took place at high temperatures of metamorphism, and immediately preceded or was synchronous with the peak of metamorphism. We will therefore equate the pressure and temperature of the metasomatic event with those deduced for the regionally metamorphosed rocks associated with the gneisses.

To the south of the York River area, calcite-dolomite geothermometry and mapping of the andalusite–sillimanite boundary (Sobol & Essene 1973) give estimates of 600 to 625°C and 3.2 to 3.3 kbar [based on Holdaway's (1971) determination of the triple point] for metamorphic conditions in that area. Consistent and not very different results were obtained by DeWitt (1976) for marbles near Haliburton, west of the York River, using calcite-dolomite geothermometry and sphalerite geobarometry. Therefore, in a preliminary model of the metasomatic process, a proposal of 600°C and 3 kbar is a reasonable one. However, for the aqueous phase, some critical experimental data are known only to 600°C and 2 kbar. Rather than attempt extrapolations of these parameters to 600°C and 3 kbar, we have used 600°C and 2 kbar as the model conditions. Not only does this choice greatly simplify the task, but the general conclusions probably would be unchanged by changes in the model T or P.

The nepheline-forming reaction

From field and textural evidence, some authors (Moyd 1949. Anderson *et al.* 1975, Mitchell & Platt 1979) have suggested that nepheline can be formed at the expense of plagioclase by a process of Na–Ca exchange, according to the reaction

$$CaAl_2Si_2O_8 + 2Na^+ = 2NaAlSiO_4 + Ca^{2+} \qquad (1)$$
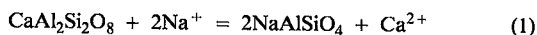
The equilibrium constant for this reaction at 600°C, 2 kbar is 0.000538 [obtained with program PTA (Brown *et al.* 1987), using the HKF model (Helgeson *et al.* 1981) for the aqueous species and the data of Berman (1988) for the minerals, with changes as noted in Appendix 4], from which it appears that rather small concentrations of calcium in solution will be able to offset large concentrations of sodium, and reduce the likelihood of nepheline being produced in this way. Of course, other reactions competing for Ca^{2+} and Na^+ also must be considered, and in the present context these are primarily the formation of chloride and

carbonate complexes. It is unlikely that the equivalent reaction involving chlorides,

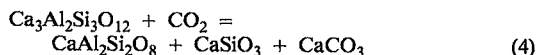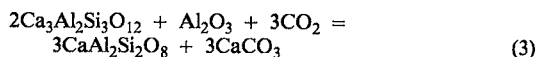$$CaAl_2Si_2O_8 + 2NaCl = 2NaAlSiO_4 + CaCl_2 \qquad (2)$$
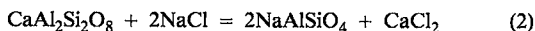
would be effective in producing nepheline, because experiments covering a wide range of conditions (Orville 1972, Debron 1965, Cermignani 1978) have shown that quite concentrated NaCl solutions can be in equilibrium with very calcic plagioclase. Dissolved Na_2CO_3 is more effective at converting anorthite to nepheline (Debron 1965, Cermignani & Anderson 1983) and, other conditions being the same, the conversion takes place at much lower salt concentrations than in the case of chloride. For example, it requires concentrations at least as low as 0.1 m at 600°C, 1 kbar (Kotov *et al.* 1978) and 0.25 m at 700°C, 2 kbar (Cermignani 1978).

The modeling attempted here therefore involves calculation (by solution of simultaneous equations, see Appendix 1) of the $a^2_{Na^+}/a_{Ca^{2+}}$ ratio in (dominantly) NaCl solutions containing both carbonate and chloride ions at the appropriate concentrations, *i.e.*, in a solution saturated with calcite, having $CO2$, Na, Ca and K contents appropriate for the observed mineral assemblages, and having various NaCl activities up to the point of sodalite stability. These $a^2_{Na^+}/a_{Ca^{2+}}$ ratios are then compared to those calculated by program PTA (Brown *et al.* 1988) for the same assemblages. We do not address other questions associated with metasomatism, such as reaction paths, kinetics, flow regimes, mass transfer, and so on, because we conclude that the metasomatic hypothesis is unlikely on chemical grounds.

CO2 concentration

The York River nepheline gneisses contain two generations of Na-rich plagioclase and nepheline, plus microcline and minor, variable quantities of pyroxene, amphibole, garnet and calcite, as the most common minor constituents (Tilley 1957, Reeve & Anderson 1976, Sylvester & Anderson 1976). It also follows from the nephelinization hypothesis that the most leucocratic of the gneisses represent the most advanced degree of metasomatism and thus that they might be expected to be closest to equilibrium with the metasomatizing solution.

The literature cited above establishes the occurrence of the assemblages nepheline + plagioclase + garnet + calcite, and, less commonly, nepheline + plagioclase + corundum + calcite. Thus an estimate of the range of possible CO_2 contents of the metasomatic fluid can be derived through the following reactions:

$$2Ca_3Al_2Si_3O_{12} + Al_2O_3 + 3CO_2 =$$
$$3CaAl_2Si_2O_8 + 3CaCO_3 \qquad (3)$$

$$Ca_3Al_2Si_3O_{12} + CO_2 =$$
$$CaAl_2Si_2O_8 + CaSiO_3 + CaCO_3 \qquad (4)$$

There are no reports of wollastonite in the nepheline gneisses, and the corundum is believed to postdate the formation of the gneisses (E.C. Appleyard, pers. comm.; Miller 1985). By setting the activities of $CaSiO_3$ and Al_2O_3 to 1.0, we therefore obtain maximum and minimum estimates for the activity of CO_2, for given activities of the other components.
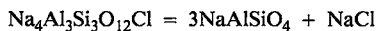
Mineral compositions in the nepheline gneisses are reported by Reeve & Anderson (1976) and Sylvester & Anderson (1976). Plagioclase compositions can range from almost pure Ab to about An_{30}, with uniformly very low Or contents. Nepheline, biotite, amphibole and garnet similarly have fairly broad ranges of compositions in the nepheline gneisses. However, in the leucocratic nepheline gneisses, these ranges are narrower; in Appendix 1 we show the compositions and component activities we have chosen as being quite typical.

Calculation of fluid compositions for reactions (3) and (4) at 600°C, 2 kbar using the activities from Appendix 1, program PTX of Perkins et $al.$ (1986) and the thermodynamic data-base of Berman (1988), results in $X(CO_2)$ values of about 0.003 and 0.01, respectively. These values incorporate the corrections for nonideality of Kerrick & Jacobs (1981) for the system CO_2–H_2O, but do not take into account the effects of NaCl. According to Bowers & Helgeson (1983, Table 5c), fugacity coefficients for CO_2 at 600°C, 2 kbar are consistently greater in $NaCl$–CO_2–H_2O solutions than in the equivalent NaCl-free solutions, an effect that leads to the overestimation of $X(CO_2)$ in the above results. A comparison of the maximum $X(CO_2)$ (0.01) (twice overestimated because of setting wollastonite activity equal to 1.0 and neglecting the NaCl content) with the data of Bowers & Helgeson (1983, Fig. 31) shows that regardless of NaCl concentration, the CO_2 content of the metasomatic solution falls well within the one-phase region, so that phase separation need not be considered. The activity of CO_2 at these concentrations in NaCl solutions is discussed in Appendix 3.

Chloride concentration

In the York River area, sodalite is a minor, but not uncommon mineral in the nepheline gneisses. Because it occurs in concentrations (Hogarth et $al.$ 1972) rather than dispersed throughout the rock, and in some cases is clearly related to fractures

(James 1965), it can be regarded as postmetasomatic. Therefore the activity of NaCl defined by the presence of both sodalite and nepheline,

$$Na_4Al_3Si_3O_{12}Cl = 3NaAlSiO_4 + NaCl$$

should be an upper limit for a_{NaCl} during metasomatism. This upper limit can be determined for pure nepheline and sodalite from the data of Wellman (1970) (about 1 m, Appendix 1). The nepheline in the gneisses have the more usual K-rich compositions, clustering around $Ne_{78}Kls_{20}Qtz_2$ (Reeve 1972), which require much higher concentrations of NaCl to be converted to sodalite (Wellman 1970, Table 2). What NaCl concentration to choose depends on how the nepheline – sodalite reaction is envisaged as proceeding. One possibility is that the K-bearing nepheline in the presence of the NaCl-rich fluid first undergoes Na-for-K exchange until it approaches the end-member, only then to alter to sodalite. At the other extreme, a much more concentrated NaCl solution could change K-bearing nepheline directly to sodalite, with release of K to the solution during sodalite formation rather than before. The study by James (1965) indicates that in this area, the former possibility is more likely.

Carbonate concentration

A carbonate-bearing solution can react with nepheline to form cancrinite-like minerals (Bariand et $al.$ 1968). In the nepheline-bearing gneisses, cancrinite is commonly developed at nepheline – calcite contacts, and occasionally as selvages between nepheline and plagioclase, and as veinlets in nepheline (Reeve 1972). There are also nepheline – calcite contacts without cancrinite. Again, data on the equilibria involved are too incomplete for quantitative analysis, but semiquantitative conclusions can be reached using data at 1 kbar, 400°C, by Zyrianov et $al.$ (1978). Their data indicate that whereas alkali chloride concentrations in excess of 1 m are required to form sodalite from nepheline + kalsilite mixtures, lower concentrations of alkali carbonates (0.25 m) are sufficient to form cancrinite from the same mixtures. That the carbonate was mostly sodium carbonate can probably be inferred from the equilibrium of two feldspars in alkali carbonate solutions at 600°C, 1 kbar, where $X(K_2CO_3)(fluid) = 0.04$ (Iiyama 1965), as compared to $X(KCl)(fluid) = 0.21$ under the same conditions.

The stable assemblages of minerals according to PTA

Given the mineral component activities listed in Appendix 1 and using parameters ($a^2_{Na^+}/a_{Ca^{2+}}$) and $a(SiO_2)(aq)$ as axes, the thermodynamic data-base of Berman (1988) and Helgeson *et al.* (1981), as used by the program PTA (Brown *et al.* 1987, 1988), predicts a distribution of fields of mineral stability as shown in Figure 3. The boundary of most interest in the present context is the anorthite – nepheline boundary, which is horizontal at a
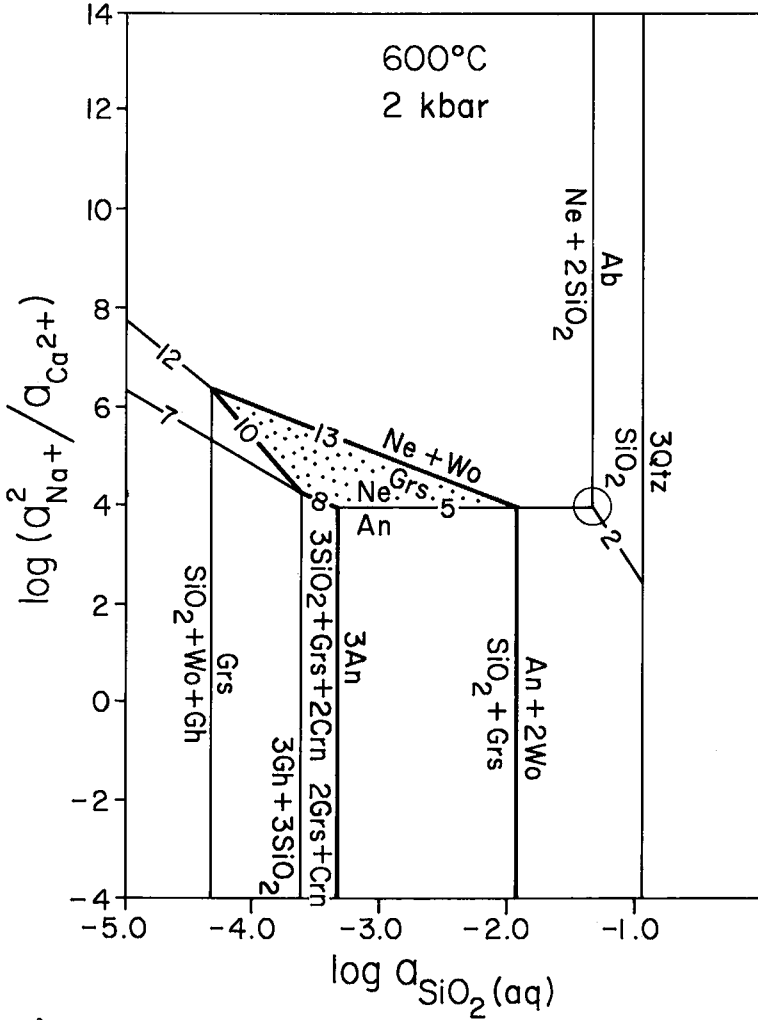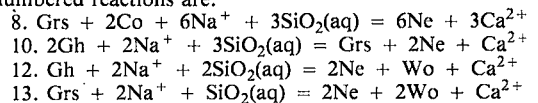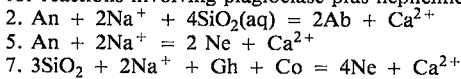

FIG. 3. A plot of ($a^2_{Na^+}/a_{Ca^{2+}}$) *versus* $a(SiO_2)$ for stable mineral assemblages in the system Na–Ca–Al–Si–O–H–C at 600°C, 2 kbar, produced by program PTA (Brown *et al.* 1988). The lines are drawn for the activities of mineral components as given in Appendix 1. The dark line outlines conditions in which garnet, plagioclase or nepheline can exist without wollastonite or melilite. The shaded area is the range of conditions in which nepheline can be produced from plagioclase without forming wollastonite. The circled point at the intersection of reactions 2, 5 and the reaction nepheline + 2 SiO$_2$ = albite is the only point on the diagram that represents stable equilibrium for reactions involving plagioclase plus nepheline. The numbered reactions are:

2. An + 2Na$^+$ + 4SiO$_2$(aq) = 2Ab + Ca^{2+}
5. An + 2Na$^+$ = 2 Ne + Ca^{2+}
7. 3SiO$_2$ + 2Na$^+$ + Gh + Co = 4Ne + Ca^{2+}
8. Grs + 2Co + 6Na$^+$ + 3SiO$_2$(aq) = 6Ne + 3Ca^{2+}
10. 2Gh + 2Na$^+$ + 3SiO$_2$(aq) = Grs + 2Ne + Ca^{2+}
12. Gh + 2Na$^+$ + 2SiO$_2$(aq) = 2Ne + Wo + Ca^{2+}
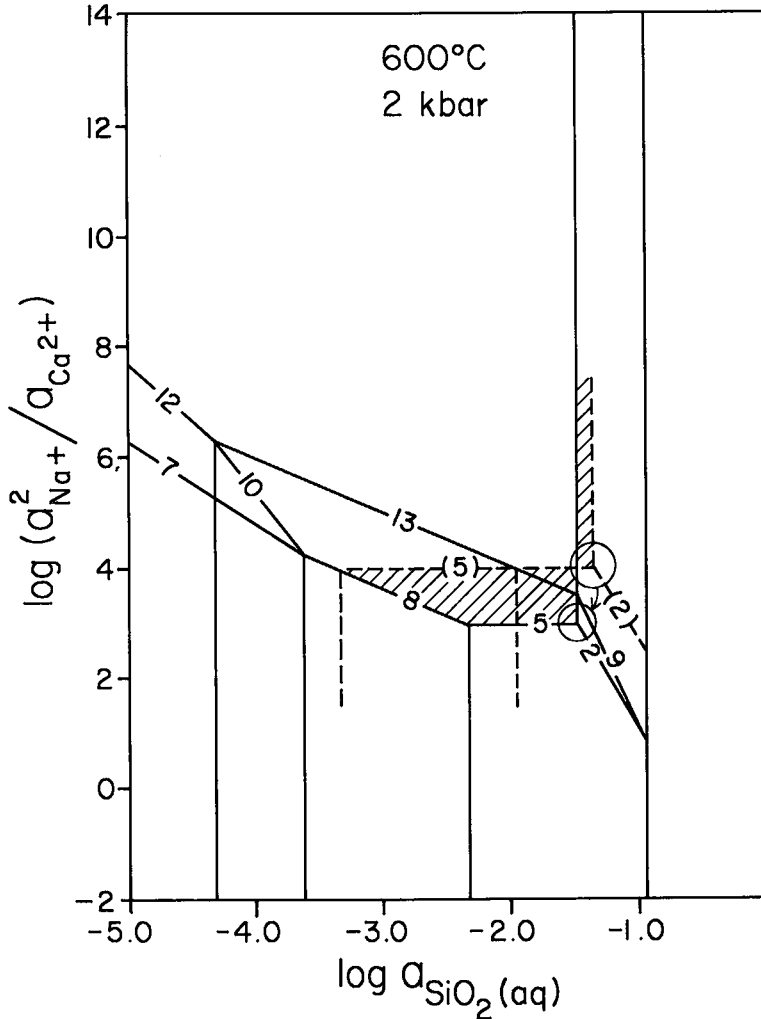13. Grs + 2Na$^+$ + SiO$_2$(aq) = 2Ne + 2Wo + Ca^{2+}

FIG. 4. Similar to Figure 3, but with activities of the albite and anorthite components both 0.5. The dotted lines show the positions of lines in Figure 3, and the ruled areas indicate the range covered by plagioclase of various activities between the ones given. The circled "equilibrium point" lies inside the garnet-stable, wollastonite-free area in this diagram. Other reactions are the same as in Figure 3, except that the reaction $Grs + SiO_2(aq) = An + Wo$ in Figure 3 becomes reaction 9 in Figure 4, which is $Grs + SiO_2(aq) + 2Na^+ = 2Ne + 2Wo + Ca^{2+}$.

$(a_{Na^+}^2/a_{Ca^{2+}})$ value of $10^{3.97}$. The dark line outlines the range of $(a_{Na^+}^2/a_{Ca^{2+}})$ and $a(SiO_2)$ values for rocks that contain nepheline or plagioclase or both, but no wollastonite or melilite. However, the fact that we have designated anorthite (activity 0.05) and albite (activity 0.95) both as reacting phases means that the only point on Figure 3 that represents stable equilibrium for reactions involving plagioclase + nepheline is the intersection of the nepheline – anorthite reaction (no. 5) and the vertical nepheline – albite reaction. This point (circled in Fig. 4) lies in a region in which wollastonite is stable but grossular is not, which indicates some conflict between our assumptions and the data in Berman (1988). The "equilibrium point" can be moved inside the grossular-stable, wollastonite-unstable area by adjusting the component activities (e.g., choosing a more anorthite-rich plagioclase) or by changing the data base. As the data for nepheline are provisional only, it seems

likely that this may be the problem. The effect of using albite and anorthite activities of 0.5 is illustrated in Figure 4.

The reaction of grossular to nepheline plus wollastonite,

$$Ca_3Al_2Si_3O_{12} + SiO_2 + 2Na^+ = \\ 2NaAlSiO_4 + 2CaSiO_3 + Ca^{2+}$$
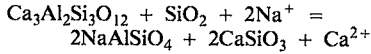
cuts across the nepheline field just above the nepheline – anorthite boundary, severely limiting the range of $(a_{Na^+}^2/a_{Ca^{2+}})$ values that could obtain during a transformation of anorthite component into nepheline, in the absence of wollastonite, at least in a fluid-dominated system (see discussion

below). It is of interest to compare the values of the ratio $(a_{Na^+}^2/a_{Ca^{2+}})$ of fluids that might be responsible for the metasomatism with those on this diagram.

To this end, we have calculated the speciation of aqueous solutions having various NaCl contents, plus an $X(CO_2)$ of 0.01, at 600°C and 2 kbar. The details of the calculation and the results are given in Appendix 2, and the $(a_{Na^+}^2/a_{Ca^{2+}})$ values of these solutions have been superimposed on the central part of Figure 3 and are shown in Figure 5. Because the $(a_{Na^+}^2/a_{Ca^{2+}})$ ratios of the mineral assemblages as determined by PTA depend on the enthalpy of nepheline, but the $(a_{Na^+}^2/a_{Ca^{2+}})$ ratios of the aqueous fluid do not, changes to the PTA data-base
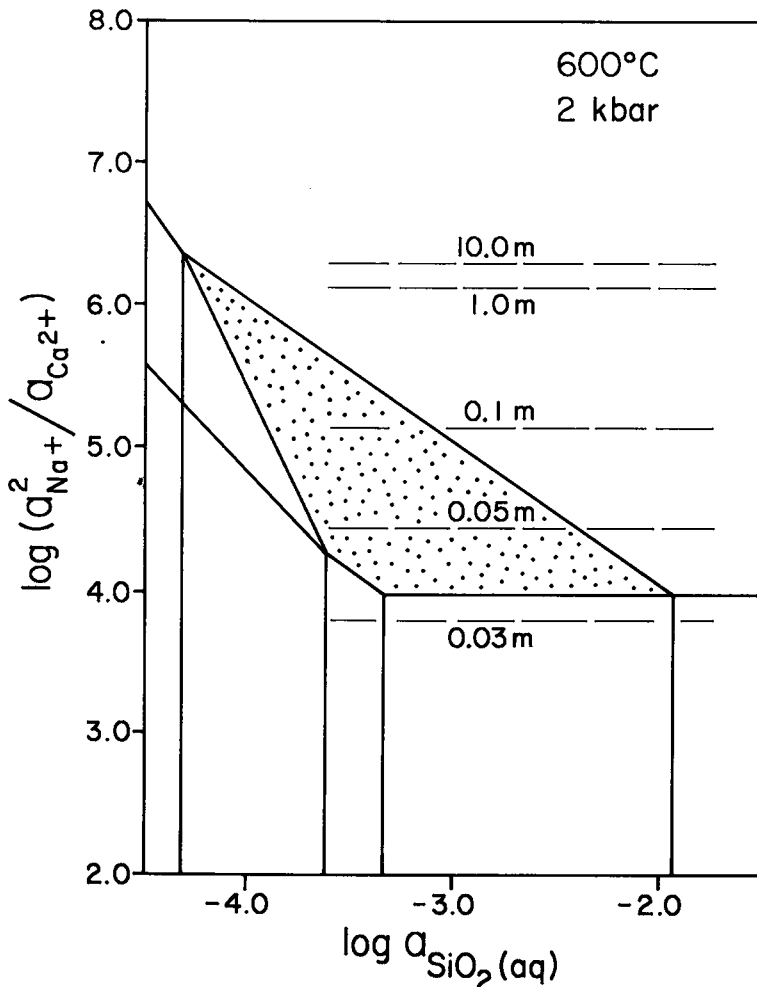

FIG. 5. The central part of Figure 3, with contours showing the $(a_{Na^+}^2/a_{Ca^{2+}})$ ratios calculated for solutions at 600°C, 2 kbar having the labeled concentrations of NaCl, K and Ca contents determined by equilibrium with feldspars, $X(CO_2)$ = 0.01, and in equilibrium with calcite. The shaded area is from Figure 3. Additional details in Appendix 2.
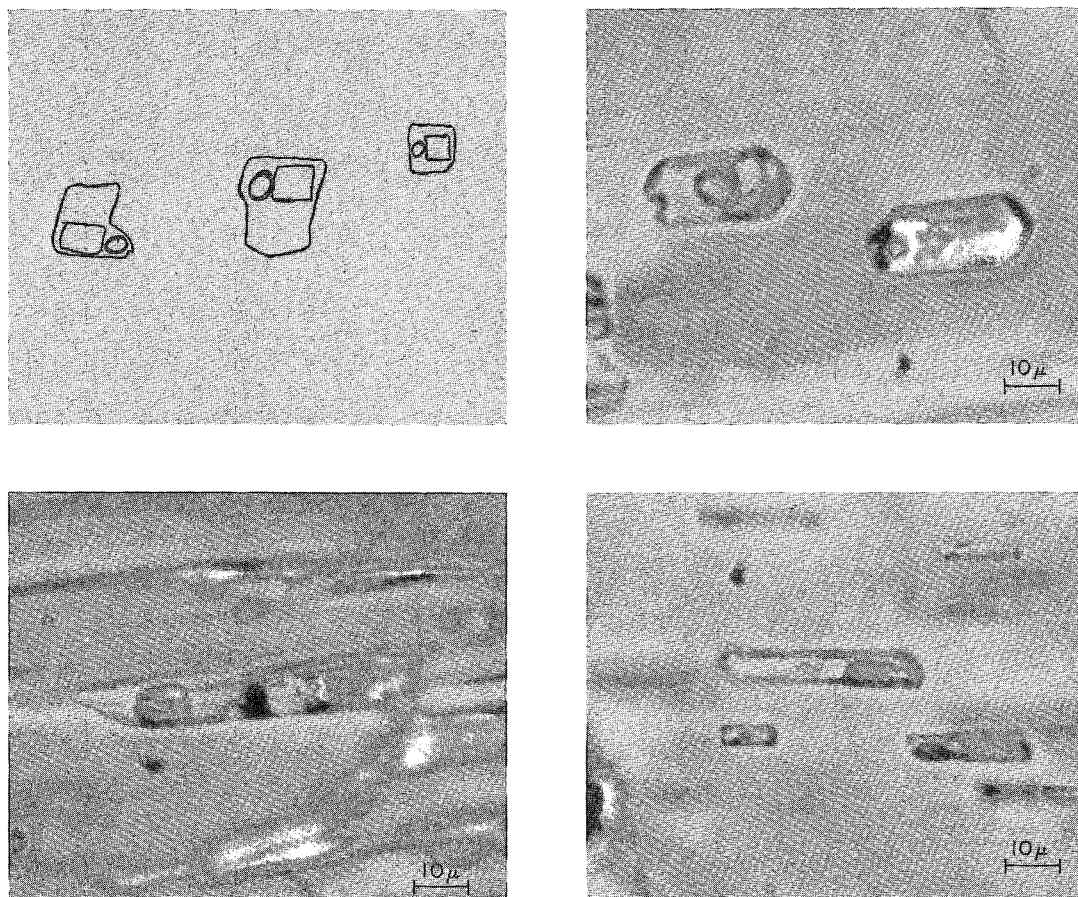
FIG. 6. In the upper left corner is a reproduction of sketches made of fluid inclusions in nepheline grains in a sample of nepheline syenite cut at 58.7 m from core from hole YR–10 (Tilley 1957). They are approximately the same size as the other inclusions shown. The other three photographs are of fluid inclusions in diopside crystals in marble from the same hole at 75.2 m.

will change the range of NaCl concentrations allowable, as discussed above. Specifically, raising the enthalpy of nepheline, which would seem to be necessary, will result in an overlap of the wollastonite-free area with much more dilute compositions of the NaCl solution.

EVIDENCE FROM FLUID INCLUSIONS

Several dozen sections were examined for fluid inclusions, mostly in material from drill hole YR–10, the hole reported on in detail by Tilley (1958). These sections were prepared from samples kindly made available by Dr. Stuart Agrell of the University of Cambridge. Although fluid inclusions containing liquid and a vapor bubble only are quite numerous, they undoubtedly are of secondary origin. Primary or pseudosecondary inclusions are extremely rare, and in fact were found in two sections only. Inclusions consisting of liquid, vapor plus a NaCl crystal were found in diopside in a marble unit intercalated with the nepheline gneisses at 58.7 m depth, and in nepheline at 75.2 m depth in the hole. The inclusions in diopside also seem to contain other crystals. Representative photographs and drawings of the fluid inclusions are shown in Figure 6. Rare though the inclusions are, they show that the nepheline and diopside did form in the presence of a highly saline fluid (e.g., >26.5 wt. % or 6.2 m NaCl if the inclusion system is H_2O–NaCl: Roedder 1984). Given the presence of microcline in the rocks, there should be a considerable proportion of KCl in the fluid.

In the absence of any compositional data on these inclusions, it is difficult to comment on their significance. Because the activity of NaCl must be extremely high to convert a potassium-bearing nepheline to sodalite, the inclusion solutions could

have been at equilibrium with the present assemblage during metamorphism. Conceivably, too, the inclusions in nepheline could represent rare survivors of an igneous premetamorphic origin. At the moment, they do not constitute evidence either for or against the idea of plagioclase – nepheline metasomatism, although given compositional determinations plus accurate thermodynamic data for nepheline, they could well be crucial.

DISCUSSION AND CONCLUSIONS

The results of the modeling as shown on Figure 5 indicate that solutions having a very restricted range of NaCl concentrations at 600°C and 2 kbar would have a tendency to change the anorthite component of an albite-rich plagioclase to nepheline, but not wollastonite, while in equilibrium with both K-feldspar and calcite, and having a $X(CO_2)$ of 0.01. The exact values of the NaCl concentration in the fluid can be determined, but they are quite sensitive to the thermodynamic data for nepheline, for which we have only provisional values.

The use of any equilibrium model for a metasomatic process can be only a beginning for the modeling process. Infiltrating fluids are not generally at equilibrium with the rocks they encounter, and the resulting reaction-paths depend on a number of factors. For example, depending on the mass ratios, the metasomatic process may be rock-dominated or fluid-dominated. In a rock-dominated system, the small window of "favorable" conditions is not necessarily detrimental to the metasomatism hypothesis, at least in the ideal sense, because fluids outside this range would produce reactions in the rocks and have their compositions "pulled into" this range, if indeed the rock lies in that range. Realistically, however, it is difficult to imagine large volumes of fluid passing through these rocks without somewhere producing conditions favoring the formation of wollastonite or sodalite (or both). But then whether or not "large volumes" are needed or could be delivered in the present case requires consideration of other aspects of the problem. The present model is a beginning only, but as such it lends little support to the nephelinization hypothesis in the sense that it shows the wide ranges of conditions favoring the formation of wollastonite.

Quite clearly, the modeling could be improved in a number of ways, but the most serious shortcoming (apart from the data for nepheline) seems to be the lack of data on carbonate complexing of Na and Ca under these conditions. Fein & Walther (1989) showed that data on carbonate complexing are not necessary to model

their results on the solubility of calcite successfully, but their concentrations are quite low compared to those considered here. The main reason for thinking that such complexing might be important is the finding of Iiyama (1965) that the $K/(K + Na)$ ratio in equilibrium with albite and K-feldspar is drastically changed (from 0.21 to about 0.04) on changing from a chloride to a carbonate system at 600°C, 1 kbar. Experimental results on associated equilibria, as noted above (Debron 1965, Cermignani & Anderson 1983), also show that carbonate-bearing solutions are quite different from chloride-bearing solutions. If these indications are valid, it would seem that inclusion of data on carbonate complexes could substantially alter the results of the speciation calculations. Although the present model does include CO_2 and calcite, removal of these makes rather little difference to the results.

Nevertheless, the topology of Figure 3 would remain the same regardless of the composition and speciation of the solutions that might interact with these rocks, and the very narrow ranges of $(a_{Na}^2 \cdot / a_{Ca^{2+}})$ and $a(SiO_2)$ allowable for the process to occur in the absence of wollastonite remains a problem for the nephelinization hypothesis.

Effect of higher pressures

After this paper was written, we became aware of the work of Anovitz & Essene (1990), who found that the pressure of metamorphism in the Haliburton – Bancroft area is probably closer to 6 kbar than to 3 kbar, as we had supposed. Fortunately, we also obtained the program SUPCRT92 (Johnson et al. 1992), which enabled us to calculate the positions of the phase boundaries in Figure 3 at pressures up to 5 kbar at 600°C, using a thermodynamic data-base which is in part quite different from that used by program PTA. Using SUPCRT92, we found that at 2 kbar, the "equilibrium point" (the intersection of reactions (5), (2) and Ne + SiO$_2$ = Ab, circled in Figures 3 and 4), lies within the shaded triangular area at both 2 and 5 kbar, as it should. In addition, although the boundaries of the shaded area shift to slightly higher SiO$_2$ values at 5 kbar, there is rather little difference in the diagrams at the two pressures, and it seems certain there would be little change in going to 6 kbar or even higher. Therefore the conclusions reached in the present context will be the same no matter what the assumed pressure of metamorphism.

work, field work and thermodynamics to answer significant geological problems. Hugh did this with matchless elegance, and is, in all the best senses of the phrase, a model petrologist. His like will not soon be seen again. We also thank S.E. Haggerty, H.C. Helgeson and R.F. Martin for their constructive comments. This research is supported by funds from the Natural Sciences and Engineering Research Council of Canada.

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APPENDIX 1.
ACTIVITIES OF MINERAL AND FLUID COMPONENTS

Albite, anorthite

The range of plagioclase compositions (An_0 to An_{30}) in the gneisses and pegmatites was shown graphically by Anderson *et al.* (1975). Leucocratic gneisses have the more Ab-rich values. As there is no unique or "best" value, we have chosen activities of 0.05 and 0.95 for $CaAl_2Si_2O_8$ and $NaAlSi_3O_8$, respectively.

Nepheline

The range of nepheline compositions also was shown by Anderson *et al.* (1975). A nepheline in the middle of the range is about $Ne_{78}Kls_{20}Qtz_2$. The activity of $NaAlSiO_4$ in a mineral of this composition at 600°C, 2 kbar is 0.50, according to the model of Roux (1979). This model accounts for the site preferences of Na and K on the basis of ion-exchange experiments, and assumes that vacancies and Ca simply reduce the number of sites available to Na and K in the larger and smaller sites, respectively.

Sodalite

The presence of both K-feldspar and albite fixes the K/(K + Na) ratio in a coexisting fluid at about 0.23 at 600°C, 2 kbar (Orville 1972). Under these conditions, the data of Wellman (1970) show the mole fraction of $Na_4Al_3Si_3O_{12}Cl$ to be 0.99. Natural sodalite is very low in Ca, but contains a variety of anions in the Cl site, so that the activity of $Na_4Al_3Si_3O_{12}Cl$ in the York River gneisses is unknown. The sodalite – nepheline boundary turns out to be not a major factor, so we have avoided assigning an activity to $Na_4Al_3Si_3O_{12}Cl$.

Grossular

Reeve (1972) and Sylvester (1973) reported all iron as ferrous in results of their electron-microprobe analyses of garnet. A more recent analysis by us, with calculation of ferrous and ferric iron from stoichiometry, shows a considerable contribution of Fe^{3+} to the total iron. The calculated composition ($Grs_{62.5}Adr_{29.9}Alm_{5.5}Fe\text{-}melan_{2.1}$) has been simplified to $Grs_{62.5}Adr_{32}Alm_{5.5}$, giving a $Ca_3Al_2Si_3O_{12}$ activity of 0.39 assuming ideal mixing on the X and Y sites. We have rounded this to 0.4. The mineral symbols used here and elsewhere in this paper are those of Kretz (1983).

Wollastonite, gehlenite, corundum

The rocks contain no wollastonite or melilite. Pure corundum occurs sparsely in the gneisses, but is generally absent. In reactions involving these minerals, $CaSiO_3$, $Ca_2Si_2O_7$ and Al_2O_3 are given activities of 1.0, as an estimate of the activities they would have if they did form.

Calcite

Calcite is abundant in the gneisses, and is quite pure. Its activity is taken as 1.0, and its presence in reaction (1) in Appendix 2 constrains the model solutions to equilibrium with calcite.

NaCl(aq)

The speciation calculations require a concentration of NaCl rather than an activity, and that is available directly from the data of Wellman (1970). He gave the equilibrium concentration of NaCl for nepheline plus sodalite and of NaCl and KCl for Ne–Kls solid solutions plus sodalite. He found an NaCl concentration of about 1.0 molal at 600°C, 2 kbar for nepheline plus sodalite. The activity of aqueous NaCl at the various conditions investigated by Wellman can be determined by applying the HKF model (Helgeson *et al.* 1981). This also has been done and may be the subject of another communication.

CO₂(aq)

The fugacity coefficients of CO_2 in concentrated NaCl solutions at several high temperatures and pressures have been calculated by Bowers & Helgeson (1983). We have converted these to activities of $CO_2(aq)$ as detailed in Appendix 3. The maximum value of $X(CO_2)$ (0.01) defined by the reactions discussed in the text corresponds to a CO_2 molality of 0.56. At 600°C, 2 kbar in pure water, this has an activity of about 0.54 (activity coefficient 0.96), using the ideal one molal standard state. The speciation calculations on the aqueous NaCl–KCl–CO_2 solutions use an activity coefficient of 1.0 for CO_2 and all other neutral species. This will not result in serious error.

APPENDIX 2.
THE SPECIATION
OF THE AQUEOUS SOLUTIONS

A. 30 unknowns

The concentrations (m_i) and activity coefficients (γ_i) of the 15 aqueous species Na⁺, K⁺, Cl⁻, NaCl°, KCl°, Ca²⁺, CaCl⁺, CaCl₂, H⁺, OH⁻, CO₂, HCO₃⁻, HCl°, NaOH°, KOH°.

B. 30 relationships

1. $a_{Ca^{2+}}a_{CO_2}/(a_{H^+}^2 a_{CaCO_3}) = K_1$
2. $a_{H^+}a_{HCO_3^-}/a_{CO_2} = K_2$
3. $a_{H^+}a_{OH^-} = K_3$
4. $a_{Na^+}a_{Cl^-}/a_{NaCl} = K_4$
5. $a_{H^+}a_{Cl^-}/a_{HCl} = K_5$
6. $a_{CaCl^+}a_{Cl^-}/a_{CaCl_2^o} = K_6$
7. $a_{Ca^{2+}}a_{Cl^-}/a_{CaCl^+} = K_7$
8. $a_{Na^+}a_{OH^-}/a_{NaOH} = K_8$
9. $a_{K^+}a_{Cl^-}/a_{KCl} = K_9$
10. $a_{K^+}a_{OH^-}/a_{KOH} = K_{10}$

In equations 1–10, $a_i = m_i \cdot \gamma_i$.

11. $m_{CO_2,total} = m_{CO_2} + m_{HCO_3^-}$
12. $m_{Ca,total} = m_{Ca^{2+}} + m_{CaCl^+} + m_{CaCl_2^o}$
13. $m_{Na,total} = m_{Na^+} + m_{NaCl^o} + m_{NaOH^o}$
14. $m_{K,total} = m_{K^+} + m_{KCl^o} + m_{KOH^o}$
15. $\sum(+charges) = \sum(-charges)$ in solution
16 to 30. $\log \gamma_i = -Z_i^2 A \bar{I}^{\frac{1}{2}}/(1 + \bar{I}^{\frac{1}{2}}) + 0.2 A Z_i^2 \bar{I}$

where Z_i is the valence of species i, A is a constant, and $\bar{I}$ is the true ionic strength.

C. Representative results:

Input:
$m_{Na,total} = 1.0$	$\log K_1 = 5.7$	$\log K_6 = -2.67$
$m_{K,total} = 0.30$	$\log K_2 = -8.0$	$\log K_7 = -5.08$
$m_{CO_2} = 0.56$	$\log K_3 = -10.853$	$\log K_8 = -2.485$
$m_{Ca,total} = 0.004$	$\log K_4 = -1.892$	$\log K_9 = -1.613$
	$\log K_5 = -3.68$	$\log K_{10} = -2.224$

Output:

	m_i	γ_i
Na^+	2.504×10^{-1}	0.40
Cl^-	2.344×10^{-1}	0.40
$NaCl^\circ$	7.442×10^{-1}	1.0
Ca^{2+}	2.849×10^{-7}	0.027
$CaCl^+$	2.124×10^{-4}	0.40
$CaCl_2^\circ$	3.787×10^{-3}	1.0
H^+	1.989×10^{-7}	0.40
OH^-	4.337×10^{-4}	0.40
CO_2	4.278×10^{-1}	1.0
HCO_3^-	1.322×10^{-1}	0.40
HCl°	3.629×10^{-5}	1.0
$NaOH^\circ$	5.395×10^{-3}	1.0
K^+	1.165×10^{-1}	0.40
KCl°	1.821×10^{-1}	1.0
KOH°	1.376×10^{-3}	1.0

$$a_{Na^+}^2/a_{Ca^{2+}} = (0.2504 \times 0.40)^2/(2.849 \times 10^{-7} \times 0.027)$$
$$= 10^{6.13} \text{ (plotted on Figure 5.)}$$

D. Notes:

1. The equations were solved with program EQBRMG, written and kindly provided by D.A. Crerar. The rather crude estimates of the activity coefficients provided by the Davies extension of the Debye-Hückel equation were used because they are very simple and are sufficient for the present purposes.

2. The values of K_3, K_4, K_5, K_8, K_9, and K_{10} are taken from Sverjensky et al. (1991). These values are similar to those from primary sources, but have been adjusted so as to be consistent with various relevant experimental data, as well as with Berman's (1988) data. Values of K_6 and K_7 are from Fein and Walther (1989). a_{H_2O} has been assumed to be 1.0.

3. The composition of a metasomatizing solution is assumed to be controlled by equilibrium with feldspars; therefore $m_{K,total}/(m_{Na,total} + m_{K,total})$ is taken as 0.23 (Orville 1963) and $m_{Ca,total}$ is taken as $(m_{Na,total}^2/249)$, where 249 is the appropriate constant at 700°C, 2 kbar, and is taken as an approximation of the constant at 600°C, 2 kbar. m_{CO_2} is constant at 0.56 ($X_{CO_2} = 0.01$). Fein & Walther (1989) found no evidence for carbonate complexing of Ca or Na at this T and P, but at much lower concentrations of Na, Ca, and CO_2.

Bowers & Helgeson (1983) provided calculated fugacity coefficients of CO_2 and H_2O in $NaCl$ – H_2O solutions at a range of temperatures, pressures, and compositions. These have been converted to activities of CO_2 and H_2O, and excess free energies calculated for each composition. The excess free energies were then fit with a two-parameter Margules equation, and the results for two concentrations of NaCl are shown in Figure 7. The lower left corner of Figure 7 is shown in Figures 8 and 9. In Figure 8, CO_2 activities in pure water at 600°C, 2 kbar, as calculated from the Margules fit parameters, are shown, together with the tangent to this curve at $X(CO_2)$ = 0. Deviations of the CO_2 activities from this tangent give Henry's Law activity coefficients. As the NaCl concentration increases, the slope of the tangent gets greater, as shown in Figure 9, but the Margules fit activities in each case are such that the Henry's Law activity coefficients at $X(CO_2) = 0.01$ are always greater than 0.95.

The Margules equation:

$$G_{CO_2}^{XS} = RT \ln \gamma_{CO_2} = (2W_{G_{H_2O}} - W_{G_{CO_2}})X_{H_2O}^2 + 2(W_{G_{CO_2}} - W_{G_{H_2O}})X_{H_2O}^3$$

The Margules parameters:

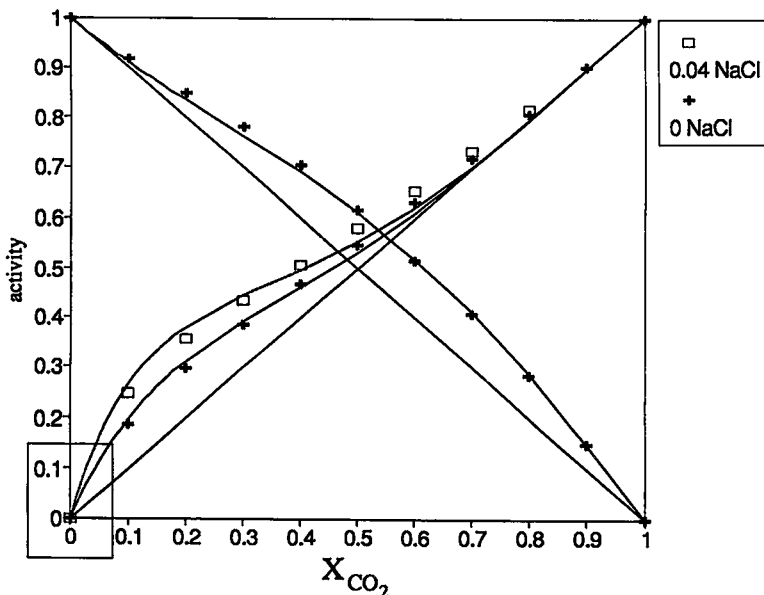| X_{NaCl}	$W_{G_{H_2O}}$	$W_{G_{CO_2}}$
0.0	1751.195	7080.569
0.01	2438.900	8323.091
0.02	2723.170	9155.435
0.03	2823.823	9759.044
0.04	2901.110	101147.356

FIG. 7. Raoult's Law activities in H_2O – CO_2 solutions at 600°C, 2 kbar, at NaCl mole fractions of 0 and 0.04. Calculated from data in Bowers & Helgeson (1983). The box at the lower left corner outlines the area of Figure 8.
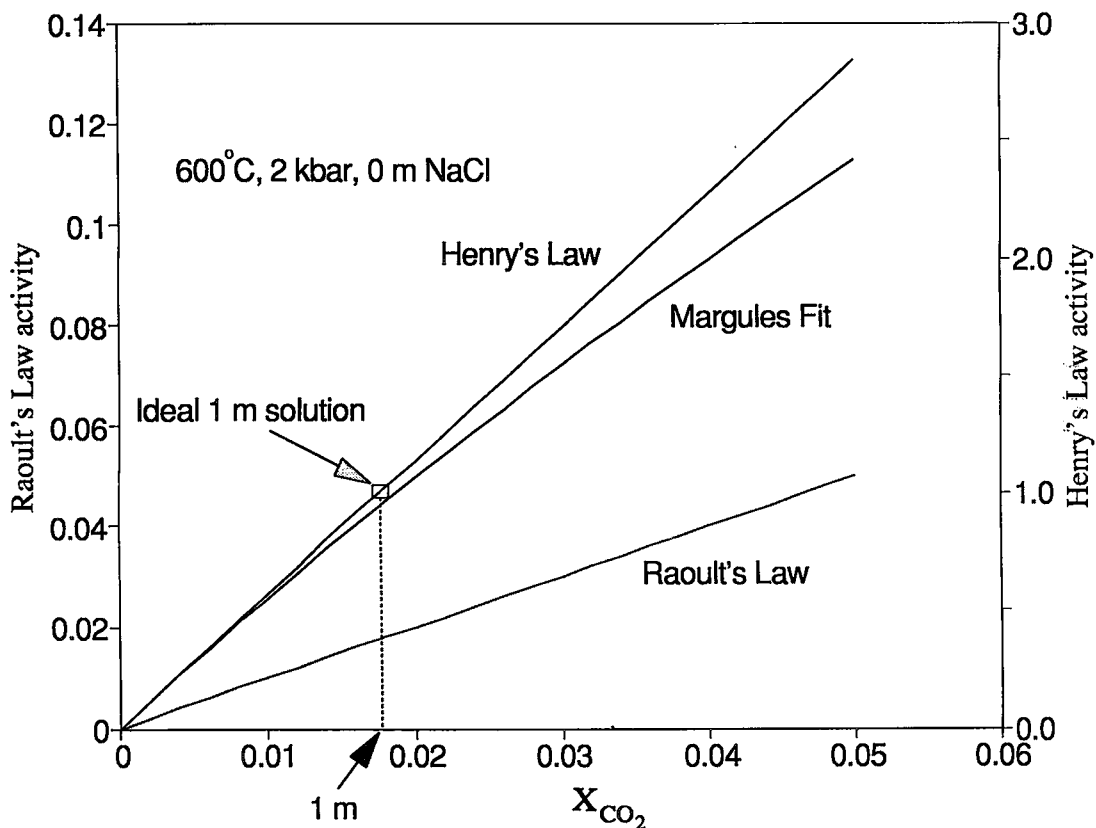
FIG. 8. Activities of CO_2 in pure water at 600°C, 2 kbar, from Figure 7. The CO_2 activities calculated from Bowers & Helgeson (1983) are labeled "Margules Fit". The tangent to this curve at $X(CO_2) = 0$ is labelled "Henry's Law". An $X(CO_2)$ of 0.0177 corresponds to 1 molal. Activities of CO_2 using the ideal 1 molal solution standard state are shown on the right-hand side of the diagram.

APPENDIX 4.
CHANGES TO THE THERMODYNAMIC
DATA-BASE OF PTA

Nepheline is not included in version 2.0 of PTA. R.G. Berman (pers. comm.) kindly supplied a provisional set of data. In the format of the PTA data-base, these are as follows:

```
–              –2087976           124.2          5.422
205.24  –759.9        –10838267      2081817344           0.0
3.15522 0.002               –0.22206        0.0006         0.0
467.15  298.15        –1.02784      0.0033945          241.835
1180.15 298.15        0.0          0.0             2393.0
```

Following the recommendation of Sverjensky et al. (1991), 1967 cal (8229.9 J) per Na atom per formula unit was then subtracted from the enthalpy of formation of all sodium-bearing minerals, in this case nepheline and low albite. Therefore, the enthalpies of nepheline and low albite used in these calculations are –2096205.9 and –3943330 J mol^{-1}, respectively.
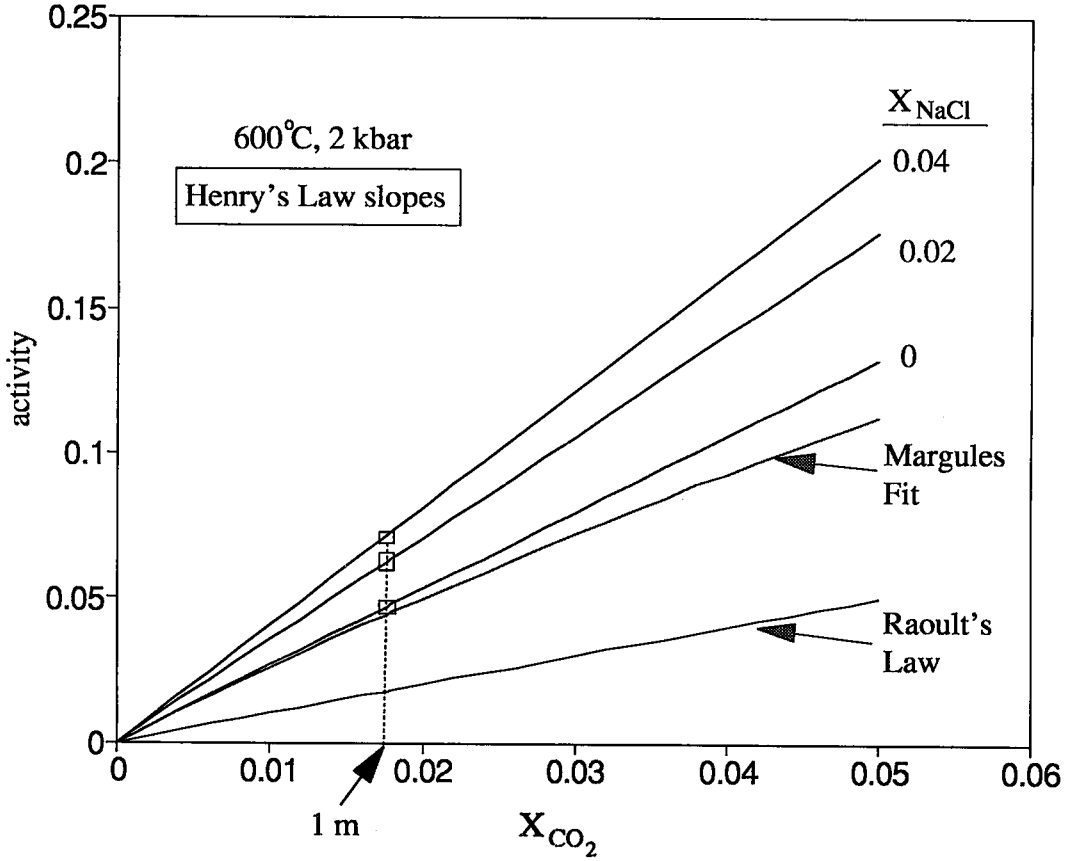
FIG. 9. Henry's Law slopes to calculated CO_2 activities in solutions having $X(NaCl)$ values of 0, 0.02 and 0.04. The calculated CO_2 activities are shown for $X(NaCl)$ = 0 only (labeled ''Margules Fit'').