*The Canadian Mineralogist*
Vol. 33, pp. 973-983 (1995)

# LOW-TEMPERATURE METAMORPHISM OF THE CROWSNEST VOLCANIC SUITE, SOUTHWESTERN ALBERTA

NORMAND J. BÉGIN, EDWARD D. GHENT AND RAYMOND E. BEIERSDORFER[1]

*Department of Geology and Geophysics, University of Calgary, Calgary, Alberta T2N 1N4*

## ABSTRACT

The analcime-phyric volcanic rocks of the Crowsnest Volcanic Suite in southwestern Alberta have been affected by low-grade metamorphism. Metamorphic mineral assemblages are characterized by analcime, which occurs as veins of analcime alone and analcime + quartz, by amygdaloidal prehnite, and by laumontite as pore-filling cement. The matrix contains a mixture of quartz, K-feldspar, albite, and chlorite. Calcite veining and pseudomorphs after igneous minerals also are common. High-silica, nonstoichiometric analcime in veins is interpreted as a product of metamorphism, not the result of igneous crystallization. Nonstoichiometric analcime may have formed as a metastable phase. The stability of laumontite + quartz restricts metamorphic temperatures to 180–280°C, for $H_2O$ pressure equal to lithostatic pressure. The presence of prehnite + laumontite + quartz in one sample constrains the pressure of metamorphism between 1.5 and 3 kbar, for $H_2O$ pressure equal to lithostatic pressure. These estimates are in consistent with maximum depths of burial of 5 to 8 km, based on structural–stratigraphic reconstruction for sedimentary rocks of the Blairmore Group, which lies stratigraphically beneath the Crowsnest volcanic suite. The restricted stability of laumontite in the presence of $CO_2$ suggests that fluids that equilibrated with laumontite were low in $CO_2$. Analcime-bearing assemblages are favored by fluids with lower $SiO_2$ and $K^+/Na^+$ activities, whereas K-feldspar – albite assemblages are favored by higher activities of $SiO_2$ and $K^+/Na^+$.

*Keywords:* Crowsnest volcanic suite, zeolites, analcime, laumontite, thermobarometry, fluid composition, low-temperature metamorphism, Alberta.

## SOMMAIRE

Les roches volcaniques à phénocristaux d'analcime de la Formation de Crowsnest, dans le sud-ouest de l'Alberta, ont subi un métamorphisme de faible température. Les assemblages de minéraux métamorphiques se distinguent par la présence d'analcime en veines avec ou sans quartz, de laumontite comme ciment dans les pores, ainsi que de préhnite amygdulaire. La matrice contient un mélange de quartz, feldspath potassique, albite et chlorite. La calcite, sous forme de veines et en pseudomorphose des minéraux ignés, est répandue. L'analcime siliceuse non stoechiométrique des veines aurait une origine métamorphique plutôt qu'ignée. Elle pourrait bien être métastable. La stabilité de laumontite + quartz limite l'intervalle des températures métamorphiques entre 180 et 300°C, pour une pression de vapeur égale à la pression lithostatique. La présence de préhnite + laumontite + quartz dans un échantillon limite la pression du métamorphisme entre 1 et 3 kbar, pour une pression de vapeur égale à la pression lithostatique. Ces estimés concordent avec une profondeur maximale dans la croûte entre 5 et 8 km, selon une reconstruction structurale et stratigraphique des roches du Groupe de Blairmore, sous-jacentes à celles de la Formation de Crowsnest. Le champ de stabilité limité de la laumontite en présence de $CO_2$ fait penser que la phase fluide coexistante avait une faible teneur en $CO_2$. Les assemblages à analcime seraient favorisés par une phase fluide à faible teneur en $SiO_2$ et faible rapport $K^+/Na^+$, tandis que les assemblages à feldspath potassique + albite seraient favorisés par une activité en $SiO_2$ et un rapport $K^+/Na^+$ plus élevés.

*Mots-clés:* roches volcaniques, Formation de Crowsnest, zéolites, analcime, laumontite, thermobarométrie, composition de fluide, métamorphisme de faible intensité, Alberta.

## INTRODUCTION

The Crowsnest Volcanic Suite (CNV) of southwestern Alberta, of Lower Cretaceous age (Norris 1964), is best known as the type occurrence of blairmorite (analcime-phyric phonolite: Peterson & Currie 1993, in prep.). The analcime-bearing volcanic rocks from the Crowsnest Pass region of Alberta were first described by Dawson (1885), Knight (1904) and MacKenzie (1914). No further work was published on the CNV until the 1960s (Norris 1964, Pearce 1967, 1970). Pearce's study emphasized the igneous petrogenesis and the volcanological and

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[1] Present address: Department of Geology, Youngstown State University, Youngstown, Ohio 44555-3612, U.S.A.

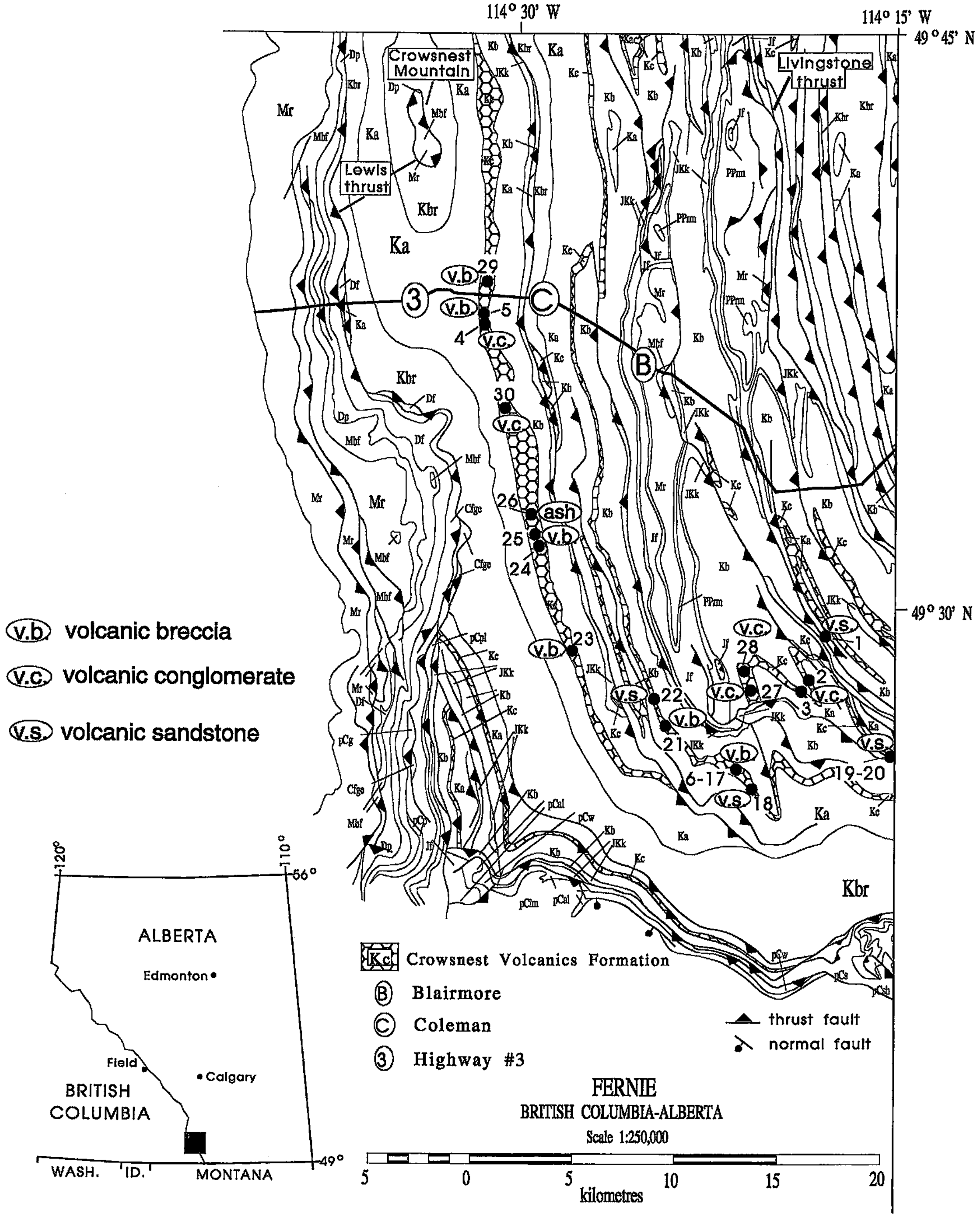

FIG. 1. Geological map of the Coleman-Blairmore area, southwestern Alberta, from the geological compilation map of the Fernie map-area (T. Peterson, pers. comm. 1993), showing the distribution of Crowsnest Volcanic Formation (patterned). Sample locations from Table 1 are indicated on the map. B: Blairmore, C: Coleman, 3: Highway 3.

sedimentological aspects. A long-standing debate concerning the primary or secondary origin of the analcime in the CNV has emerged over the years (MacKenzie 1914, Pirsson 1915, Ferguson & Edgar 1978, Karlsson & Clayton 1991, 1993, Pearce 1993). Goble *et al.* (1993) and Peterson & Currie (1993, in prep.) suggested that analcime phenocrysts crystallized from a melt, and are not the result of a replacement of primary leucite phenocrysts, as proposed by Karlsson & Clayton (1991) and others. Peterson & Currie (manuscript in prep.) have recently reviewed the mineralogical, petrological and geochemical data and have concluded that the analcime studied by Karlsson & Clayton (1991) was of primary igneous origin, but had been modified by subsolidus reactions. Important aspects of this problem are the character and extent of the low-temperature metamorphism of the CNV (recognized by several investigators). No one has documented the nature and extent of the metamorphic mineral assemblages and the physical conditions [P, T, activity of $H_2O$ $a(H_2O)$] attending the low-temperature metamorphism. In this paper, we present relevant new data and interpretations of the low-temperature metamorphism.

## GEOLOGICAL SETTING AND PETROGENESIS OF THE CNV

The CNV occurs as a series of westward-dipping, north-striking, *en échelon* thrust sheets (Fig. 1). The unit ranges up to more than 400 m in thickness (Norris 1964, Pearce 1970). The CNV consists of volcanic breccia, agglomerate, volcanogenic conglomerate, crystal tuff and tuffaceous sandstone (Norris 1964), and shows at least incipient metamorphism throughout the map unit (Fig. 1). The unit is lithologically heterogeneous over short vertical and lateral distances. On the basis of fossil flora, Norris (1964) assigned the CNV to the Albian stage of the Lower Cretaceous. Isotopic ages from extrusive fragments in the CNV are consistent with this assignment (Norris 1964). The base of the CNV is in gradational contact with volcanogenic nonmarine sandstones of the Blairmore Group (Lower Cretaceous). The top of the CNV is marked by a disconformity, above which lie marine shale and siltstone of the Blackstone Formation (Upper Cretaceous). Only the easternmost part of the CNV is exposed, as the region to the west of the study area is covered by Paleozoic and older rocks of the Lewis thrust sheet (Fig. 1). The CNV igneous lithologies have been divided into three types according to the phenocryst assemblages recognizable in the field (Peterson & Currie 1993): 1) trachyte with sanidine + melanite garnet; 2) analcime phonolite with sanidine + analcime, and 3) blairmorite with analcime cumulates only. Based on the assumption that the analcime in the CNV crystallized from a magma, several investigators (Pearce 1967, 1970, Ferguson & Edgar 1978, Peterson & Currie 1993) have concluded that the CNV originated by fractionation of a parental alkali basalt magma at depths greater than 20 km. The analcime-bearing rocks would have formed as differentiates from the fractionation of a trachytic melt (Ferguson & Edgar 1978).

## SAMPLING STRATEGY, SAMPLE PREPARATION AND ANALYTICAL PROCEDURES

The goal of field sampling of the CNV was to obtain representative samples over the entire area of outcrop. Each thrust slice was sampled at several localities along strike. A larger number of samples was obtained from the Coleman thrust slice (Fig. 1). One hundred and five hand samples were collected from 30 different localities (Fig. 1). During thin-section preparation, the epoxy was cured slowly (one week) at low temperature (<50°C) to avoid any alteration of the zeolites. Selected minerals in fifteen samples were analyzed using an ARL–SEMQ electron-probe microanalyzer, equipped with nine wavelength-dispersion spectrometers at the University of Calgary. Analytical conditions were: accelerating potential 15 kV and beam current 0.15 nA. Spot size was 1 μm for all minerals except analcime (7 μm). Counting time per analysis was 20 seconds. Silicates were used as standards, and the data were reduced using the methods of Bence & Albee (1968) and the programs outlined in Nicholls & Stout (1988). Nineteen samples were chosen for X-ray diffraction studies (XRD). The crushed sample was sieved, and a <2 μm fraction was separated by centrifuge methods. Samples were glycol-solvated at 60°C for at least 12 hours and heat-treated at 550°C for 30 minutes. A light mineral-fraction (specific gravity <2.45) was separated from the 100–200 mesh sieved portion using heavy liquids. A Philips–Norelco X-ray diffractometer with Fe$K\alpha$ radiation was operated at 40 kV accelerating potential and 20 mA current.

## PETROGRAPHY OF THE CNV AND CHEMISTRY OF METAMORPHIC MINERALS

Mineral assemblages encountered at each locality are listed in Table 1 (available from the Department of Unpublished Data, Document Delivery, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2). Igneous minerals are represented by euhedral crystals of sanidine, melanite, aegirine-augite and analcime. Titanite also is common in most samples examined. Oriented laths of sanidine define a trachytic texture in the matrix. Heterolithic fragments containing some of the minerals listed above were observed in a few samples. Xenocrystic garnet and pyroxene are present in several samples. Opaque minerals are rare and consist of pyrite with some ilmenite. For more detailed descriptions of the igneous petrography, see Pearce (1967, 1970) and Ferguson & Edgar (1978).

In most localities, the rocks of the CNV exhibit incipient to weak metamorphism. Igneous phenocrysts appear relatively unaltered. The most advanced degree of alteration occurs in finer-grained epiclastic rocks, where much of the matrix consists of calcite, chlorite and albite. Other metamorphic minerals described below, *e.g.*, laumontite, have been identified in only one or two samples.

### *Quartz*

Quartz occurs as radiating aggregates of bladed or columnar hypidioblastic crystals in the matrix (Fig. 2A), in veins of pure quartz, and in the center of a vein that is lined with analcime (see Fig. 2D). Quartz is also an abundant clastic mineral in some of the epiclastic rocks.

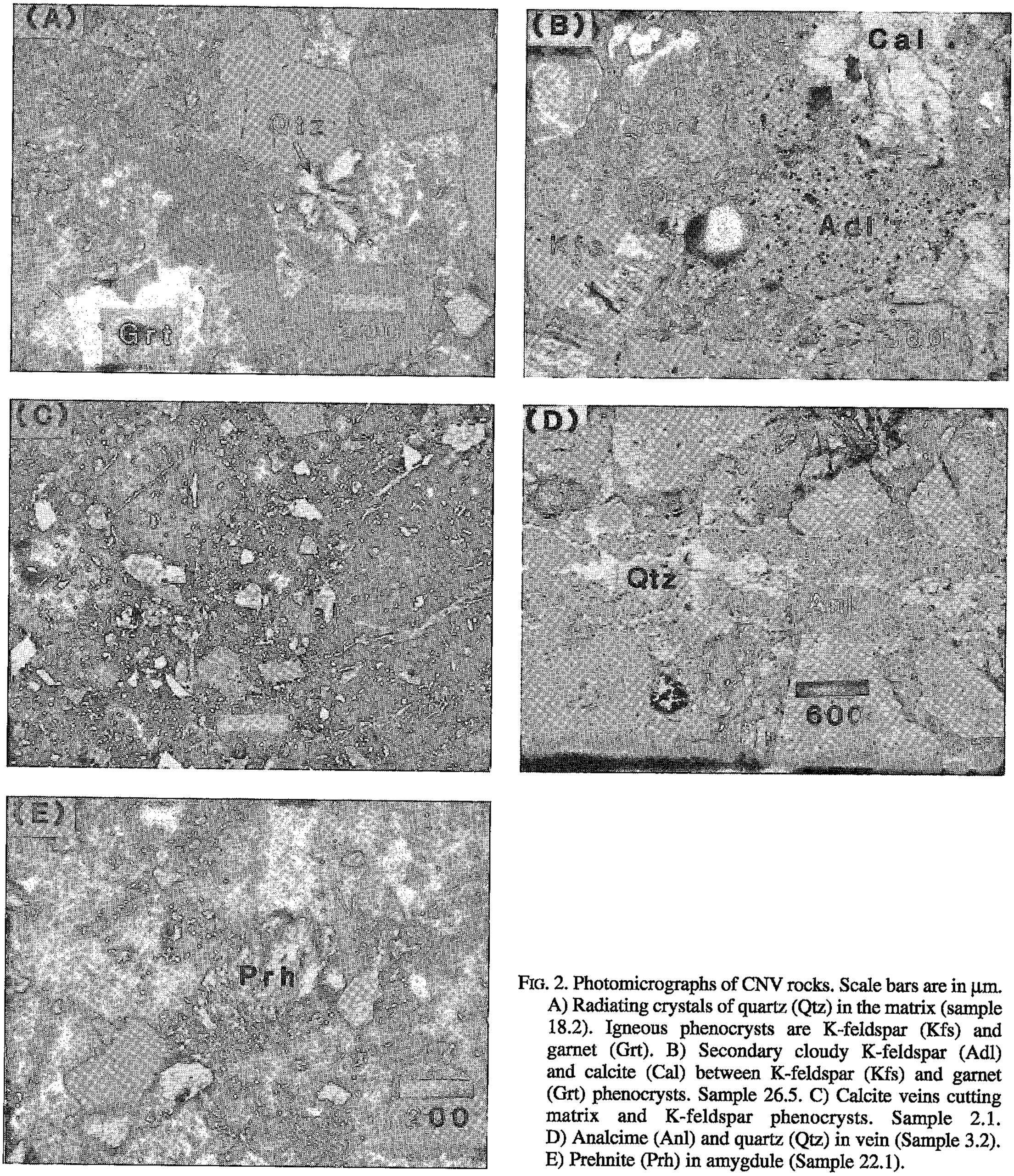

FIG. 2. Photomicrographs of CNV rocks. Scale bars are in µm. A) Radiating crystals of quartz (Qtz) in the matrix (sample 18.2). Igneous phenocrysts are K-feldspar (Kfs) and garnet (Grt). B) Secondary cloudy K-feldspar (Adl) and calcite (Cal) between K-feldspar (Kfs) and garnet (Grt) phenocrysts. Sample 26.5. C) Calcite veins cutting matrix and K-feldspar phenocrysts. Sample 2.1. D) Analcime (Anl) and quartz (Qtz) in vein (Sample 3.2). E) Prehnite (Prh) in amygdule (Sample 22.1).

TABLE 2. ELECTRON-MICROPROBE DATA ON ANALCIME, ALBITE, AND K-FELDSPAR FROM THE CROWSNEST VOLCANIC SUITE

| Sample | 10.1 anl p | 26.5 anl p | 3.2 anl p | 19.1 anl p | 3.2 anl v | 10.1 ab v | 18.2 Kfs am | 18.2 Kfs m | 26.5 Kfs m |
|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 57.35 | 58.45 | 58.55 | 56.27 | 58.64 | 68.95 | 65.03 | 63.78 | 65.98 |
| $Al_2O_3$ | 21.65 | 22.56 | 20.09 | 21.75 | 20.76 | 19.65 | 18.21 | 19.04 | 18.62 |
| $Fe_2O_3{}^a$ | 0.12 | 0.08 | 0.00 | 1.57 | 0.01 | | | | |
| CaO | 0.01 | 0.05 | 0.00 | 0.07 | 0.00 | 0.07 | 0.14 | 0.17 | 0.20 |
| $Na_2O$ | 12.31 | 10.42 | 11.66 | 12.46 | 10.65 | 11.52 | 1.95 | 1.09 | 3.75 |
| $K_2O$ | 0.02 | 0.05 | 0.35 | 0.13 | 0.65 | 0.08 | 13.95 | 14.47 | 11.43 |
| $H_2O^b$ | 8.24 | 8.34 | 7.89 | 8.06 | 8.19 | | | | |
| sum | 99.70 | 99.95 | 98.22 | 100.3 | 98.92 | 100.3 | 99.28 | 98.55 | 99.98 |

Number of atoms calculated on the basis of 8 oxygen atoms (O + OH) for analcime and 8 oxygen atoms for feldspars

| Sample | 10.1 anl p | 26.5 anl p | 3.2 anl p | 19.1 anl p | 3.2 anl v | 10.1 ab v | 18.2 Kfs am | 18.2 Kfs m | 26.5 Kfs m |
|---|---|---|---|---|---|---|---|---|---|
| Si | 2.085 | 2.100 | 2.141 | 2.053 | 2.136 | 2.999 | 3.004 | 2.972 | 2.999 |
| Al | 0.928 | 0.955 | 0.866 | 0.935 | 0.891 | 1.007 | 0.991 | 1.046 | 0.997 |
| Fe | 0.003 | 0.002 | 0.000 | 0.043 | 0.000 | | | | |
| Ca | 0.000 | 0.002 | 0.000 | 0.003 | 0.000 | 0.003 | 0.007 | 0.008 | 0.010 |
| Na | 0.868 | 0.726 | 0.827 | 0.882 | 0.752 | 0.972 | 0.175 | 0.098 | 0.331 |
| K | 0.001 | 0.002 | 0.016 | 0.006 | 0.030 | 0.004 | 0.822 | 0.860 | 0.663 |
| Si/Al | 2.247 | 2.199 | 2.472 | 2.196 | 2.397 | | | | |

All oxides expressed as weight percent. a - total Fe expressed as $Fe_2O_3$. b - calculated from stoichiometry. anl p - analcime phenocryst. anl v - analcime in vein, average of three analyses. ab v - albite in vein. Kfs am - K-feldspar in amygdule. Kfs m - K-feldspar in matrix.

### *K-feldspar*

K-feldspar occur as colorless clusters of radiating aggregates filling amygdules (Fig. 2B). Microprobe analyses of amygdaloidal K-feldspar (Table 2) indicate that the composition is closer to end-member K-feldspar, in contrast to igneous sanidine, which shows more extensive solid-solution with albite (*e.g.*, Pearce 1970, Table 2).

### *Albite*

Albite occurs as microlaths in the matrix and in amygdules. It is also found as veins in two samples (4.2 and 10.1). Electron-microprobe analyses (Table 2) indicate relatively pure albite, containing only trace amounts of K (0.05 wt.% $K_2O$) and Ca (0.09 wt.% CaO). Albite also occurs as patches within sanidine phenocrysts, probably the result of exsolution (Pearce 1970).

### *Analcime*

In addition to its occurrence as phenocrysts, analcime was observed in veins in two samples (3.2 and 26.5). In one sample (3.2), analcime occurs as idioblastic equant isotropic crystals lining a vein with quartz in the center (Fig. 2D). The other sample (26.5) contains veins composed solely of colorless interlocking xenoblastic analcime that exhibits faint birefringence. The occurrence of analcime in veins is interpreted as a product of metamorphism, not a product of igneous crystallization. Similar distinct generations of analcime have recently been described by Goble *et al.* (1993) in an analcime phonolite sill from the Proterozoic Purcell Supergroup of southwestern Alberta. The analcime in veins (Table 2) has slightly higher Si/Al and Na/(Na+K) values than in the phenocrysts. It is difficult to analyze analcime because there is likely to be appreciable loss of Na due to heating by the electron beam. Consequently, when one compares compositions documented by different investigators, it is likely that the Si/Al atomic ratio will be the least affected by the electron-microprobe analytical technique. Peterson & Currie (in prep.) reported an average ratio of Si/Al for analcime phenocrysts of 2.1, which is near the stoichiometric value. In contrast, Wilkinson & Hensel (1994) reported an Si/Al ratio of 2.9 for low-temperature analcime from a vug in a tinguaite. According to Coombs & Whetten (1967), nonstoichiometric Si-rich analcime typically occurs in sedimentary and burial metamorphic rocks, but it must be noted they considered only chemically analyzed mineral separates.

Peterson & Currie (in prep.) indicated that unaltered analcime phenocrysts contain up to 1.9 wt.% $Fe_2O_3$, but that recrystallized analcime has a low Fe content (about 0.2 wt.% $Fe_2O_3$). We also recorded very low Fe contents in vein analcime (Table 2).

### *Phyllosilicates*

Chlorite occurs as cryptocrystalline aggregates throughout the matrix of clastic rocks and as a replacement of relict phases in the groundmass of some samples. Average compositions of chlorite from four samples are listed in Table 3. Chlorite formulae were

TABLE 3. ELECTRON-MICROPROBE DATA ON PREHNITE, CELADONITE, AND CHLORITE FROM THE CROWSNEST VOLCANIC SUITE

| Sample | 22.1 prh | 27.1 cel | 3.2 chl | 5.1 chl | 19.1 chl | 22.1 chl |
|---|---|---|---|---|---|---|
| $SiO_2$ | 44.56 | 54.76 | 28.28 | 26.05 | 27.64 | 30.69 |
| $Al_2O_3$ | 20.30 | 18.53 | 19.21 | 16.30 | 18.66 | 17.83 |
| $FeO^a$ | 4.13 | 9.60 | 35.01 | 39.71 | 34.17 | 31.50 |
| MnO | 0.09 | 0.11 | 0.60 | 1.16 | 1.00 | 1.38 |
| MgO | 0.02 | 2.72 | 6.21 | 6.47 | 7.40 | 7.90 |
| CaO | 26.19 | 0.14 | 0.10 | 0.07 | 0.17 | 0.25 |
| $Na_2O$ | 0.10 | 0.67 | 0.00 | 0.00 | 0.00 | 0.00 |
| $K_2O$ | 0.00 | 9.07 | 0.56 | 0.02 | 0.08 | 1.15 |
| $H_2O^b$ | 4.28 | 4.36 | 10.89 | 10.70 | 10.87 | 11.21 |
| sum | 99.67 | 99.92 | 100.86 | 100.46 | 100.17 | 101.81 |

Number of atoms based upon 12 oxygens (O + OH) for prehnite, 11 oxygens (O + OH) for celadonite, and 14 oxygens (O + OH) for chlorite.

| Sample | 22.1 prh | 27.1 cel | 3.2 chl | 5.1 chl | 19.1 chl | 22.1 chl |
|---|---|---|---|---|---|---|
| Si | 3.105 | 3.743 | 3.055 | 2.923 | 2.994 | 3.225 |
| Al | 1.667 | 1.493 | 2.447 | 2.156 | 2.408 | 2.210 |
| Fe | 0.217 | 0.550 | 3.164 | 3.727 | 3.096 | 2.774 |
| Mn | 0.005 | 0.006 | 0.055 | 0.110 | 0.092 | 0.123 |
| Mg | 0.002 | 0.278 | 1.000 | 1.082 | 1.195 | 1.241 |
| Ca | 1.956 | 0.010 | 0.011 | 0.008 | 0.019 | 0.028 |
| Na | 0.013 | 0.088 | 0.000 | 0.000 | 0.000 | 0.000 |
| K | 0.000 | 0.791 | 0.078 | 0.003 | 0.010 | 0.152 |

All oxides in weight per cent. a - total Fe expressed as FeO. b - $H_2O$ estimated from stoichiometry. prh - prehnite. cel - celadonite. chl - chlorite.

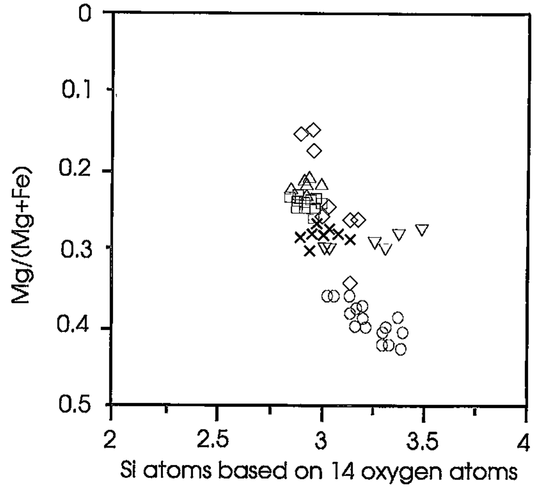

FIG. 3. Plot of Si atoms per 14 atoms of oxygen *versus* Mg/(Mg + Fe) for chlorite of the CNV. See text for discussion of calculation. Symbols: ◇ sample 3.2, △ sample 5.1, ○ sample 18.2, □ sample 19.1, ▽ sample 22.1, and × sample 27.1.

recalculated assuming 14 atoms of oxygen per formula unit, with all iron treated as $Fe^{2+}$. The chlorite contains no detectable Na, but has variable Ca and K; the calculated proportions of Si, in cations per 14 oxygen atoms, are equal to or greater than 3.0 atoms per formula unit, indicating the presence of smectite interlayers in the chlorite (Bettison & Schiffman 1988). The proportion of chlorite ($x$) in a mixed-layer smectite–chlorite can be calculated, assuming that base phases are trioctahedral. The mineral formula used by Bettison & Schiffman is: $(K,Na,Ca_{0.5})_{z-y}[(Mg,Fe,Mn)_{6-y}Al_y][Si_{8-z}Al_z]O_{20}(OH)_4{\cdot}x[(Mg,Fe)_6(OH)_{12}]$. The noninterlayer cations are (Si + Al + Fe + Mn + Mg). An end-member chlorite ($x$ = 1) would have 10 noninterlayer cations per 14 atoms of oxygen, whereas a smectite with $x$ = 0 would have 8.91 noninterlayer cations. The average proportion of chlorite in the CNV chlorite has been interpolated between these two extremes. Values of $x$ for chlorite compositions listed in Table 3 range from 0.61 to 0.91, indicating the presence of significant proportions of smectite interlayers. Chlorite compositions plotted in terms of Si cations per 14 atoms of oxygen *versus* Mg/(Mg+Fe) (Fig. 3) exhibit relatively low Mg/(Mg+Fe) values, ranging from 0.23 to 0.31.

Celadonite was identified by electron-microprobe analysis in one sample (27.1; Table 3), where it occurs as an olive-green to brown fine-grained aggregate replacing groundmass analcime. Fine-grained white mica with a ~10 Å diffraction peak is common (Table 1), but we have not chemically analyzed the phase.

### *Calcite*

Calcite is commonly observed in the CNV, as veins (Fig. 2C), in the groundmass, as replacement of igneous phenocrysts and as poikiloblastic cement.

### *Prehnite*

Prehnite was observed in only two samples (18.2 and 22.1). It occurs as colorless, radiating aggregates of bladed or columnar hypidioblastic crystals, filling amygdules (Fig. 2E). Microprobe analyses of prehnite (Table 3) indicate an average $X_{Fe}$ of 0.12, which is comparable to the $X_{Fe}$ reported for other very-low-temperature metamorphic (*e.g.*, zeolite facies) terranes (*e.g.*, Cho *et al.* 1986, Bevins *et al.* 1991).

### *Laumontite and heulandite*

Laumontite was not recognized in thin section, but was identified by X-ray diffraction in the low-specific-gravity fraction (<2.45) separated from sample 22.1, one of the two prehnite-bearing samples. Laumontite of near end-member composition was described by Miller & Ghent (1973) and Ghent & Miller (1974) as a pore-filling cement in the nonmarine sandstones of the Blairmore Group, stratigraphically underlying the CNV. Norris (1964) reported heulandite from the CNV, but we were unable to confirm this occurrence. Miller & Ghent (1973) and Ghent & Miller (1974) reported the presence of Ba–Sr-rich heulandite as a pore-filling cement in the Blairmore sandstones.

## PETROGENETIC CONSTRAINTS ON THE LOW-GRADE METAMORPHISM OF THE CNV

Although diagnostic low-variance assemblages have not been observed in the CNV, the pressure and temperature of metamorphism for the prehnite–laumontite-bearing samples can be estimated from the petrogenetic grid of Frey *et al.* (1991) and from the recent review of experimental studies for some Ca-zeolites by de Capitani & Liou (1995). The P–T stability field of laumontite is limited by the following equilibria:

$$\text{Lmt} = \text{Wa} + 2\,H_2O \quad (1)$$

$$\text{Lmt} = \text{Lws} + 2\,\text{Qtz} + 2\,H_2O \quad (2)$$

$$\text{Stb} = \text{Lmt} + 3\,\text{Qtz} + 3\,H_2O \quad (3)$$

$$\text{Hul} = \text{Lmt} + 3\,\text{Qtz} + 2\,H_2O \quad (4)$$

(Abbreviations are: Lmt laumontite, Wa wairakite, Lws lawsonite, Stb stilbite, Hul heulandite, and Qtz quartz).

Laumontite-bearing equilibria have been examined

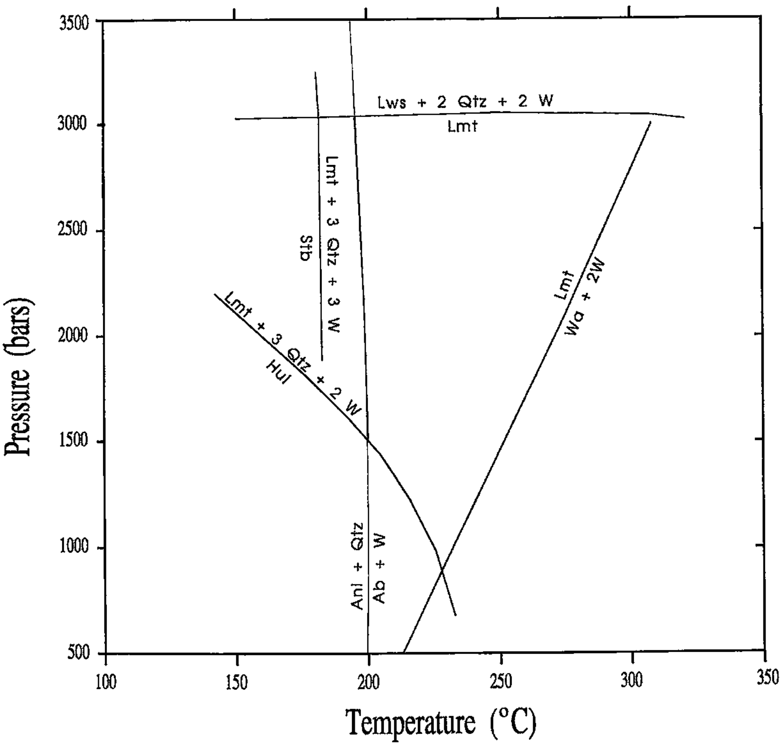

FIG. 4. Pressure – temperature diagram for mineral equilibria relevant to the metamorphism of the CNV rocks. P–T curves calculated using the program TWEEQU of Berman (1991). Thermodynamic properties of the phases in the system $CaO–Al_2O_3–SiO_2–H_2O$ are from de Capitani & Liou (1995). Thermodynamic properties of stoichiometric analcime are discussed in the text.

by de Capitani & Liou (1995). Because of the absence of stilbite and wairakite in the CNV, the stability field of laumontite and quartz is restricted to 180–300°C at 1.5–3 kbar (150–300 MPa) for $P(H_2O) = P_S$, where $P(H_2O)$ is $H_2O$ pressure, and $P_S$ is lithostatic pressure (Fig. 4). Temperatures based on chlorite thermometry (Cathelineau & Nieva 1985) from matrix chlorite give scattered results in the range of 150–300°C (Fig. 5). Geothermometry using chlorite compositions has been critically reviewed by de Caritat *et al.* (1993), who questioned the reliability of some of the calibrations. In addition, the presence of interlayers of a smectite-group mineral would cast doubt upon the reliability of the estimates. The presence of prehnite and laumontite in sample 22.1 constrains the pressure for the metamorphism between 0.9 and 2.9 kbar, for a temperature range of 200 to 250°C (Frey *et al.* 1991). This range of pressure estimates for these samples is consistent with that of maximum depths of burial, between 4.7 and 7.8 km, based upon structural–stratigraphic reconstruction (Ghent & Miller 1974) for rocks of the Blairmore Group, which stratigraphically underlie the CNV rocks. Ghent & Miller (1974) documented the occurrence of laumontite + albite + quartz assemblages in the sandstones of the underlying Blairmore Group. They detected no analcime in these rocks. Vitrinite reflectance and coal-rank in the Mesozoic sedimentary rocks underlying the CNV are consistent with laumontite + albite + quartz stability (see summary in Greenwood *et al.* 1992, p. 542-543).

The occurrence of albite or analcime and quartz in veins (*e.g.*, sample 3.2, Fig. 2D) can also be used to set limits on the P–T conditions of metamorphism. Experimental data of Liou (1971) and others indicate that the equilibrium:

$$\text{analcime} + \text{quartz} = \text{albite} + H_2O \qquad (5)$$

lies near 200°C and 1 kbar. We used the heat capacity and entropy of analcime calculated by Berman & Brown (1985) and adjusted the enthalpy ($\Delta H^0_{f,298}$ = –3307050 Joules) of stoichiometric analcime in equi-

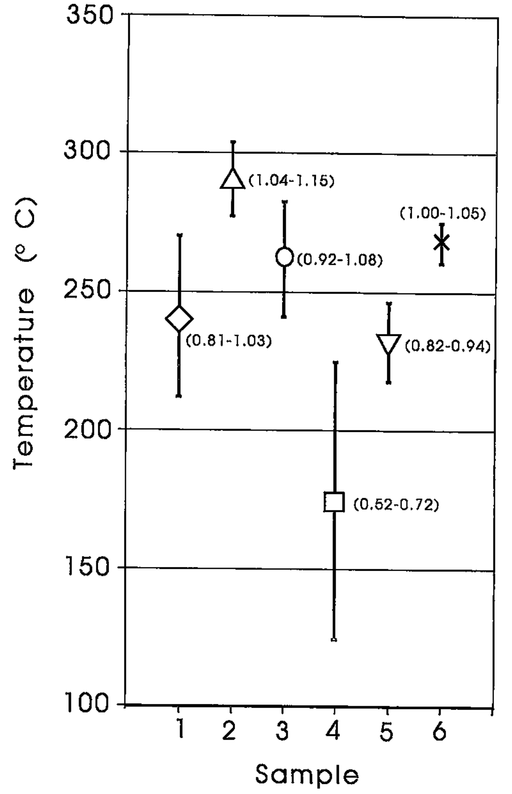

FIG. 5. Estimate of temperatures based on chlorite thermometry for matrix chlorite from the CNV. Calibration of Cathelineau & Nieva (1985). In parentheses, range of $^{IV}$Al atoms per 14 atoms of oxygen. Symbols: ◇(1) sample 3.2, Δ(2) sample 5.1, ○(3) sample 19.1, □(4) sample 22.1, ∇(5) sample 27.1, ×(6) sample 29.6B.

librium (5) until it passes through 200°C at 1 kbar, using the multiequilibrium program TWEEQU of Berman (1991).

Helgeson *et al.* (1978) argued that on the basis of the available experimental data, stoichiometric analcime could not be in equilibrium with albite at any temperature. They argued that the experimental data of Liou (1971) could be interpreted to indicate a solid solution between $NaAlSi_2O_6 \cdot H_2O$ and $SiO_2 \cdot 0.5\ H_2O$. The stability field of nonstoichiometric higher-silica analcime (+ quartz) relative to albite + $H_2O$ is displaced toward higher temperatures. Their treatment implies that higher temperature favors nonstoichiometric analcime, yet metamorphic and sedimentary analcime is typically nonstoichiometric high-Si analcime, and higher-temperature analcime is typically closer to being stoichiometric. We suggest the possiblity that the low-temperature, nonstoichiometric analcime grows and persists as a metastable phase, relative to stoichiometric analcime (+ $SiO_2$ + $H_2O$). Because of the very small $\Delta S$ and $\Delta V$ of equilibrium (5), this should not be surprising. According to the ideal-solution calculations of Helgeson *et al.* (1978), a small amount of solid solution with $X_{anl} \approx 0.99$ would displace equilibrium (5) by tens of degrees. This is a very small difference in free energy, about 40 J at 200°C (from $RT\ln X_{anl}$), and suggests that the reaction was not far from equilibrium.

The presence of nonstoichiometric metastable analcime + quartz in some veins and albite in other veins suggest that the P–T conditions of vein formation will be difficult to constrain. Variable composition of the fluid phase is another possible control (see section below).

The minimum temperature of this episode of metamorphism is difficult to constrain, particularly without independent estimates of $a(H_2O)$. In addition, many mineral reactions at *low temperatures* are *not reversible*, that is, the reactant solid phases are typically far outside of their pressure – temperature – fluid composition stability fields. Consequently, these reactants cannot be produced from the product phases by small changes in the pressure, temperature, or fluid composition. For example, the production of laumontite + albite from oligoclase (detrital) + quartz + $H_2O$ would clearly not be a reversible reaction, because one could not produce oligoclase + quartz from laumontite + albite at these low temperatures. The documented production of laumontite at temperatures of 100°C or less (Liou *et al.* 1987) is an example of this problem.

## FLUID COMPOSITION ATTENDING METAMORPHISM AND OXYGEN ISOTOPE EXCHANGE BETWEEN ANALCIME AND WATER

The presence of laumontite suggests that the fluid phase attending metamorphism of the underlying Blairmore Group locally was low in $CO_2$ (*e.g.*, Ghent & Miller 1974). The occurrence of extensive veining and amygdules in the CNV indicates the presence of an active fluid phase during metamorphism. Calculations of log ($a$K$^+$/$a$Na$^+$)–log $a$SiO$_2$ diagrams using the program TWEEQU suggest that analcime-bearing assemblages would be favored by lower values of log $(a_{K+}/a_{Na+})$. K-feldspar – albite assemblages would be favored by higher log $(a_{SiO2})$ and higher values of log $(a_{K+}/a_{Na+})$ (Fig. 6). Variable $SiO_2$ and $K^+/Na^+$ activities for the fluids must have occurred throughout the metamorphic process, since both K-feldspar – albite and analcime-bearing assemblages are observed in the CNV on a regional scale. One sample (3.2, Table 1) contains the assemblage Ab + Kfs + Qtz + Anl, which plots on an isobaric–isothermal invariant point (Fig. 6).

Stable isotopic data have been collected on analcime and sanidine from the CNV (Karlsson & Clayton 1991, Peterson & Currie, in prep.) and these data can also be used to constrain the metamorphic fluid composition

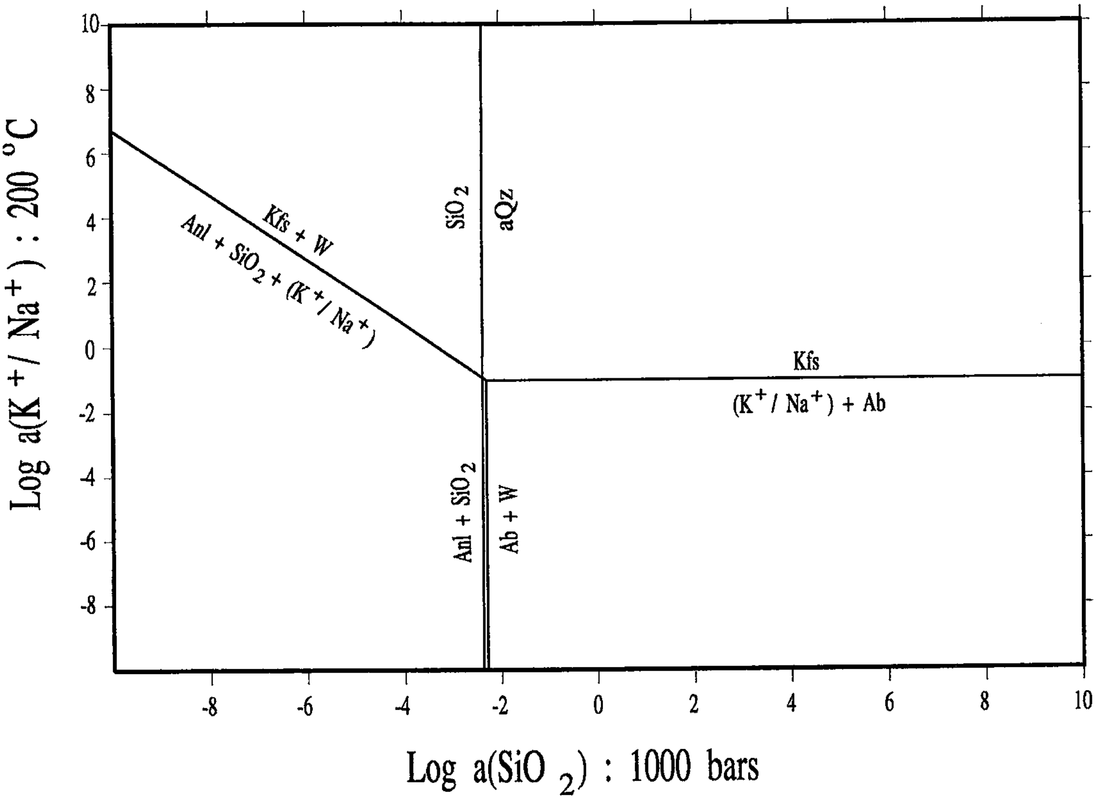

FIG. 6. Activity–activity diagram plotting log ($aK^+/aNa^+$) against log $a$SiO$_2$, calculated using the program TWEEQU of Berman (1991) at 200°C, 1 kbar and the thermodynamic properties of stoichiometric analcime discussed in the text. SiO$_2$ aqueous refers to SiO$_2$ in an aqueous solution. The quartz saturation line is indicated.

(or temperature). Oxygen isotope analyses of loosely bonded $H_2O$ molecules in analcime suggest that the analcime has exchanged with local groundwater. Isotopic analyses of framework oxygen, however, indicate that some analcime phenocrysts have retained a higher-temperature oxygen isotope signature, *e.g.*, $\delta^{18}O = 9.4‰$, whereas others have exchanged oxygen at a lower temperature (range of $\delta^{18}O = 12.2$ to 14.2‰: Karlsson & Clayton 1991, Peterson & Currie, in prep.). Karlsson & Clayton (1990a) have suggested that analcime fractionates framework oxygen isotopes with respect to water in a similar way to calcite–water. If we assume a Lower Cretaceous $\delta^{18}O$ of groundwater of −10‰ (F. Longstaffe, pers. comm., 1995), the fractionation will yield a *minimum* temperature of oxygen isotope exchange. This is because fractionation of oxygen isotopes between a solid and water should make the water heavier. For a $\delta^{18}O$ of analcime of 12.2 to 14.2‰, this yields a *minimum* temperature of about 75°C (Karlsson & Clayton 1990b).

## CONCLUSIONS

We have documented low-temperature assemblages of metamorphic minerals in the volcanic rocks of the CNV of southwestern Alberta. Analcime occurring in veins, with or without quartz, is evidence for a secondary origin. Other low-grade metamorphic minerals are laumontite in amygdules, prehnite and albite in veins and chlorite in the matrix. Given the occurrence of laumontite – prehnite – quartz, pressures of metamorphism are constrained to have been between 1.5 to 3 kbar. This is consistent with evidence from stratigraphic–structural reconstructions, suggesting an upper limit of about 2 kbar. Minimum temperatures are difficult to constrain, but maximum temperatures probably did not exceed 250–300°C. Although there is abundant calcite veining and alteration in the CNV, low contents of $CO_2$ for the metamorphic fluids are indicated by the presence of laumontite. The metamorphic fluids must have had variable activities of $SiO_2$ and $K^+/Na^+$, given the presence of analcime-bearing and K-feldspar – albite secondary assemblages.

## ACKNOWLEDGEMENTS

This project was part of an investigation on the mineralogy, geochemistry and economic mineral potential of the Crowsnest volcanic suite, as a contribution to the Canada–Alberta Mineral Development Agreement. Funding was provided by the Geological Survey of Canada to NJB and REB, and by an NSERC Research Grant (A–4379) to EDG. The authors are grateful to J.G. Liou, W.E. Trzcienski, Jr., and R.F. Martin for their helpful reviews of this paper.

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*Received January 20, 1995, revised manuscript accepted June 3, 1995.*