

Analcime phenocrysts in igneous rocks: Primary or secondary?

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ABSTRACT

The origin of analcime phenocrysts in volcanic rocks is problematic. Are they primary minerals crystallized directly from melts or are they secondary minerals formed from preexisting igneous minerals such as leucite? To address this question, we have obtained stable isotope (H, N, O), electron microprobe, and ion microprobe data for analcime-bearing samples from the Crowsnest Formation in Canada and the Colima volcanic complex in Mexico. Isotopic ratios were obtained for the framework ($\delta^{18}\text{O}_f$) and the channel water ($\delta^{18}\text{O}_{cw}$, δD) for two Crowsnest samples and one Colima sample. Both O and H isotopic ratios of channel water in all three samples fall on the meteoric water line, reflecting local meteoric water, and are clearly not magmatic. The $\delta^{18}\text{O}_f$ values for Crowsnest (13.6 and 14.2‰) and Colima (8.7‰) indicate that these analcime samples have either exchanged with external fluids at subsolidus temperatures or have formed from a preexisting igneous mineral such as leucite. Elevated $\delta^{18}\text{O}$ values of sanidine phenocrysts (8.2 and 10.9‰) demonstrate O isotopic exchange with an external reservoir in two Crowsnest trachytes. Evidence of low-temperature water-rock interaction is also found in the Colima minette SAY-104. Its whole-rock $\delta^{18}\text{O}$ value (7.6‰) is significantly higher than those of associated basanites and leucite basanites (5.2–6.1‰), and the high N content (6 ppm) and low $\delta^{15}\text{N}$ value (3.4‰) imply interaction with water either during magma genesis, transport, or postextrusion. The glass matrix in the Colima minette is also unusually H_2O rich (4 wt%) suggesting posteruption, glass-fluid interaction. Collectively our data for the Crowsnest and Colima samples favor a secondary origin for analcime in these rocks.

INTRODUCTION

Analcime phenocrysts occur most commonly in volcanic alkalic rocks such as phonolites and lamprophyres. The origin of these phenocrysts has perplexed geologists since the turn of the century (Knight, 1904; Daly, 1912; Washington, 1914; MacKenzie, 1915; Prisson, 1915). Did the crystals grow as a primary phase from a melt or did they form as a secondary phase as a result of postmagmatic alteration? If the analcime is magmatic, then H_2O -rich magmas are implied.

In an attempt to place quantitative constraints on the origin of analcime in volcanic rocks, stable isotope (H, N, O), electron microprobe, and ion microprobe data were collected from two well-documented analcime occurrences: Crowsnest Formation, Alberta, Canada and Colima volcanic complex, Jalisco, Mexico. O isotope analyses were obtained of analcime frameworks, and both O and H isotope analyses were obtained of channel water from two Crowsnest samples, 2a and PN-39E, and one Colima analcime separate from sample SAY-104. Feld-

spar phenocrysts handpicked from four Crowsnest rocks were analyzed for O isotope ratios (1e, PN-39E, WR-4, and WR-11). Additional data were also collected for the Colima sample, including whole-rock O and N isotope analysis, electron and ion microprobe measurements of various phases in SAY-104, including H_2O content and major- and trace-element concentrations.

PRIMARY IGNEOUS VS. SECONDARY REPLACEMENT HYPOTHESES

Two hypotheses have emerged to explain the origin of analcime phenocrysts in igneous rocks: the primary igneous hypothesis and the secondary replacement hypothesis. In the primary igneous hypothesis, analcime is postulated to crystallize directly from a silicate melt without the formation of any intermediate minerals. Proponents of the igneous hypothesis (Larsen and Buie, 1938; Wilkinson, 1968; Pearce, 1970; Cundari, 1973; Roux and Hamilton, 1976; Woolley and Symes, 1976; Ferguson and Edgar, 1978; Church, 1978, 1979; Edgar, 1979; Luhr and Carmichael, 1981) give one or more of the following as evidence for a primary igneous origin: (1) the crystals are euhedral, (2) the host rock is fresh and other associated

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igneous phases, in particular glass and olivine, show no visible signs of alteration, (3) other hydrous minerals such as amphibole are present, suggesting a hydrous magma, (4) differentiation trends are controlled by Na enrichment, and (5) analcime can crystallize from liquids in simple experimental systems. The following evidence is used against an igneous origin: (1) the host rock is frequently altered, (2) the experimentally determined stability of analcime is relevant within extremely limited ranges in pressure, temperature, and whole rock composition, (3) other igneous hydrous minerals are absent, indicating absence of H_2O , and (4) the differentiation trends are not controlled by Na enrichment (Nakamura and Yoder, 1974; Wilkinson, 1977; Henderson, 1984).

An alternative explanation for the origin of analcime in igneous rocks is that the analcime is secondary and has formed from a preexisting igneous mineral, most likely leucite. According to the leucite transformation hypothesis, the analcime is formed by the ion exchange reaction $leucite + Na^+ + H_2O = analcime + K^+$ at subsolidus temperatures. This transformation can occur either during cooling of the magma or after the host rock has solidified. It has been known since the experiments of Lemberg (1876) that this reaction can occur rapidly in salt solutions at low temperatures. Gupta and Fyfe (1975) recently demonstrated that the leucite transformation can go to completion in a matter of days even in dilute salt solutions at 150 °C.

Proponents of the leucite transformation hypothesis (Prisno, 1915; Gupta and Fyfe, 1975; Taylor and MacKenzie, 1975; Wilkinson, 1977; Comin-Chiaromonti et al., 1979) give the following arguments in its favor: (1) experiments show that leucite can be transformed into analcime by simple ion exchange with Na-rich fluids, and (2) the transformation is extremely rapid even on a laboratory time scale and should therefore easily go to completion over short geological time scales. Opponents of the leucite transformation hypothesis (MacKenzie, 1915; Larsen and Buie, 1938; Lyons, 1944; Wilkinson, 1968; Pearce, 1970; Woolley and Symes, 1976; Ferguson and Edgar, 1978; Luhr and Carmichael, 1981) argue against it for the following reasons: (1) leucite and analcime are rarely seen in the same rock and partially transformed leucite is quite rare, (2) analcime occurs in rocks where there is no obvious source of Na-rich fluids, (3) the transformation of leucite to analcime is accompanied by a 10% volume increase so there should be expansion cracks in the vicinity of the analcime and disruption of inclusions originally present in the leucite and that these are not observed, and (4) differentiation trends should be controlled by leucite crystallization, e.g., K depletion.

PREVIOUS WORK

Many workers have attempted to link the chemistry and the origin of analcime, motivated primarily by the experimental work of Saha (1959, 1961). He synthesized analcime in the system $NaAlSi_4O_{10}$ (nepheline)- $NaAlSi_3O_8$ (albite)- H_2O with Si/Al ratios ranging from ~1.4 to 3,

which clearly deviate from that of ideal analcime, $[Na(AlSi_2O_6) \cdot H_2O]$, in which the Si/Al ratio is 2. Saha (1961) suggested that the Si/Al ratio of natural analcime might be a useful geothermometer, although, as he pointed out, the apparent correlation of Si/Al with temperature might be spurious since his experiments were unreversed. Indeed, Coombs and Whetten (1967) concluded on the basis of about 50 analcime samples from a variety of parageneses that the silica content of analcime is influenced by the chemical environment in which analcime crystallizes as well as by the temperature. On the other hand, Ferguson and Edgar (1978) argued that the Si/Al ratio of analcime could still be used to characterize primary analcime, even though they were unable to separate igneous analcime from diagenetic analcime (see Fig. 3 in Ferguson and Edgar, 1978).

Luhr and Kyser (1989) suggested that primary igneous analcime is generally higher in Fe than secondary hydrothermal analcime (see Fig. 4 in Luhr and Kyser, 1989). It is likely, however, that the apparent difference in Fe contents reflects impurities (e.g., oxide inclusions) as noted by Coombs and Whetten (1967).

A few workers have searched for clues to the origin of analcime among minor and trace elements such as K, Ba, Cs, Sr, Rb, and Li that can substitute for the Na atoms located in the channels of the analcime structure (Larsen and Buie, 1938; Lyons, 1944; Ferguson and Edgar, 1978; Barberi and Penta, 1984; Keith et al., 1983; Luhr and Kyser, 1989). Based on the results of experimental ion exchange studies, the large ion lithophile (LIL) elements [e.g., K^+ (1.33 Å), Ba^{2+} (1.34 Å), and Cs^+ (1.82 Å)] enter analcime channels only at elevated temperatures (>200 °C) (Barrer, 1978; Keith et al., 1983), so that abnormally high concentrations of LIL elements would support a magmatic origin. Because of a lack of data, however, nobody knows what constitutes "abnormally high." Moreover, these elements may have been inherited from preexisting minerals (e.g., nepheline or leucite). Ferguson and Edgar (1978) argued against a secondary origin of analcime from the Crowsnest Formation because it has very low Rb contents (37 ppm) relative to analcime formed from leucite at Vico Volcano, Italy (4003 ppm). Comparison of trace elements in analcime from different localities is inappropriate as the trace element concentrations depend on the concentration in the host rock and possibly the precursor mineral.

Studies of the equilibrium phase relations in the quaternary system nepheline ($NaAlSi_3O_8$)-kalsilite ($KAlSi_3O_8$)-silica (SiO_2)- H_2O (Ne-Ks-Si- H_2O) and its subsystems indicate that the conditions under which analcime can coexist with a melt are very restricted in terms of pressure (5–12 kbar P_{H_2O}), temperature, and melt composition (Peters et al., 1966; Kim and Burley, 1971; Roux and Hamilton, 1976; Zeng and MacKenzie, 1984). This restricts magmatic analcime crystallization from a hydrous magma at depths of 20–50 km and at 600–660 °C which poses a serious problem to those proposing an igneous origin of analcime phenocrysts in extrusive rocks. Rapid

transport from depth of such H₂O-rich magmas would require explosive volcanism. Church (1978) has argued that analcime could not survive such violent treatment without rounding or shattering. It should be noted, however, that the synthetic systems are highly simplified and do not include important chemical components such as Mg, Fe, Ca, F, or Cl. It is unclear whether or not the addition of these components could raise the liquidus temperature of analcime by 450 °C, lower the liquidus pressure by 5 kbar, or both.

Karlsson et al. (1985) and Luhr and Kyser (1989) proposed that primary igneous and secondary analcime might have distinctive framework O isotope ratios ($\delta^{18}\text{O}_f$). Because of the structural and chemical similarities between analcime and albite, it is reasonable to assume that they should have similar O isotopic fractionation curves. Hence, primary igneous analcime should have $\delta^{18}\text{O}_f$ values between 6 and 7‰ analogous to igneous albite. Karlsson et al. (1985) determined $\delta^{18}\text{O}_f$ values ranging from 8.8‰ to 24.1‰ in seven analcime samples from igneous, hydrothermal, and sedimentary environments with $\delta^{18}\text{O}_f$ values correlated to formation temperature. Luhr and Kyser (1989) obtained a similar range in $\delta^{18}\text{O}_f$ (9.2–21.0‰) for six analcime samples. Based on their data and that of Karlsson et al. (1985), Luhr and Kyser (1989) concluded that purportedly primary igneous analcime, such as those at Colima, cannot be distinguished from hydrothermal analcime based on O isotopes alone. Karlsson and Clayton (1990a) reported $\delta^{18}\text{O}_f$ values ranging from 4.3‰ to 26.6‰ for roughly 50 analcime samples from a variety of geologic environments. Their results, reproduced in Figure 1, clearly show that $\delta^{18}\text{O}_f$ of primary igneous analcime and secondary hydrothermal or sedimentary analcime all overlap.

MATERIALS AND METHODS

Samples

Descriptions of samples and their localities are given by Pearce (1970) for PN-39E; Ferguson (1977) and Ferguson and Edgar (1978) for 2a, 1e, WR-4, and WR-11; Luhr (1980), Luhr and Carmichael (1981), and Luhr and Kyser (1989) for SAY-104.

Stable isotope analysis

Details of the experimental procedures are given by Karlsson (1988) and Karlsson and Clayton (1990a). Following Karlsson (1988), framework and channel water constituents were separated by dehydrating analcime samples in a separate vacuum line outside the fluorination lines. Karlsson (1988) showed that negligible O isotope exchange occurs between framework and channel water upon dehydration. Hence, it is possible to obtain not only precise ($1\sigma < 0.2\text{‰}$), but also accurate $\delta^{18}\text{O}_f$ values for analcime. Powdered samples (10–80 mg) were loaded into a special dehydration vessel, evacuated at room temperature for 1 h, and then heated to 2–4 °C/min to 450 °C under vacuum ($\sim 10^{-5}$ torr), at which tem-

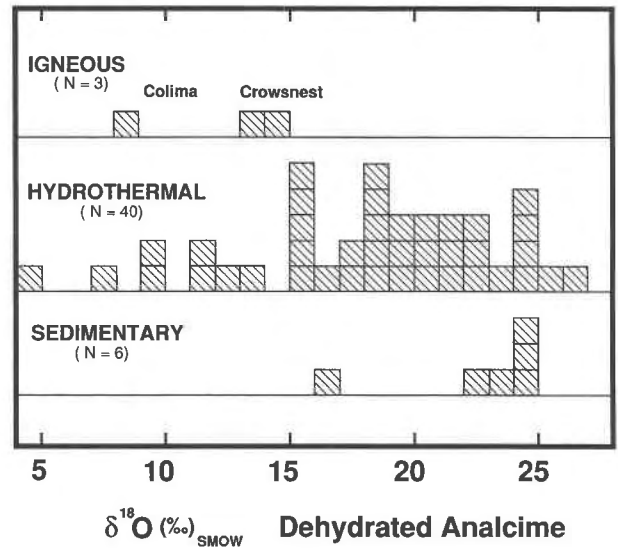


Fig. 1. Range of O isotope ratios of analcime frameworks from various environments (adapted from Karlsson and Clayton, 1990a). The figure demonstrates that the origin of igneous analcime cannot be uniquely determined solely on the basis of O isotopes.

perature dehydration was complete. Analcime loses little or no channel water up to 150 °C even under high vacuum and must be heated to at least 350 °C to ensure complete dehydration (Karlsson, 1988; Karlsson and Clayton, 1990a). During dehydration, the channel water (1.4–3.3 mg) was collected by condensing it into a cold-trap at liquid N temperatures thus isolating it for isotopic analysis. O₂ was extracted from feldspars and dehydrated analcime using the BrF₃ method of Clayton and Mayeda (1963). Channel water was either reacted with BrF₃ to liberate O₂ following O'Neil and Epstein (1966) or equilibrated with small quantities of CO₂ using the procedures of Kishima and Sakai (1980). H₂ was released from channel water by reaction with U at 700 °C (see, e.g., Bigeleisen et al., 1952).

For the whole-rock O and N isotope analyses of sample SAY-104, a rock chip was finely ground (60–200 mesh) and splits of the powder taken for each isotope analysis. Prior to analysis, both powders were outgassed under high dynamic vacuum ($\sim 10^{-5}$ torr) at 350 °C in order to rid the analcime of channel water, which might otherwise interfere with the O isotope results. Details of methods used for extraction and analysis of N₂ content and isotope ratios are given by Zhang (1988).

Isotopic measurements were obtained with ratio isotope mass spectrometers. The stable isotope results are reported in the conventional δ -notation (Craig, 1957). Values for $\delta^{18}\text{O}$ and δD are relative to SMOW, whereas $\delta^{15}\text{N}$ values are relative to AIR.

Electron microprobe analysis

Back-scattered electron images (BSE) and X-ray elemental maps (K and Na) were obtained for sample SAY-

104 using a Cameca SX-5 electron microprobe with an operating voltage of 15 kV and beam currents ranging from 0.7 to 6 nA. Spot analysis of individual phases are consistent with those reported by Luhr and Carmichael (1981) and by Luhr and Kyser (1989).

Ion microprobe analysis

Major oxide compositions, trace element concentrations, and H₂O content of some groundmass glass, analcime, olivine, and pyroxene in sample SAY-104 were determined using an AEI-IM20 ion microprobe. Analyses were performed with a 25 μ m diameter primary beam of ¹⁶O⁻ ions. Secondary ions of high energy (35–50 eV) were used during analysis in order to minimize interferences from molecular ions. Synthetic borosilicate glasses, natural analcime (SAY-104), natural staurolite, natural apatite, and CaF₂ were used as standards for oxides, H, Li, Cl, and F, respectively. Ion yields of the borosilicate glasses were normalized to the ion yield of Si. The oxide concentrations in analcime, glass, and anhydrous minerals were normalized to 91 wt%, 95 wt%, and 100 wt%, respectively. In the calculations it was assumed that ion yields for H₂O were similar for the glass and for the analcime.

CROWNSNEST ANALCIME

Introduction

The Crowsnest Formation in southwestern Alberta, Canada, is renowned for the occurrence of abundant analcime phenocrysts in its volcanics (MacKenzie, 1915; Pearce, 1970; Ferguson and Edgar, 1978). The analcime phenocrysts reach a diameter of 3 cm and the total amount of analcime in these rocks can locally be as high as 60 vol% (Pearce, 1970; Ferguson and Edgar, 1978).

The formation, which is of Lower Cretaceous age, consists mainly of agglomerates, volcanic sandstones, and tuffs, all of which are interbedded with rare lava flows and are intruded locally by dikes. The volcanic rocks in lower parts of the formation are dominantly trachyte; blairmorite occurs in the upper and younger parts of the formation. Although analcime is pervasive in the groundmass of most rocks throughout the Crowsnest Formation, analcime phenocrysts are found primarily in the analcime phonolites and blairmorites. Blairmorite is an extrusive rock type characterized by the predominance of analcime as phenocrysts and in the matrix, with only minor amounts of sanidine, pyroxene, and garnet phenocrysts. Analcime phonolite is distinguished from blairmorite by having abundant phenocrysts of sanidine, in addition to analcime (Pearce, 1970). The predominance of pyroclastics in the Crowsnest Formation, suggests that the eruptive style was predominantly explosive rather than effusive. The formation is usually interpreted as having resulted from the eruption of volcanoes located on a flood plain. The presence of water is inferred from the occurrence of sandstones and water-worked volcanic tuffs and agglomerates, although it is not known whether it was primarily marine or fresh.

Within the Crowsnest volcanics, there is widespread evidence of low-temperature alteration in veins carrying secondary minerals such as zeolites and by the alteration of primary igneous minerals such as sanidine to albite and olivine to iddingsite (Pearce, 1970; Ferguson and Edgar, 1978). Leucite, nepheline and hydrous igneous minerals are notably absent in the Crowsnest volcanics (Pearce, 1970; Ferguson and Edgar, 1978).

Results and discussion

The results of our isotopic work on minerals from the Crowsnest Formation are summarized in Table 1. The analcime framework $\delta^{18}\text{O}$ values, which are intermediate, 13.6–14.3‰ (Fig. 1), clearly lie within the range observed for hydrothermal analcime (4–27‰) as shown by Karlsson (1988) and Karlsson and Clayton (1990a). Hence the analcime phenocrysts have either undergone subsolidus exchange or formed from a preexisting igneous mineral such as leucite (Karlsson et al., 1985; Karlsson, 1988). Data from Luhr and Kyser (1989) on secondary analcime from Roccamonfina, Italy, suggest that conversion of leucite to analcime is accompanied by partial O isotopic exchange of the leucite framework. Subsidius exchange could have occurred during cooling, later during the low-temperature metamorphic event, or during both. The rapid exchange rates observed between analcime and H₂O at 300 °C are consistent with either type of subsolidus exchange (Karlsson et al., 1988; Karlsson and Clayton, 1990b). Ferguson and Edgar (1978) concluded that the Crowsnest rocks had not exchanged O isotopes with an external reservoir because pyroxene from the formation have normal igneous values of $\delta^{18}\text{O}$ (5.1–5.6‰). Pyroxene, however, is among the most resistant silicates to O isotope exchange whereas feldspars, feldspathoids, and analcime exchange much more readily (Taylor and Forrester, 1971; Karlsson and Clayton, 1990b). To test the possibility that O isotopes in the feldspars and analcime in the Crowsnest volcanics were much more extensively exchanged than pyroxene, we analyzed four sanidine separates (Table 1). Since sanidine and albite have identical O isotope fractionation curves, it is possible to use the albite-diopside equation of Chiba et al. (1989) to check the potassium feldspar data. According to this equation, the sanidine-pyroxene fractionation is 1.1‰ at magmatic temperatures (1300 K) and hence sanidine in equilibrium with pyroxene of 5.6‰ should have a $\delta^{18}\text{O}$ value of 6.7‰. The observed values ranging between 6.6 and 10.8‰ (Table 1) indicate that sanidine in 1e and PN-39E shows effects of low-temperature exchange whereas sanidine in WR-4 and WR-11 does not. The variation in the $\delta^{18}\text{O}$ values may reflect the varying extent to which the potassium feldspars have been albitized. In sample PN-39E, where O isotope ratios are available both for the potassium feldspar and the analcime, the analcime is 5.4‰ more enriched in $\delta^{18}\text{O}$ than is the associated potassium feldspar. This result is in good agreement with experimental data showing that analcime exchanges O isotopes more readily than feldspars do (Karlsson and Clayton,

TABLE 1. Values for $\delta^{18}\text{O}$ of minerals from the Crowsnest Formation

Rock type	Sample	$\delta^{18}\text{O}$ (‰) relative to SMOW		
		Potassium feldspar	Analcime frw	Analcime cw*
blairmorite	2a		14.3	-20.4
blairmorite	WR-4	6.6		
analcime phonolite	WR-11	6.6		
trachyte	1e	10.9		
trachyte	PN-39E	8.2	13.6	-22.2**

Note: The abbreviations frw and cw refer to framework and channel water, respectively.
 * Precision (esd) $\pm 0.3\text{‰}$.
 ** δD measured for the same H_2O sample is $-166 \pm 3\text{‰}$.

1990b). The main argument leveled against the formation of analcime from leucite is that Na was not available for the conversion to analcime since the water in contact with these rocks was nonmarine (MacKenzie, 1915; Pearce, 1970; Ferguson and Edgar, 1978). Albitization of sandine, however, shows that Na must have been mobile in these rocks during the low-grade metamorphism (Pearce, 1970). The channel water $\delta^{18}\text{O}$ (-22‰) and δD (-166‰) values of Crowsnest analcime (see Table 1) fall close to the meteoric water line (Craig, 1961), well outside the field proposed for magmatic water (Fig. 2), indicating a secondary origin of the channel water. This result agrees with those of Karlsson and Clayton (1990a) who showed that analcime channel water reflects the meteoric water of the sample locality. To conclude, the O isotope results indicate that the analcime phenocrysts in the Crowsnest Formation have either suffered subsolidus O isotope exchange or formed from the transformation of leucite or nepheline to analcime. The absence of hydrous primary igneous minerals such as mica or amphibole indicates that the magma was not H_2O saturated suggesting that the formation of analcime from leucite is a more viable explanation.

COLIMA ANALCIME

Introduction

The Colima minettes provide an unparalleled opportunity to determine whether or not analcime can crystallize directly from hydrous silicate melts. The analcime occurs in rock series whose mineralogy, petrochemistry, and geochemistry have been thoroughly documented (Luhr, 1980; Luhr and Carmichael, 1981, 1987; Heatherington et al., 1987). The Colima volcanic complex, situated in the Colima graben in southern Jalisco, Mexico, includes Late Quaternary (<20000 years) cinder and lava cones which form a transitional basic alkalic suite of basanites, leucite basanites, and analcime-bearing minettes. Volatile and incompatible element concentrations are high in these rocks, especially in the latter two rock types. The whole-rock compositions and mineralogies of the leucite basanites and the minettes are virtually identical, the only difference being that the leucite basanites contain leucite

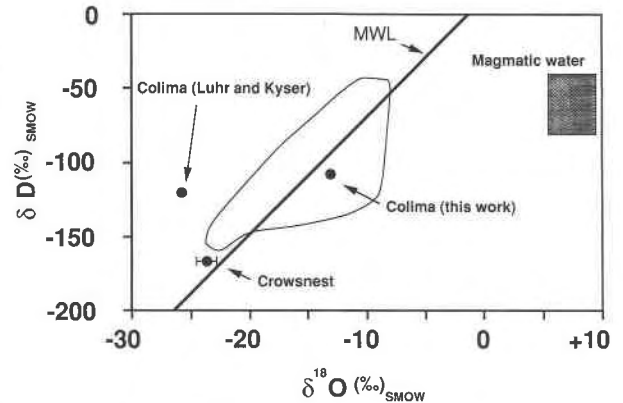


Fig. 2. Relationship between $\delta^{18}\text{O}$ and δD in analcime channel water. MWL = meteoric water line (Craig, 1961). Envelope encloses compositions of secondary hydrothermal and sedimentary analcime analyzed by Luhr and Kyser (1989) and Karlsson and Clayton (1990a). Field of magmatic water is from Sheppard (1986). Error bar shows 1σ standard deviation.

and phlogopite in their groundmass whereas the minettes contain analcime in their groundmass and phlogopite phenocrysts. Analcime and leucite have not been observed together in the same sample. Petrographically analcime and leucite cannot be distinguished from one another since they have the same appearance and mode of occurrence in thin section. Both minerals occur as round to euhedral microphenocrysts, reaching ~ 0.1 mm, in the groundmass and both contain pyroxene and titanomagnetite inclusions. Luhr and Carmichael (1981) thus failed to find any characteristic textural features that distinguished the two minerals. They could be identified only by electron microprobe analysis.

The presence of highly forsteritic (Fo_{90-94}) olivine phenocrysts with chrome-spinel inclusions in the Colima minettes suggests that the minettes are mantle-derived magmas (Luhr and Carmichael, 1987). Maximum depth of origin is limited to about 100 km by the top of the subducted Cocos plate (Heatherington et al., 1987).

One particular minette sample, SAY-104, has drawn considerable attention (Luhr and Carmichael, 1981; Karlsson et al., 1985; Hay, 1986; Karlsson, 1988; Luhr and Kyser, 1989). The sample contains analcime microphenocrysts up to 0.16 mm in diameter relatively free of inclusions and enclosed in glass, which appears fresh (Figs. 3a, 3b). Hay (1986) concluded that sample SAY-104 gives unequivocal proof of igneous origin. Luhr and Carmichael (1981) and Luhr and Kyser (1989) advocated an igneous origin (melt temperatures: $1125\text{--}1150^\circ\text{C}$) for the Colima analcime, although the former did not rule out leucite transformation as long as the transformation took place during the late stages of the crystallization of a hydrous melt.

Results

O and H isotopes. Results of O isotope analyses for the analcime framework are given in Table 2. Also included

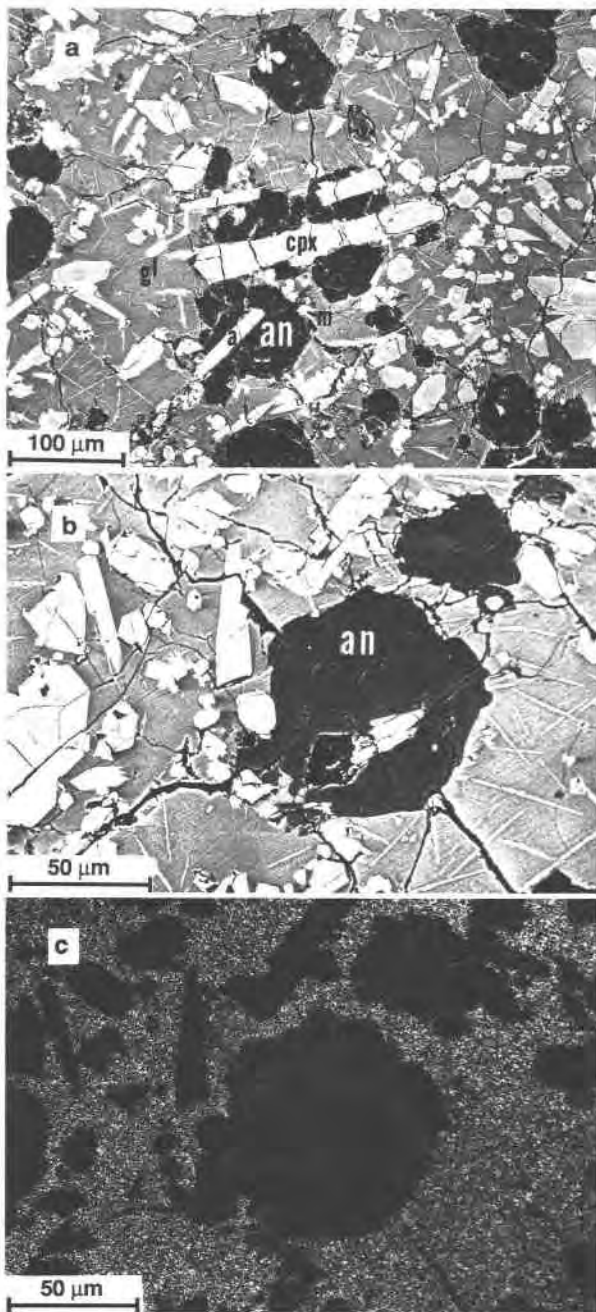


Fig. 3. Microphotographs of Colima minette SAY-104. (a) Backscattered-electron image. Microphenocrysts of analcime (an) and augite (cpx) along with apatite (a) and titanomagnetite (m) in a groundmass of glass (gl). Note that major fractures appear to radiate from analcime grains (expansion cracks?). (b) Backscattered-electron image. Close-up of an analcime microphenocryst (an). (c) X-ray elemental map. Concentration of K in the same region shown in b. K is most concentrated in glass (7 wt%) whereas little K occurs in the analcime (0.3 wt%). K is evenly distributed throughout glass and zoning is absent. Similar results were obtained on a large scale and for Na. Precision ± 0.5 wt%.

in Table 2 are O isotope data from Luhr and Carmichael (1981) and Luhr and Kyser (1989). The whole-rock $\delta^{18}\text{O}$ value for SAY-104 (7.6‰) is somewhat higher than that of other minettes (5.3 and 6.4‰), basanites (5.7 and 6.1‰), or leucite basanite (5.2‰). Except for analcime, $\delta^{18}\text{O}$ values of mineral separates ranging from 4.8 to 6.1‰ are similar to those observed in other igneous rocks (Taylor, 1968). Our $\delta^{18}\text{O}$ value of 8.7‰ for the analcime framework of sample SAY-104 is in excellent agreement with results of Luhr and Kyser (1989) after allowance for difference in SMOW standards (see note in Table 2).

O and H isotope ratios for the analcime channel water are given in the last footnote in Table 2. Isotopic ratios of channel water were also reported by Luhr and Kyser (1989) for this same sample. Although our δD value, -108‰ , agrees well with the value, -119‰ , obtained by Luhr and Kyser (1989), our $\delta^{18}\text{O}_{\text{cw}}$ value, $-13 \pm 0.3\text{‰}$ (1σ) is considerably higher than theirs, $-26 \pm 1\text{‰}$ (1σ) (Fig. 2). This discrepancy in $\delta^{18}\text{O}_{\text{cw}}$ values is far outside the analytical errors and must stem from differences in sample dehydration. We consider our value for $\delta^{18}\text{O}_{\text{cw}}$ to be more appropriate than Luhr and Kyser's since the SAY-104 sample analyzed by Luhr and Kyser (1989) behaved somewhat unusually compared to other analcimes in that most of the channel water degassed abruptly at 400–450 °C instead of between 300 and 350 °C (J.F. Luhr, personal communication, 1989). This suggests that Luhr and Kyser (1989) heated their sample too fast inducing O isotope exchange between the channel water and framework. In our experiments most of the channel water degassed gradually between 150 and 300 °C (Karlsson, 1988). The isotopic composition of channel water is close to the meteoric water line as has been observed for other analcime samples as shown in Figure 2 (Karlsson, 1988; Luhr and Kyser, 1989; Karlsson and Clayton, 1990a), and our measured $\delta^{18}\text{O}_{\text{cw}}$ value is in good agreement with a value calculated through mass balance from measured hydrated and dehydrated analcime SAY-104 (Karlsson, 1988). According to Luhr and Kyser (1989) the $\delta^{18}\text{O}$ of local ground water at Colima is -8.5‰ . Based on experimentally determined partitioning of O isotopes between analcime channel water and bulk water in the temperature range 25–400 °C, channel water in analcime is depleted in ^{18}O relative to bulk water by a constant value of $\sim 5\text{‰}$ essentially independent of temperature (Karlsson et al., 1988; Karlsson and Clayton, 1990b). Hence, if the channel water is in isotopic equilibrium with the local ground water it should have a value of -13.5‰ , in excellent agreement with $\delta^{18}\text{O}_{\text{cw}}$ value observed in this study.

N isotopes and concentration. Sample SAY-104 has 6.0 ± 0.3 ppm N_2 and a $\delta^{15}\text{N}$ value of $3.4 \pm 0.1\text{‰}$. The N_2 content is significantly higher than that of midocean ridge basalts (MORBs) and the $\delta^{15}\text{N}$ value is somewhat lower (Fig. 4).

Ion microprobe. The results of ion microprobe analyses of four analcime samples, three glasses, two augites, and one olivine in sample SAY-104 are shown in Tables 3–

TABLE 2. Compilation of $\delta^{18}\text{O}$ values of rocks and minerals from the Colima volcanic complex

Rock type	Sample	$\delta^{18}\text{O}$ (‰) relative to SMOW*						Source
		wr	grm	ol	cpx	phlog	an	
leucite basanite	SAY-5A	5.2						**
basanite	510	5.7	5.5	5.0				†
basanite	500	6.1	5.6	4.8	5.4			†
minette	8H	5.3	4.9	5.0		5.5		†
minette	7E	6.4	6.2	5.2	6.1	6.0		†
minette	SAY-104	7.6					8.7‡	This work

Note: The $\delta^{18}\text{O}$ values obtained from others have been lowered by 0.5‰ in order to readjust their numbers to an $\alpha(\text{CO}_2\text{-H}_2\text{O})$ of 1.0407 used in this study.

* Abbreviations: wr = whole rock, grm = groundmass, ol = olivine, cpx = clinopyroxene, an = analcime, phlog = phlogopite. Precision of analysis $\pm 0.2\text{‰}$.

** Analysis of T.K. Kyser. J.F. Luhr (personal communication 1989).

† Analyses by T.K. Kyser and J.R. O'Neil. From Luhr and Carmichael (1981).

‡ Framework. Isotopic measurements on the same channel water sample yield $\delta^{18}\text{O}_{\text{ow}} = -13 \pm 0.3\text{‰}$ and $\delta\text{D} = -108 \pm 3\text{‰}$.

5. Olivine and pyroxene were analyzed in order to measure background concentration of H_2O and in order to investigate the partitioning of trace elements among various phases in sample SAY-104 (Table 5). Electron microprobe analyses of the analcime and the glass from Luhr and Kyser (1989) are included for comparison. Given the limitations of the standards for the ion probe, the agreement between major element concentrations as obtained with the electron probe is satisfactory.

Ion microprobe analysis of the glass yields H_2O contents ranging from 2.9 to 4.3 wt% (Table 4). The H_2O values are considered reliable to $\pm 50\%$ or better. Minor and trace elements are in good agreement except for Sr and Cl where the electron microprobe values are higher.

Li was not detected in either glass or minerals. Small amounts of B in the glass (~ 30 ppm) and in the analcime (~ 15 ppm) are most likely contamination introduced during the sample preparation. Rb is concentrated in the analcime (189 ppm) relative to other phases (Rb ~ 82 ppm in the glass and not detected in olivine and augite). Sr, F, and Cl are strongly enriched in the glass (Sr = 3600 ppm; F = 4100 ppm; Cl = 700 ppm) relative to other phases (≤ 310 ppm).

Electron microprobe. Results of the back-scattered imaging and elemental mapping are shown in Figure 3. Analcime crystals stand out in the BSE photomicrographs because of their low mean atomic weight relative to other phases present (Figs. 3a, 3b). The X-ray map reveals no significant zonation in Na and K either in the glass or in the analcime.

Discussion

The $\delta^{18}\text{O}$ and δD values (-13‰ , -108‰) of the analcime channel water fall close to the meteoric water line and well outside the range of magmatic water compositions (Craig, 1961), indicating that the channel water is of meteoric origin and almost certainly not magmatic (Fig. 2). It is possible to estimate what the framework $\delta^{18}\text{O}$ of analcime SAY-104 as a primary igneous mineral should be by combining the results of Karlsson and Clayton

(1990a) and Chiba et al. (1989). Karlsson and Clayton (1990b) showed that analcime- H_2O fractionation curve is similar to that of calcite- H_2O . Assuming that analcime was in equilibrium with pyroxene with $\delta^{18}\text{O}$ of 6.1‰ (Table 2) and given that the calcite-diopside fractionation (Chiba et al., 1989) is 1.4‰ at magmatic temperatures (1300 K), the analcime should have framework $\delta^{18}\text{O} = 7.5\text{‰}$. The observed framework $\delta^{18}\text{O}$ value, 8.7‰ (Fig. 1), is somewhat higher than the 7.5‰ value, suggesting that the analcime has either undergone subsolidus exchange or formed from a preexisting igneous mineral such as leucite. As in the case of Crowsnest, evidence for low-temperature water-rock interaction can also be found in sample SAY-104.

Both the concentration and isotopic composition of N_2 in sample SAY-104 are indicative of interaction with water. Recently, Zhang et al. (1987) and Zhang and Clayton (1988) showed that the content and isotopic ratios of N_2 in igneous rocks can be a useful indicator of water-rock interaction. Mantle-derived rocks such as MORB typically contain small amounts of N_2 (< 1 ppm) and their $\delta^{15}\text{N}$ (relative to AIR) values range from 7 to $+15\text{‰}$ (Zhang, 1988). Any subsequent interaction with atmospheric N_2 ($\delta^{15}\text{N} = 0.0\text{‰}$) through contact with water or assimilation of N_2 -rich sediments will therefore result in an increase in the N_2 content and a lowering of the $\delta^{15}\text{N}$ value. The high concentration of N_2 indicates substantial interaction with a N_2 -rich source (Fig. 4). There are three possible N_2 sources. First, N_2 could have been added to the rock at the source region by fusion of N_2 -rich sediments on top of the subducted Cocos plate. Second, N_2 could have been introduced into the magma during its ascent to the surface from its source region by interaction with waters or assimilation of N_2 -rich country rocks. Third, N_2 could have been incorporated into the rock after extrusion during hydration of the glass. Posteruption hydration of the glass is supported by the increased whole-rock $\delta^{18}\text{O}$ value relative to the basanites, leucite basanite, and other minettes (Table 2). Such increases in $\delta^{18}\text{O}$ values have commonly been observed for rocks undergoing hydration (see, e.g., Muehlenbachs, 1987). Sample SAY-

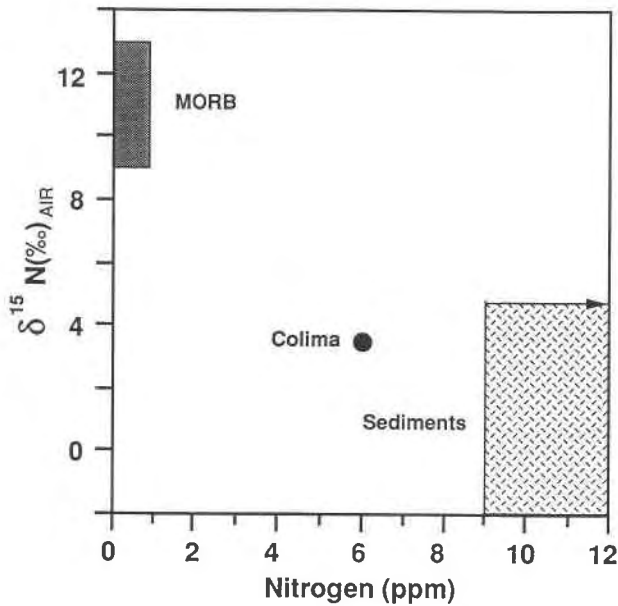


Fig. 4. Relationship between $\delta^{15}\text{N}$ and N_2 concentration in Colima sample SAY-104. MORB is average mid ocean ridge basalt. The figure suggests that sample SAY-104 has interacted with a N_2 -rich and $\delta^{15}\text{N}$ -low source such as water, sediments, or both (adapted from Zhang, 1988).

104 has suffered some loss of olivine crystals (Luhr and Carmichael, 1981). However, removal of olivine from the minettes cannot account for the observed $\delta^{18}\text{O}$ enrichment of 1.2–2.3‰, since the difference between the $\delta^{18}\text{O}$ of the olivine (mean: +5.1‰) and the groundmass $\delta^{18}\text{O}$ (mean: +5.6‰) is small. Addition of H_2O directly into the magma is also unlikely; since ground waters normally have negative $\delta^{18}\text{O}$ values, the whole-rock $\delta^{18}\text{O}$ val-

ue would have been lowered rather than increased. If the posteruption hydration hypothesis is correct then a considerable amount of H_2O must have entered the glass while leaving no visible trace of alteration.

In fact, the glass in sample SAY-104 contains an unusually high amount of H_2O , 4 wt% (Table 4), which supports a posteruption hypothesis. Unfortunately, data on H_2O solubilities in phonolitic melts are scanty and none have been obtained at 1100 °C. There is only a single low-temperature measurement by Dingwell et al. (1984). They found that a synthetic phonolite can incorporate up to 5 wt% H_2O at 1 kbar and 800 °C. Since the solubility of H_2O in melts generally decreases with increasing temperature (Burnham and Jahns, 1962; McMillan and Holloway, 1987), it seems reasonable to assume that pressures higher than 1 kbar are needed to dissolve 4 wt% in phonolitic melts at 1100 °C. By comparison it would require pressures in excess of 1.5 kbar to dissolve the same amount of H_2O in a basaltic melt at 1100 °C (Burnham and Jahns, 1962; Hamilton et al., 1964). Although some H_2O must have been present in the magma, as is evidenced by the existence of hydrous igneous minerals such as phlogopite, the bulk of H_2O in sample SAY-104 must have been added after the eruption, otherwise the eruptive mode would have been explosive rather than effusive.

In conclusion, the whole-rock N, O isotope data and the H_2O content of the glass collectively suggest that minette sample SAY-104 has interacted with water at one stage or another in its posteruption history and that the analcime is secondary. The most likely precursor mineral is leucite as this phase is present in nearby leucite basanites. Both rock types have very similar compositions and mineralogies. Leucite in the basanites is petrographically indistinguishable from analcime in the minettes.

TABLE 3. Results of ion microprobe analysis of analcime in sample SAY-104

Oxide (wt%)	IMPA*			mean	$\pm 1\sigma$	EMPA**
	1	2	3			
Li_2O	n.d.†	n.d.	n.d.	n.d.		
B_2O_3	<0.0003	<0.0007	<0.00044	0.0005	0.0002	
Na_2O	12.2	12.1	11.7	12.0	0.26	12.40
MgO	0.026	0.033	0.037	0.032	0.006	
Al_2O_3	19.9	20.0	20.1	20.0	0.1	21.59
SiO_2	57.7	57.3	57.7	57.57	0.23	55.66
K_2O	0.523	0.473	0.457	0.49	0.03	0.30
CaO	0.161	0.226	0.213	0.200	0.03	0.23
TiO_2	0.183	0.157	0.146	0.162	0.019	
MnO	0.029	0.021	0.027	0.026	0.0042	
FeO	0.9	0.8	0.74	0.81	0.08	1.17‡
Rb_2O	n.d.	n.d.	0.0189	0.0189		
SrO	n.d.	n.d.	0.031	0.031		0.12
Total				91.33		91.48
F	<0.0007	0.0026	<0.0005	<0.0072	0.0119	0.00
Cl	<0.011	<0.022	n.d.	<0.015	0.006	0.00
$\text{H}_2\text{O}\S$				8.66		8.52

* Ion microprobe analysis. For experimental conditions see text.

** Electron microprobe analysis by Luhr and Carmichael (1981) who also reported BaO content of 0.01 wt%.

† n.d. = not detected.

‡ FeO as Fe_2O_3 .

§ By difference.

TABLE 4. Results of ion microprobe analysis of glass in sample SAY-104

Oxide (wt%)	IMPA*					EMPA**	
	1	2	3	mean	$\pm 1\sigma$	Mean	$\pm 1\sigma$
Li ₂ O	n.d.†	n.d.	n.d.				
B ₂ O ₃	<0.0031	<0.0027	<0.0028	<0.0029	0.0002		
Na ₂ O	5.06	4.16	5.40	4.87	0.64	5.53	0.14
MgO	2.06	3.88	3.18	3.04	0.92	1.25	0.16
Al ₂ O ₃	16.4	15.2	15.2	15.60	0.69	18.0	0.26
SiO ₂	55.0	50.6	53.8	53.13	2.27	53.9	0.65
P ₂ O ₅						0.60	
K ₂ O	8.32	8.02	4.84	7.06	1.92	6.76	0.24
CaO	2.34	3.00	6.19	3.84	2.06	2.58	0.27
TiO ₂	1.71	1.93	1.54	1.73	0.20	1.83	0.10
MnO	0.09	0.15	0.12	0.12	0.03	0.11	0.01
FeO	3.50	8.44	4.71	5.55	2.57	2.74	0.13
Rb ₂ O	n.d.	n.d.	<0.0082	<0.0082			
SrO	n.d.	n.d.	0.36	0.36		0.69	
BaO						0.44	
Total	94.5	95.4	95.0	95.3		95.3	
F	0.18	<0.82	0.22	41	0.36	0.42	
Cl	<0.019		<0.12	<0.05	0.06	0.24	
H ₂ O	4.30	2.90	3.98	3.73	0.73	4.7‡	

* Ion microprobe analysis. For experimental conditions see text.

** Electron microprobe analysis by Luhr and Kyser (1989). The glass total also includes 0.19 wt% SO₃.

† n.d. = not detected.

‡ By difference.

Such similarities, especially in the mode of occurrence of leucite and analcime, seem highly fortuitous if the melts that generated these rocks differed only in their H₂O contents, but would be expected if the analcime formed from the leucite. The transformation of leucite to analcime must have occurred at some stage during cooling of the lava flow after eruption. The question is when and how the hydration of the glass fits into this scheme. Since glass is present, the lava must have cooled rapidly. However, this does not imply that the lava temperature fell abruptly from ~1100 °C to ambient temperature, but only that the temperature dropped sharply below the transition point of the glass. Hence, the lava may have first cooled rapidly by several hundred degrees and then cooled at a slower rate. Thus, there could have been sufficient time to allow the leucite-analcime transformation to go to completion. Taylor and MacKenzie (1975) demonstrated experimentally that this transformation can occur upon cooling. They held charges of the appropriate compositions such that leucite was stable in the Ne-Ks-Si system at 2 kbar P_{H_2O} and 840 °C for a specified number of hours. Subsequently the samples were cooled to room temperature at varying rates. In all their experiments they observed glass and leucite in the products. Moreover, the leucite was in varying stages of reacting to analcime. Taylor and MacKenzie (1975) noted that the exsolution rate was very fast and might ultimately lead to the generation of analcime phenocrysts. However, such subsolidus transformation of leucite into analcime probably did not occur in minette SAY-104 since the scheme of Taylor and MacKenzie (1975) requires a high initial concentration of H₂O in the melt. It is more likely that the leucite-analcime transformation in SAY-104 and the hydration of the glass were contemporaneous.

The leucite-analcime transformation is accompanied by a 10% volume increase. If the mineral transformation occurred after the glass had solidified, as has been maintained here, then some expansion cracks could have resulted. Although Figure 3 shows that cracks are indeed present in sample SAY-104, it remains to be determined whether they could have resulted from such an expansion. If the leucite was transformed to analcime in sample SAY-104 it must have done so without leaving obvious remnants of the preexisting leucite or marked traces of K- or Na-zoning in the glass (Figs. 3b, 3c).

The two most serious objections that can be raised to

TABLE 5. Results of ion microprobe analysis of olivine and pyroxene in sample SAY-104

Oxide (wt%)	Olivine	Pyroxene	
		1	2
Li ₂ O	n.d.*	n.d.	n.d.
B ₂ O ₃	n.d.	n.d.	n.d.
Na ₂ O	0.02	0.44	0.15
MgO	39.1	12.5	16.4
Al ₂ O ₃	0.03	5.86	1.48
SiO ₂	45.9	43.8	51.8
K ₂ O	0.02	0.17	0.02
CaO	0.23	24.1	21.5
TiO ₂	0.02	1.88	0.71
MnO	0.29	0.18	0.20
FeO**	14.9	11.4	7.73
Rb ₂ O	n.d.	n.d.	n.d.
SrO	n.d.	n.d.	n.d.
Total	100.2	100.3	100.0
F < 0.0006	<0.013	<0.0039	
Cl < 0.0050	<0.0024	<0.0050	
H ₂ O	<0.048	<0.36	<0.090

* n.d. = not detected.

** FeO as Fe₂O₃.

the hypothesis of post-hydration transformation of leucite to analcime are the apparent freshness of the glass and the survival of leucite in the leucite basanites. As was discussed earlier, there are no visible signs of alteration in sample SAY-104 in either the primary minerals or the glass. However, hydration and increases in $\delta^{18}\text{O}$ in volcanic glasses can occur with no petrographically detectable alteration (see, e.g., Kyser et al., 1986 and Muehlenbachs, 1987).

A second objection involves survival of leucite in the leucite basanites. A possible explanation is that the leucite basanites underwent less posteruption hydration than the minettes. A whole-rock wet chemical analysis (see Table 3 in Luhr and Carmichael, 1981) and the low whole-rock $\delta^{18}\text{O}$ value of leucite-basanite SAY-5A both suggest negligible hydration (Table 2). Modal analysis by Luhr (1980) and Luhr and Carmichael (1981) revealed that the leucite basanites contain little or no glass in their groundmass while at least half of the minettes contain glass. The difference in the hydration levels of the leucite basanites may thus stem from the amount of glass present. A leucite enclosed in hydrous glass is presumably much more readily transformed into analcime than a leucite located in holocrystalline matrix of ferromagnesian minerals, principally because the raw material necessary to complete the leucite-analcime transformation is more readily available in a glass than in a holocrystalline matrix. Further studies of the leucite-analcime transformation are needed in order to clarify the transformation process.

CONCLUSIONS

Our results show that the Crowsnest and Colima analcime samples have either undergone subsolidus O isotopic exchange or formed from preexisting leucite crystals. Evidence exists for low-temperature water-rock interaction in analcime-bearing rocks from both locales. At Crowsnest, primary igneous $\delta^{18}\text{O}$ values of some sanidine phenocrysts have been perturbed. At Colima, minette SAY-104 has an elevated whole-rock $\delta^{18}\text{O}$ value compared to associated basanites and leucite basanites and a high whole-rock N_2 content coupled with a low $\delta^{15}\text{N}$ value compared to MORB. Its glass is unusually rich in H_2O .

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