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Primary igneous analcime: The Colima minettes

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Abstract

Major-element compositions, cell constants, and oxygen- and hydrogen-isotope compositions are presented for six analcimes from differing geologic environments, including proposed primary (P-type) analcime microphenocrysts from a late Quaternary minette lava near Colima, Mexico. The Colima analcime has $X_{\mathrm{Si,tet}} = 0.684$, $a_0 = 13.712$ Å, and one of the lowest $\delta^{18}O$ values yet recorded for analcime (+9.2‰). The major difficulty in identifying primary (P-type) igneous analcime is distinguishing it from analcime formed by ion-exchange conversion of leucite (L-type analcime) or other precursor minerals. Petrographic criteria are shown to be unreliable in discriminating P and L analcimes, although the higher K_2O and Rb contents and $\delta^{18}O$ values of L-type crystals may be diagnostic. P- and L-type analcimes can be distinguished from classic hydrothermal varieties (H-type) by the lower Fe contents of the latter. H-type analcimes, however, can have $\delta^{18}O$ values as low as 8.9‰ and cannot be distinguished from P-type analcimes by this criterion. Analcimes formed from volcanic glass or zeolite precursors in saline, alkaline lakes (S-type) or metamorphic sequences (M-type) can be distinguished from other varieties by their higher silica contents, smaller cell constants, and higher $\delta^{18}O$ values of >+17.7‰. For all types of analcime, $\delta^{18}O$ of the channel water does not correlate with $\delta^{18}O$ of the framework oxygen. With the exception of the P-type Colima sample, analcime channel waters have $\delta^{18}O$ and δD values that fall on the meteoric water line, but differ from modern meteoric water at the individual sample sites. The channel waters may reflect fluids that entered the analcime shortly after the mineral formed and have not been replaced by more modern waters. The Colima analcime has $\delta^{18}O$ slightly higher than expected for magmatic analcime, based on exchange partitioning with mafic minerals in the Colima minettes. This enrichment in framework $\delta^{18}O$ and the distinct isotopic composition of the channel water in the Colima analcime indicates that exchange between channel water and framework oxygen has occurred.

In previous discussions of primary igneous analcime, most attention has focused on blairmorites and analcimites containing centimeter-sized euhedral phenocrysts of analcime in the absence of other primary hydrous minerals. We consider these rocks to be unlikely hosts for P-type analcime, which is far more likely to occur as microphenocrysts and groundmass microlites in mica- or hornblende-bearing lamprophyres, magmas characterized by high water contents and silica undersaturation. The Quaternary minettes from Colima are the youngest and freshest lamprophyres yet described and appear to represent the strongest case for primary igneous analcime.

Introduction

Historically, petrographers have interpreted euhedral phenocrysts or microphenocrysts of analcime in mafic alkalic igneous rocks as primary (P-type) crystals that precipitated directly from a silicate melt (Pirsson, 1896; Washington, 1914; Tyrell, 1928; Larsen and Buie, 1938; Lonsdale, 1940; Harker, 1954; Wilkinson, 1965, 1968; Pearce, 1970; Williams et al., 1982). In this view, analcime is stable from late magmatic stages through low-temperature dueteric processes, and the different environments of analcime formation can be distinguished by microscopic texture (Lonsdale, 1940). In the last few decades, however, experimental results have turned the tide of opinion away from the concept of primary, magmatic analcime. Experiments have shown that leucite, nepheline, albite, and other minerals can be rapidly converted to analcime by reaction with aqueous solutions at low temperatures (Saha, 1961; Gupta and Fyfe, 1975). In addition, phase-equilibrium experiments in the synthetic system $NaAlSiO_4$-$KAlSiO_4$-SiO_2-H_2O have demonstrated that analcime and silicate melt cannot coexist above 650 °C or below about 5-kbar pressure under water-sat-

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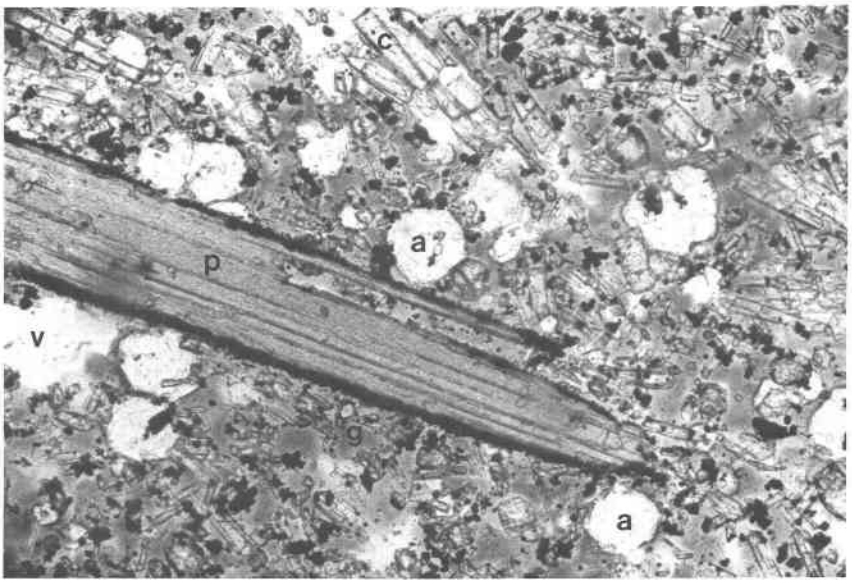

Fig. 1. Photomicrograph of proposed primary (P-type) analcime microphenocrysts (a) in Colima minette SAY-104. Also present are phlogopite (p), clinopyroxene (c), and titanomagnetite microlites in clear brown glass (g) with vesicles (v). Field of view = 0.35 mm.

urated conditions (Peters et al., 1966; Morse, 1968; Boettcher and Wyllie, 1969; Kim and Burley, 1971; Liou, 1971; Roux and Hamilton, 1976). In hydrothermal experiments on a natural analcime-bearing crinanite from the Dippin sill, analcime was absent above 400 °C (Henderson and Gibb, 1977). Because the crystallization temperatures of most analcime-bearing igneous rocks are thought to be much higher, euhedral analcime crystals in igneous rocks are now generally explained as low-temperature alteration products of leucite, nepheline, or other precursor minerals (Rock, 1977; Wilkinson, 1977; Comin-Chiaramonti et al., 1979).

Although we concur with this interpretation for most analcime-phyric samples described in the literature, we argue that the most likely rock types to contain primary igneous analcime are lamprophyres. These are mafic alkalic rocks containing phenocrysts of Mg-mica or amphibole and groundmass feldspars (Williams et al., 1982), features consistent with high magmatic water contents. Unfortunately, most lamprophyres occur as dikes that are very old and substantially altered, thus rendering them ill-suited to test for primary analcime. Luhr and Carmichael (1981) described Quaternary basanites gradational to analcime-bearing minettes near Volcan Colima in western Mexico. Minettes are the most common variety of mica lamprophyre, with K/Na > 1 and characteristically high Ba and Sr contents. The Colima samples are the youngest and freshest minettes yet reported, and we consider them the best candidates for primary analcime. In this paper, the proposed primary (P-type) analcime from Colima is compared with analcimes from other geologic environments, using major-element compositions, cubic cell constants, and oxygen- and hydrogen-isotope compositions.

Samples studied and techniques

Analcime characteristically forms as a secondary mineral from alteration of zeolites, volcanic glass, feldspathoids, or feldspars in a broad range of geologic and hydrologic environments. These include saline, alkaline lakes (S-type), hydrothermal veinlets (H-type), low-grade burial metamorphic sequences (M-type), pelagic sedimentary rocks (Hay, 1966, 1978, 1986), and from precursors of primary leucite and perhaps other feldspathoids in igneous rocks (L-type). In addition to the proposed P-type analcime from Colima, five other analcimes were investigated, representing L, S, and H varieties:

1. Colima minette *SAY-104* was chosen to represent the proposed primary (P-type) analcime. The sample location is shown on the map of Luhr and Carmichael (1981). Whole-rock and glass analyses for lava sample SAY-104 are given in Table 1. SAY-104 differs from other Colima minettes in its lack of feldspars. In addition to olivine (5.1 vol%) with spinel inclusions, clinopyroxene (16.6%), phlogopite (0.4%), and apatite, SAY-104 contains more than 8.3% euhedral analcime microphenocrysts (up to 0.16 mm diameter) encased in clear brown glass (Fig. 1). These crystals are completely homogeneous and unaltered and may contain small clinopyroxene and titanomagnetite inclusions, identical to microlites in the surrounding glass. The lack of feldspars and the large size of analcimes in SAY-104 may have resulted from the failure of feldspars to nucleate upon eruptive quenching, a common development in experimental cooling-rate studies (Lofgren, 1980). A histogram of K/Na ratios for the various Colima alkaline samples is shown in Figure 2. Surprisingly, there is no systematic difference in K/Na between the basanites and minettes, although the three highest ratios are clearly related to high abundances of phenocrystic phlogopite.

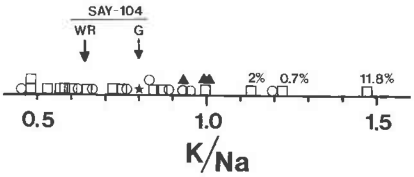

Fig. 2. Whole-rock molar K/Na ratios for 27 basanite-minette samples from Colima (Luhr and Carmichael, 1981; Luhr, 1980). Open circles are basanites, open squares are minettes, and closed triangles show three leucite-bearing basanites. The three minettes with the highest K/Na values have the highest modal phlogopite contents as labeled (2 vol%, 0.7%, 11.8%). The whole-rock (WR) and glass (G = star) analyses of SAY 104 from Table 1 are indicated. [The Na_2O and K_2O values for Colima samples SAY-5A and SAY-6E were reversed in the above references: SAY-5A—2.55 wt% Na_2O, 3.85% K_2O; SAY-6E—2.77% Na_2O, 4.16% K_2O.]

Table 1. Colima minette SAY-104: whole-rock and glass analyses (wt%)

SAY-104	Whole rock	Glass
SiO_2	50.20	53.91(0.65)
TiO_2	1.80	1.83(0.10)
Al_2O_3	13.05	18.03(0.26)
FeO_T	7.79	2.74(0.13)
MnO	0.14	0.11(0.01)
MgO	8.58	1.25(0.16)
CaO	9.56	2.58(0.27)
Na_2O	3.79	5.53(0.14)
K_2O	3.72	6.76(0.24)
SO_3	n.d.	0.19(0.04)
Total	100.00	95.32
LOI	2.94	n.d.
K/Na (molar)	0.65	0.80

Note: Whole-rock analysis by XRF (normalized anhydrous) on pressed powder with wet-chemically analyzed minette standards used to define working curves. Loss on ignition (LOI) determined at 950 °C.

Mean analysis (8 points) and 1 std. dev. (in parentheses) of brown glass in SAY-104 (Fig. 1) determined by electron microprobe: 15-kV accelerating potential, 8-nA sample current, with beam rastered over 20 × 20 μm area. Na and K count rates were constant during analysis. Glass total also includes 0.44 wt% BaO, 0.69% SrO, 0.60 wt% P_2O_5, 0.42% F, and 0.24% Cl.

The three leucite-bearing, analcime-phlogopite–free basanites have high K/Na ratios of about 1, whereas the majority of basanites and minettes range to lower values. SAY-104 is typical of the latter group with K/Na = 0.65. These lower values for the minettes might be argued to result from analcimization of leucite, but that argument cannot be applied to the analcime-leucite–free basanites. In addition, the glass of SAY-104 has K/Na of only 0.80, demonstrating that values less than unity are indeed magmatic.

2. Milk-white, L-type analcime *R-36* completely replaced centimeter-sized leucite phenocrysts in a 1 Ma leucite tephrite lava flow from the Quaternary volcano Roccamonfina in western Italy (Giannetti, 1982). R-36 was collected near the city Vologno. Analcimization of leucite is a widespread phenomenon among the potassic Italian volcanoes (Cundari and Graziani, 1964; Passaglia and Vezzalini, 1985; Luhr and Giannetti, 1987). Because of great similarities in optical properties, analcime has been confused with either leucite (Washington, 1914) or glass (Pirsson, 1896) in numerous igneous rocks.

3. Vesicle-filling and veinlet-forming analcime *BPF* in Tertiary basaltic lavas of the Bald Peak Formation in Tilden County Park, California (University of California, Berkeley, UCB no. 16642), is typical of the earliest-recognized type of analcime, the hydrothermal (H) variety (Mumpton, 1977; Hay, 1978). H-type analcimes presumably precipitate from hydrothermal fluids and are not dependent upon a local precursor mineral or glass.

4. Veinlet-forming (H-type) analcime *KH* is from the Kilpatrick Hills, Scotland. (UCB no. 16658).

5. Sample *ST* is from the analcime diagenetic facies of the Miocene Skyline tuff (Sheppard and Gude, 1969), from the Barstow Formation at Rainbow Gulch, near Barstow, California. This is typical of sedimentary analcime formed in saline, alkaline lakes (S-type) (Surdam, 1977).

6. Sample *WMT* (S-type) is from the analcime diagenetic facies of the upper Jurassic White Mesa tuff (Brushy Basin Member, Morrison Formation, near San Ysidro, New Mexico; Turner-Peterson, 1985; Hay, 1986).

Each sample was crushed and sieved to 100–200 mesh, and the analcime was concentrated to >95% using magnetic and density separation techniques. The cubic cell constant was determined for each analcime by least-squares refinement of 15 major reflections measured using a Guinier (Jago) powder camera with Si metal as a standard and FeKα, radiation. Only analcime reflections were observed for each sample. Major-element analyses of the analcimes and the glass of SAY-104 were determined by electron microprobe at 15 kV-accelerating potential and a sample current of 8 nA. With the beam rastered over an area of 20 × 20 μm, the Na count rates were constant during the 20–s analyses.

Oxygen isotopes were measured on dehydrated analcime using the BrF_5 procedure of Clayton and Mayeda (1963). The analcimes were dehydrated by heating the samples in vacuum at 100 °C for 2 h to remove any surface water and then heating to 400 °C during which the channel water was released and collected. The oxygen- and hydrogen-isotope compositions of the channel water were measured using the micro–CO_2-H_2O equilibration technique of Kishima and Sakai (1980).

Isotopic compositions are reported in the familiar δ notation in units of per mill relative to SMOW. Duplicate analyses indicate a reproducibility of δD and $\delta^{18}O$ of channel water of 10 and 2‰ respectively, and 0.3‰ for the $\delta^{18}O$ value of the dehydrated analcime. The $\delta^{18}O$ value of NBS-28 quartz standard is 9.6‰ in the Saskatoon laboratory. All mineralogical, chemical, and isotopic results on analcime are given in Table 2.

RESULTS

Cell constants and chemical compositions

Saha (1959, 1961) synthesized solid solutions of analcime under hydrothermal conditions from glasses ranging across the binary system $NaAlSiO_4$ (nepheline)–$NaAlSi_3O_8$ (albite). He demonstrated a systematic decrease in the cell constant a_0 with increasing silica, an effect caused by the shorter distance of the stronger Si–O bonds versus the Al–O bonds. Recognizing the wide range of conditions for analcime formation, attempts have been made to use compositional parameters or the cubic cell constant to characterize particular environments. For example, Fornaseri and Penta (1960) found high Rb in L-type analcimes in Italian volcanics; Hay (1966) and Coombs and Whetten (1967) noted that S- and M-type analcimes are the most siliceous, reflecting their origins from silica-rich volcanic glass precursors; and Keith et al. (1983) found high concentrations of Cs in H-type analcimes. Figure 3 is a plot of a_0 versus mole fraction tetrahedral Si (X_{Si}) for the six analcimes from this study and 23 analyses from the literature, including S, M, H, and suggested P types. As expected, the most siliceous analcimes are S and M types; S-type analcimes are also the most compositionally inhomogeneous, with the largest standard deviation values in Table 2. The Colima analcime falls near the center of the range in Figure 3 (a_0 = 13.712 Å), along with the L- and H-type analcimes and other possible primary analcimes from the Crowsnest Formation, southeast Queensland (Wilkinson, 1977), northwest Iran (Comin-Chiaramonti et al., 1979), and the Highwoods Mountains, Montana (Wilkinson, 1968). Three analcimes from the Square Top intrusion of New South Wales (Wilkinson, 1965) have significantly lower Si contents and larger cell edges. From Figure 3, it is clear that S- and M-type analcimes can generally be distinguished from other types by Si content and cell constant, but primary analcime cannot be distinguished from either L or H types by these means.

H-type analcimes can be distinguished from P and L types by the very low Fe contents (presumably tetrahedral Fe^{+3}) of the former (Fig. 4). S- and M-type analcimes are also generally low in Fe, with the exception of an S-type sample near Wikieup, Arizona, reported by Ross (1928) and Coombs and Whetten (1967). The Colima analcime is high in Fe_2O_3 (0.98 wt%), as are feldspars and leucites (0.48–1.71 wt%) from the high-temperature Colima basanite-minette suite (Luhr and Carmichael, 1981). Other

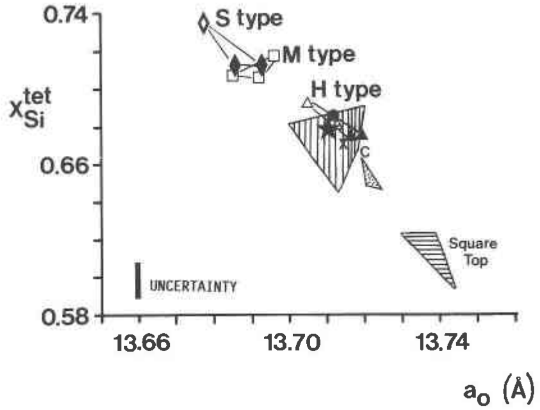

Fig. 3. Mole fraction of Si in the tetrahedral site (X_{Si}) of analcime versus cubic cell constant a_0. Solid symbols represent the six samples from this study: dot = P-type analcime SAY-104; star = L-type analcime R-36; diamonds = S-type samples ST and WMT; triangles = H-type analcimes BPF and KH. Open symbols and letters are data from the literature: open diamond = S-type analcime; open squares = M-type analcimes; and open triangles = H-type analcimes (Coombs and Whetten, 1967). Suggested P-type analcimes from the literature: C = Crowsnest Formation (Wilkinson, 1968); X = Queensland analcimite (Wilkinson, 1977); vertically ruled field outlines analcimes from the Azerbaijan, Iran, tephrites, phonolites, and analcimites (Comin-Chiaramonti et al., 1979); stippled field = analcimites and analcime phonolites from the Highwoods Mountains and analcime tinguaite from the Otago Harbor (Wilkinson, 1968); horizontally ruled field = three analcimes from the Square Top Intrusion (Wilkinson, 1965). Error bar indicates uncertainties from Table 2.

TABLE 2. Electron-microprobe analyses (wt%), formulae, cell constants (Å), and $\delta^{18}O$ and δD values of analcimes

Sample number:	SAY-104	R-36	BP	KH	ST	WMT
Analcime type:	P	L	H	H	S	S
SiO_2	55.28(0.28)	56.37(0.27)	54.06(0.37)	54.87(0.19)	57.10(0.91)	61.62(1.48)
Al_2O_3	21.04(0.16)	22.12(0.16)	22.49(0.17)	22.21(0.17)	19.41(0.28)	19.50(0.83)
Fe_2O_3	0.98(0.08)	0.27(0.03)	0.03(0.02)	0.02(0.02)	0.10(0.01)	0.20(0.07)
CaO	0.26(0.04)	0.09(0.04)	0.18(0.07)	0.02(0.01)	0.02(0.02)	0.10(0.06)
Na_2O	11.58(0.26)	11.46(0.12)	13.20(0.12)	13.03(0.09)	11.47(0.16)	11.02(0.63)
K_2O	0.38(0.05)	1.03(0.09)	0.05(0.02)	0.14(0.04)	0.15(0.06)	0.27(0.11)
Total	89.52	91.34	90.01	90.29	88.25	92.71
On the basis of six oxygens						
Si	2.065(0.011)	2.062(0.010)	2.015(0.014)	2.035(0.007)	2.143(0.034)	2.189(0.053)
Al	0.927(0.007)	0.954(0.007)	0.988(0.008)	0.971(0.007)	0.859(0.012)	0.817(0.035)
Fe	0.028(0.002)	0.007(0.001)	0.001(0.001)	0.001(0.001)	0.003(0.001)	0.005(0.002)
Ca	0.010(0.002)	0.004(0.002)	0.007(0.003)	0.001(0.001)	0.001(0.001)	0.004(0.002)
Na	0.839(0.019)	0.813(0.009)	0.954(0.009)	0.937(0.007)	0.835(0.012)	0.759(0.043)
K	0.018(0.002)	0.048(0.004)	0.002(0.001)	0.007(0.002)	0.007(0.003)	0.012(0.005)
Sum	3.886	3.888	3.968	3.951	3.847	3.786
$X_{Si,tet}$	0.684(0.009)	0.682(0.009)	0.671(0.011)	0.677(0.007)	0.713(0.028)	0.727(0.049)
Cubic cell constant						
a_0	13.712(0.001)	13.710(0.001)	13.716(0.004)	13.720(0.001)	13.686(0.001)	13.693(0.002)
Isotopic data						
$\delta^{18}O$ analcime (‰)	+9.2	+11.1	+13.9	+20.4	+21.0	+17.7
Channel H_2O (wt%)	3.1	4.0	1.1	6.2	3.6	3.4
δD channel H_2O (‰)	−119	−136	−155	−89	−112	−63
$\delta^{18}O$ channel H_2O (‰)	−26	−20	−20	−12	−19	−9
$\delta^{18}O$ modern meteoric water* (‰)	−8	−10	−6	−8	−10	−8

* Measured directly or estimated from Dansgaard (1964).

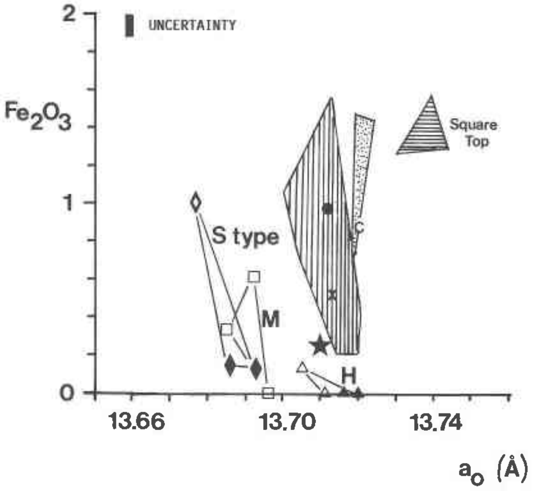

Fig. 4. Fe_2O_3 content of analcime (wt%) versus cubic cell constant a_0. Symbols as in Fig. 3.

suggested primary analcimes are also rich in Fe_2O_3 (Fig. 4: 0.2–1.56%). The L-type analcime from Roccamonfina falls at the low end of this range (0.27%), a value presumably inherited from the precursor leucite. Thus, Fe content may be effective in distinguishing P- and L-type analcimes from S, M, and H varieties. The L-type analcime has significantly higher K_2O content than the Colima analcime, consistent with the high Rb contents of L-type crystals described by Fornaseri and Penta (1960). K and Rb abundances may prove effective in discriminating P- and L-type analcimes, although analcime formed from nepheline or other precursor minerals would probably show different inherited enrichments.

$\delta^{18}O$ of framework oxygen

Oxygen-isotope values are plotted versus cell constants in Figure 5 for the six analcimes of this study. The lowest $\delta^{18}O$ value is for the Colima specimen (+9.2‰). Karlsson et al. (1985) dehydrated this same sample and measured a value of +8.8‰ on the framework oxygen. This small discrepancy is related to the different methods used in calculating $\delta^{18}O$ values of silicates relative to the SMOW standard. We assume that the $\delta^{18}O$ value of framework oxygen in primary igneous analcime should be similar to the feldspar $\delta^{18}O$ values. Kyser et al. (1981) measured $\delta^{18}O$ of +6‰ in clinopyroxene phenocrysts from other Colima basanites and minettes. Based on oxygen-isotope partitioning between clinopyroxene and plagioclase, we expect primary Colima analcime to have $\delta^{18}O$ of about +7‰. The higher value of the Colima analcime (+9.2‰), therefore, is inconsistent with simple magmatic equilibration. The L-type analcime from Roccamonfina is somewhat more ^{18}O rich at +11.1‰ and is not in the range of fresh leucites (+7.6 to +9.0‰) at Roccamonfina (Taylor et al., 1979). This indicates that simple ion-exchange conversion of leucite to analcime was accompanied by partial disruption of the Si-Al-O framework.

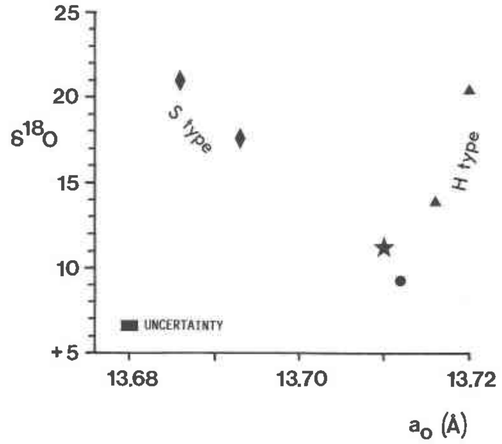

Fig. 5. $\delta^{18}O$ values of analcime versus cubic cell constant for the six samples of this study. Symbols as in Fig. 3.

The S- and H-type analcimes have much higher $\delta^{18}O$ values (+13.9 to +21.0‰), as expected if they equilibrated with surface waters at relatively low temperatures. Karlsson et al. (1985) reported similar $\delta^{18}O$ values for S-type analcimes, but their values for H-type analcimes ranged from +12.3‰ down to +8.9‰, below our value for the Colima analcime. Staudigel et al. (1981) and Alt et al. (1986) measured $\delta^{18}O$ values of +18 to +24‰ for H- or M-type analcime from veinlets in altered oceanic crust. These results are broadly consistent with the negative correlation between $\delta^{18}O$ of framework oxygen in analcime and temperature of formation as suggested by Karlsson et al. (1985), although this relationship is somewhat confused by the overlap between H-type and proposed P-type analcimes. Karlsson et al. (1985) also reported intermediate values (+13.6 to +14.3‰) for analcime from the Crowsnest Formation (Pearce, 1970), clearly demonstrating the nonprimary nature of these analcime phenocrysts in which framework oxygens have apparently been partially exchanged with fluids. In summary, based on available results, oxygen-isotope compositions appear to be usable for distingishing P-type analcime from L- and S-types and can be used to deny primary status to most analcimes. Overlap exists, however, for $\delta^{18}O$ values of P-type and some H-type analcimes.

$\delta^{18}O$ and δD in channel water

The water extracted from analcime channels below 400 °C could originate from either (1) the fluid from which the analcime originally crystallized or (2) a later fluid that has replaced the channel water but not substantially affected the framework oxygen. Karlsson et al. (1985) reported that the $\delta^{18}O$ values of channel water in analcimes from a variety of environments do not correlate with those of the framework oxygen, a result that is confirmed by the data of this study (Table 2). For example, S-type analcime WMT has a $\delta^{18}O$ value of −9‰ for the channel water and a $\delta^{18}O$ value of +17.7‰ for the framework oxygen. H-type analcime KH presumably formed at a higher temperature than the S-type samples, and isotopic fractionations between analcime and water should be smaller. KH has a $\delta^{18}O$ value of −12‰ for channel water, but a higher $\delta^{18}O$ value of +20.4‰ for the framework oxygen. These results suggest that the channel water in many analcimes does not represent the fluid from which the analcime originally formed.

The mobility of water in zeolites is slowest for analcime (Dyer and Molyneux, 1968), but the analcime channels provide a pathway for faster exchange between water and the framework oxygen than does lattice diffusion. If channel-water diffusion and exchange with framework oxygen is fast at relatively low temperatures, the isotopic composition of the channel water should correlate with both local meteoric water and framework oxygen. As discussed above, however, neither parameter is well correlated with $\delta^{18}O$ of the channel water, suggesting that exchange between local water, channel water, and framework oxygen is slow at low temperatures, and that the channel water has not equilibrated with local meteoric water.

Inasmuch as the isotopic compositions of channel water in most samples plot on the meteoric line (Fig. 6) but differ from modern meteoric water in the area from which the samples were collected, the channel water must represent an ancient meteoric water that has neither been replaced by modern water nor appreciably exchanged with the framework oxygen. As such, the isotopic composition of channel water probably reflects a paleoclimate, although the age of this paleoclimate would be difficult to determine. The only channel water that falls off the meteoric line is from the Colima analcime, which plots to the left. Because meteoric water can be affected in this way by a limited number of processes (e.g., Welhan, 1987), the most likely explanation for the isotopic composition of the channel water from the Colima analcime is that the water has become ^{18}O-depleted because of either low-temperature precipitation or exchange with a silicate phase, such as the analcime itself. This would result in a slight ^{18}O enrichment in analcime and perhaps raise the $\delta^{18}O$ value of the Colima analcime from the presumed magmatic value of about +7‰ to the observed value of +9.2‰.

Discussion

Petrographers have traditionally relied on the fresh appearance of certain euhedral analcime crystals in igneous rocks to argue for a primary origin (Washington, 1914). The Colima analcime of Figure 1, however, is petrographically indistinguishable from many L-type analcimes. A photomicrograph of virtually identical L-type analcime from the 0.38 Ma Brown Leucitic Tuff of Roccamonfina is given in Luhr and Giannetti (1987). Textural arguments in favor of primary analcime, therefore, are not definitive.

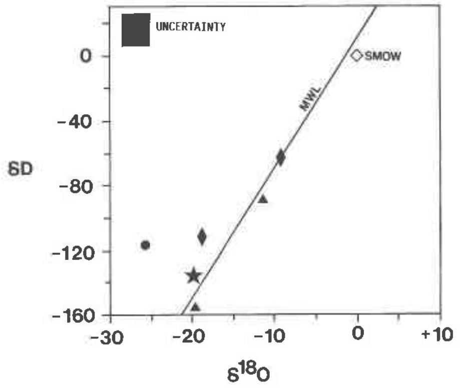

Fig. 6. δD and $\delta^{18}O$ values of channel water extracted from various types of analcime (Table 2). Symbols as in Fig. 3. All channel waters except that of P-type analcime from the Colima minette (SAY-104) have isotopic compositions similar to modern meteoric waters (MWL = meteoric water line from Craig, 1961), but typically different from modern water in the local area. Open diamond indicates standard mean ocean water (SMOW).

Igneous rocks in which analcime has been considered as a primary mineral can be divided into the broad groups: (1) blairmorites (Pearce, 1970; Woolley and Symes, 1976), analcimites (Wilkinson, 1968, 1977), phonolites, and tephrites (Comin-Chiaramonti et al., 1979) in which analcime forms large euhedral phenocrysts up to 3 cm in diameter and (2) minettes, monchiquites, and other lamprophyres in which analcime occurs as discrete microphenocrysts or groundmass crystals (Jahns, 1938; Rock, 1977, 1984; Williams et al., 1982) as well as a diffuse groundmass phase, apparently a replacement of original glass.

Without exception, the blairmorites and other igneous rocks with phenocrystic analcime are lavas that are associated with only minor pyroclastic material. They lack mica, hornblende, or other hydrous minerals and can be construed to have formed from relatively anhydrous magmas. These magmas probably crystallized in the stability field of leucite or other feldspathoids, and their analcime (L-type) formed from these primary minerals by low-temperature ion exchange. The very low silica contents and large cell constants for analcimes from the Square Top intrusion (Fig. 3) may reflect formation from a low-silica precursor such as nepheline or kalsilite instead of leucite.

The petrography of lamprophyres, on the other hand, requires very hydrous magmatic conditions. High water contents stabilize mica or amphibole and couple with relatively low magmatic Al contents to contract the stability fields for feldspars and leucite. We suggest that primary analcime can become stable instead of leucite in hydrous magmas of appropriate mafic alkalic composition. The upper temperature limit of analcime stability in synthetic systems (650 °C) might be enhanced in natural lamprophyric magmas by the presence of Ca, Fe, Ti, and other elements and by slightly water-undersaturated conditions that are known to increase the thermal stability of hornblende and other hydrous minerals (Allen and Boettcher, 1978). The Colima basanites and minettes have high contents of Mg, Cr, and Ni, with olivine (Fo$_{90-94}$) and Cr-rich spinel as the earliest-formed minerals. Oxygen-isotope partitioning among phenocrysts in these samples yields equilibration temperatures of 1000 to 1200 °C (Kyser et al., 1981). The water-saturated solidus temperatures of basalts at crustal pressures are as low as 700 to 800 °C (Yoder and Tilley, 1962; Holloway and Burnham, 1972; Stern et al., 1975). Thus, the Colima minettes may have encountered the stability field of primary analcime on approaching solidus temperatures near the Earth's surface.

CONCLUSIONS

1. The proposed P-type analcime from Colima can be distinguished from most S- and M-types by the lower Si content and larger unit cell of the former.

2. P-type analcime can be distinguished from H-type analcime by the much higher Fe content of the former, although $\delta^{18}O$ values may overlap.

3. P-type analcime should have low $\delta^{18}O$ values similar to magmatic feldspars (+6 to +8‰). The Colima analcime, which has a $\delta^{18}O$ value of +9.2‰, may have formed as a magmatic phase, but has undergone a limited amount of low-temperature exchange with its channel water resulting in a slight $\delta^{18}O$ enrichment.

4. We investigated a single sample of L-type analcime, derived from leucite. It has higher $\delta^{18}O$ than both the presumed precursor leucite and the P-type Colima analcime, although P- and L-type varieties are identical in cell constant and in petrographic appearance. As a corollary, textural arguments in favor of primary analcime cannot be definitive. In addition to higher $\delta^{18}O$ values, K_2O and Rb contents appear to be systematically higher in L-type analcimes. These three parameters may prove the only reliable discriminators of P- and L-type analcimes.

5. Primary analcime is most likely to occur in lamprophyres, alkali-rich, silica-undersaturated magmas whose high water contents are essential for the stability of analcime and other hydrous minerals. The Quaternary Colima minettes seem to be the best candidates for primary analcime.

6. Analcimites, blairmorites, and related lavas containing analcime phenocrysts in the absence of other hydrous minerals are unlikely hosts for primary analcime. With increasing temperature of alteration, these analcimes range from strict L-types to H and M varieties having heavier oxygen-isotope compositions.

7. The hydrogen- and oxygen-isotope compositions of channel water in all but P-type analcime fall on the meteoric water line and may record the composition of meteoric water at the time of analcime formation. The $\delta^{18}O$ values of the channel water do not generally correlate with either the values of modern meteoric water in the environs of each sample or with the $\delta^{18}O$ value of the framework oxygen, suggesting that exchange between groundwater, channel water, and framework oxygen is slow.

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