# Analcime phenocrysts in igneous rocks: Primary or secondary?—Discussion

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## Abstract

There are two major hypotheses of origin for the rare occurrence of analcime phenocrysts in sodic volcanic rocks. They are either primary analcime or replacement pseudomorphs of leucite. The preponderance of experimental, isotopic, chemical, textural, and field evidence supports the primary analcime hypothesis for the analcime from the Crowsnest Formation, Alberta, Canada. O isotope data are permissive evidence for either replacement of leucite or isotopic alteration of analcime, as is the case with sanidine phenocrysts, which coexist with the analcime but are igneous in origin. Most of the analcime in the Crowsnest Formation shows signs of alteration; only a small amount is pristine. Textural observations of thermal alteration place the analcime in the volcanic environment immediately after eruption (while the rocks were still hot) and are the most persuasive evidence of the sequence of events by which the primary analcime was partially preserved in the Crowsnest flows, tuffs, and agglomerates.

## Introduction

Karlsson and Clayton (1991) have recently published work in this journal based mainly on O isotopic data, in which they conclude that the data "collectively" favor a secondary origin for the analcime of the Crowsnest Formation, Alberta, and the Colima volcanic complex, Mexico. I provided the Crowsnest material to Karlsson and Clayton for their study, but I must disagree with their conclusions. I believe the data they use are, at best, only permissive evidence for a secondary origin. There are further data (not considered in their paper) that seem to me to imply a primary origin, at least for the Crowsnest analcime. In this discussion, I will review the evidence bearing on the origin of igneous analcime, concentrating on the empirical evidence that I have personally verified.

I spent several years studying the Crowsnest Formation in both the field and laboratory (Pearce, 1967, 1970a, 1970b), but I have not seen the Colima material. This discussion emphasizes the Crowsnest locality, which, in any event, contains the foremost example of primary igneous analcime. One other location of blairmorite is known from the Lupata Gorge, Mozambique.

## Features of the Crowsnest Formation

Karlsson and Clayton have admirably summarized the essential features of the Crowsnest volcanics. However, there are certain important features that should be emphasized. The Crowsnest Formation (estimated at 209 km³) is essentially the eroded remains of an alkaline volcanic center that was erupted in a fluvial environment in which the Lower Cretaceous, nonmarine, Blairmore Group was being deposited. The Crowsnest volcanoes formed a local topographic high that was reduced to a fairly level plain (35 m of relief) by postvolcanic erosion.

Some important features of the Crowsnest Formation are outlined below: (1) The formation is nonmarine and was deposited on the fluvial sands of the Blairmore Formation. As early as 1885, Dawson (1885) reported finding in the Crowsnest Formation fossil leaves, branches, twigs, and other pieces of wood often replaced by calcite (see comments on carbonatites below). (2) The volcanism was essentially pyroclastic (agglomerates, tuffs), probably accompanied by lahars with no pumice. (3) There was probably a carbonatitic phase of the volcanism, since there are carbonate-bearing tuff beds with sufficient calcite to react visibly with HCl. Most of the reported alteration in the formation is calcareous and, in my experience, relates to the carbonate-bearing tuffs. (4) There is some evidence of reworking by $H_2O$ consistent with intermittent streams on the flanks of a volcano. There is no evidence of lakes nor evidence of extensive water-working of the volcanic detritus. (5) The chemistry of the Crowsnest rocks is relatively normal but rather sodic (nepheline syenite); only the mineral content is unusual (Pearce, 1967). (6) The freshest sanidine (Pearce, 1970a, 1970b) occurs in the analcime-bearing rocks (blairmorite and analcime phonolite), which, according to the leucite replacement hypothesis, are the most altered rocks (having undergone extensive Na metasomatism).

## The Crowsnest Analcime

The analcime of the blairmorites and analcime phonolites of the Crowsnest Formation is the most spectacular example of primary igneous analcime. Blairmorite, the analcime-phyric rock named from the town of Blairmore in Alberta, is a rare rock known only from one other occurrence—the Lupata Gorge in Mozambique (Woolley and Symes, 1976). The Crowsnest blairmorites have eu-
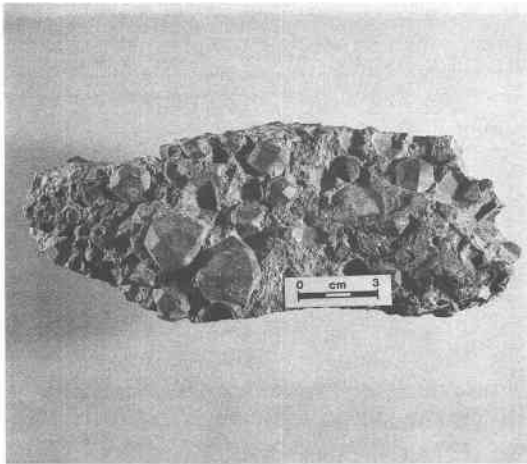
Fig. 1. A hand specimen of blairmorite (PN-15D) from a bomb in an agglomerate southwest of Coleman, Alberta. The large trapezohedral analcime phenocrysts are clear honey color in thin section with no trains of inclusions, as is common in leucite. Minor constituents of this rock are sanidine, aegirine-augite, melanite garnet, and magnetite.

hedral trapezohedrons of analcime up to 2.5 cm in a matrix containing analcime (75% of the total mode in some cases). Figure 1 shows an example of a blairmorite bomb in agglomerate containing the largest reported primary analcime crystals. These crystals are brown in color and contain 1–2% $Fe_2O_3$ (Pearce, 1970a). Karlsson and Clayton appear to be of the opinion (following Coombs and Whetten, 1967) that the Fe reported in analcime is present as inclusions. This is not true for the Crowsnest isotropic brown analcime (of the type illustrated in Fig. 1). The mineral contains no trains of inclusions, as is common with leucite. This is an important observation, as magmatic leucite typically contains inclusions in a radial pattern so characteristic that it may be used to help identify the mineral (Deer et al., 1963). Analcime formed by alteration of leucite (Luhr and Giannetti, 1987) retains these inclusions. Crowsnest analcime, in contrast, is optically clear, and X-ray diffraction studies show no additional phases. There is no reason to doubt that the brown color is caused by structural Fe or that the analcime was ever anything but analcime. In the altered varieties referred to below, particularly the red analcime, it appears that the Fe has come out of solution and is present as discrete inclusions (hematite?), thus giving a red stain to the crystals. It is worth noting here that the Lupata Gorge material similarly has red analcime and presumably has an Fe content similar to that of the Crowsnest material. Both known occurrences of blairmorite have red Fe-bearing analcime. In contrast, analcime pseudomorphous after leucite in volcanic rocks is typically white. Luhr and Giannetti (1987), for example, report "milk-white" analcime (with rare cores of leucite) as a replacement for leucite. Brown and yellow colors reported by these authors

are due to alteration of glass rather than alteration of analcime.

Although the Crowsnest locality is noteworthy for its large fresh analcime crystals, such pristine analcime is actually rare within the formation. Most of the analcime is altered in some fashion. It might be stressed here that the alteration of the analcime is not the well-known pseudoleucite alteration of magmatic leucite. In hand specimen the altered analcime is most commonly red, but orange or green varieties are locally present. In thin section the altered analcime is anisotropic, twinned, and locally decomposed (Pearce, 1970a). The fresh analcime is brown in hand specimen and a clear honey color in thin section. Only the brown analcime is isotropic in thin section.

From petrographic observations and textural considerations as well as thermal experiments, it appears that the brown isotropic analcime was the original material and the anisotropic varieties are alteration products of it. Some of the brown analcime has a dark brown rim, and studies have shown (Pearce, 1970a) that this contains 10% less $H_2O$ than the core of the crystal. This observation is consistent with analcime becoming unstable and losing $H_2O$.

There is one sample (PN-27A; see Fig. 10 in Pearce, 1970a) whose features bear on the question of the origin of the analcime. This sample was a bomb (0.25 m long) in an agglomerate. On the outside of the bomb, the analcime is orange and has a distinctly charred appearance. Inside, the analcime is mainly red except at the center (of the bomb), where some variegated red and brown crystals occur. In these latter crystals the isotropic brown material is in the cores, giving the appearance that the red alteration proceeded inward from the outside of the crystals.

I consider this occurrence to be in the nature of a smoking gun. In this one sample, we have fresh isotropic analcime in the core with progressively more altered analcime towards the rim of the bomb and the most altered analcime at the surface. Furthermore, the distinctive orange discoloration can be reproduced by heating brown analcime to red heat in air (Pearce, 1970a). These features are consistent with the primary analcime hypothesis. Analcime is not stable under volcanic conditions of low pressures and high temperatures. Since its decomposition involves the loss of $H_2O$, any alteration involving dehydration must necessarily proceed from the outside of the bomb inward. It seems to me that the most straightforward interpretation of this occurrence is that the analcime was injected from the volcano and began to decompose, but the bomb cooled sufficiently rapidly that decomposition was not complete. Thus the various stages of alteration were preserved, and the incomplete transition process has been fossilized. This textural evidence is both simple and compelling.

On the other hand, if we were to assume that the bomb PN-27A was leucite bearing when ejected from the volcano, there is no reason to suppose that the leucite would show this alteration pattern, as it is perfectly stable under volcanic conditions. If the leucite were then altered to

analcime at a low temperature, then how do we explain the thermal discoloration and decomposition of the analcime? The alteration pattern of the analcime from the outside inward is also difficult to explain. Analcime would be perfectly stable under these low temperature conditions and should not be altered at all. In occurrences in which leucite has been altered to analcime, it is the leucite that is altered, not the analcime. It is this textural and chemical evidence of decomposition of analcime that I consider the most serious problem for the leucite hypothesis.

## Sr isotope data

Karlsson and Clayton appear to have overlooked the Sr isotope data (Pearce et al., 1971) on the crystals and rocks of the Crowsnest Formation. In fairness, it might be noted that these data, as well as other data indicating the legitimate igneous nature of analcime, have also been overlooked by all textbook authors in the past few years. I present here in Table 1 revised data on selected Crowsnest material. The $^{87}Sr/^{86}Sr$ ratios for all of the Crowsnest material fall within the accepted range for mantle material. There is no convincing evidence that the rocks have been altered by pervasive fluids of crustal origin, as this would be expected to change the $^{87}Sr/^{86}Sr$ ratios of altered material toward crustal values ($>0.705$). One could argue that the altered analcime (PN-27) has a ratio less mantlelike than the fresh analcime (PN-15D). This might indicate that, during alteration, the analcime acquired a small amount of crustal Sr; however, the amounts are small.

The calcite-bearing tuffs that occur in several places in the Crowsnest formation have the same mantle $^{87}Sr/^{86}Sr$ ratios as the other rocks of the formation. Therefore, it is considered that they are carbonatites rather than nonmarine tuffaceous limestones. It is this carbonatitic phase of the volcanism which appears to be the source material for much of the alteration in the formation.

### The putative transforming solution

Karlsson and Clayton are remarkably silent concerning the source, chemical composition, and timing of the transforming solution. If we accept their conclusion, then 200 km³ of predominantly potassic, leucite-bearing volcanics were transformed into 200 km³ of predominantly sodic, analcime-bearing volcanics. Although this is not, in itself, impossible, we should look very carefully at such a hypothesis. Although the details of the transforming solution are vague in their hypothesis, we can place some constraints on the hypothetical solution from the observed facts. The solution that transformed the leucite to analcime was apparently a rather unusual solution. It had meteoric O (not unusual in itself), mantle-derived Sr, and relatively large amounts of Na (in spite of being in a very K-rich, i.e., leucite-bearing, volcanic formation). If all the analcime were originally leucite, then the volcanic material (including glass and leucite) would be extremely K-rich. $H_2O$ from any source permeating and equilibrat-

**TABLE 1.** Crowsnest Sr isotopes

| Sample | Description | Initial $^{87}Sr/^{86}Sr$ |
|---|---|---|
| **Phenocrysts** | | |
| PN-15D | blairmorite, fresh brown analcime phenocryst | 0.7034 |
| PN-27A-A | blairmorite, altered red analcime phenocryst | 0.7046 |
| PN-27A-F | blairmorite, sanidine phenocryst | 0.7041 |
| PN-20 A-F | trachyte, sanidine phenocryst | 0.7034 |
| Cl/X-1B | trachyte, garnet phenocryst | 0.7038 |
| **Rocks** | | |
| PN-15B-M | analcime phonolite matrix | 0.7042 |
| PN-20A-M | trachyte flow | 0.7046 |
| PN-39C | felsite dike | 0.7042 |
| PN-31D | garnet trachyte | 0.7044 |
| Cl/X-5K | carbonatite tuff | 0.7041 |
| PN-42D | carbonatite tuff | 0.7045 |
| PN-27A-M | blairmorite matrix | 0.7027 |

*Note:* All values normalized to $^{87}Sr/^{86}Sr = 0.1194$, Eimer and Amend interlaboratory standard $^{87}Sr/^{86}Sr = 0.7081 \pm 0.0002$. The precision on all values is better than $\pm0.0003$.

ing with such material would be K-rich rather than Na-rich. Ion exchange within the formation's rocks can not produce Na from K. It seems, therefore, necessary to have an external source for the solution. If ground $H_2O$ and ion exchange in leucite-bearing rocks were all that is necessary to change leucite to analcime over a period of time, then almost all occurrences of leucite should be converted to analcime. Clearly this is not the case; leucite is very common, whereas phenocrysts of red or brown analcime (as in blairmorite) are only known from two locations worldwide.

There are two possible sources for the putative transforming solution—groundwater and Blackstone sea water. The first source would have the correct isotopic signature (for O, not Sr) but probably the wrong chemical composition (not saline). The second source has the correct major-element composition and O isotope signature; however, it seems to me highly unlikely that the upper Cretaceous Blackstone sea had mantle Sr isotopes.

### Phase relations of analcime

The reason that analcime is not readily accepted as an igneous phase appears to be the tacit assumption that analcime, $NaAlSi_2O_6 \cdot H_2O$, a hydrous mineral usually classified as a zeolite, cannot be stable under magmatic conditions. This argument is reminiscent of the argument that muscovite could not be an igneous phase because it breaks down at a few hundred degrees (depending on the $H_2O$ pressure). The muscovite "problem" was resolved by experimental evidence indicating that elevated $H_2O$ pressures stabilize muscovite at the liquidus. A similar argument may be made for analcime.

Morse (1969), Pearce (1967), Roux and Hamilton (1976), and Kim and Burley (1971) have all shown that there is a primary phase field for analcime in hydrous nepheline syenite compositions. Morse's work detailed the extent of the narrow analcite primary phase field at $P_{H_2O} = 5$ kbar and also showed isothermal isobaric sec-

tions at 600, 640, and 655 °C. Analcime in Morse's experiments coexisted with a K-rich alkali feldspar ($Or_{80+}$). These are the exact major phases in many Crowsnest rocks. Roux and Hamilton (1976) found that analcime melts congruently in the range 5–13 kbar at 640–600 °C. Above 13 kbar, jadeite is stable rather than analcime. From this latter work, it is likely that the Crowsnest analcime phenocrysts grew at a depth exceeding 18 km.

The available experimental evidence, which, in fairness, it must be admitted has been overlooked by a number of petrologists and all the textbook authors, shows that analcime is a legitimate igneous phase in magmas of nepheline syenite composition under conditions of $H_2O$ pressure corresponding to depths of about 18 to 30 km in the crust. Since it is not stable at lower pressures, analcime can only be preserved if it is erupted explosively and quenched at the surface. Presumably this accounts for the rarity of blairmorites and related rocks. It is not often that a mineral assemblage stable at high $H_2O$ pressures can successfully make the relatively rapid passage to the surface of the earth. Indeed, in the case of the Crowsnest analcime, most of the analcime did not survive without some evidence of alteration.

## DISCUSSION

The O isotope data of Karlsson and Clayton (1991) are permissive of either primary analcime (with isotopic exchange by meteoric $H_2O$) or secondary analcime. The O isotope data do not prove either case. They refer to O exchange in sanidine as well as analcime, but they do not suggest that the sanidine is secondary after some other mineral. That said, pseudomorphism is known to occur. However, in cases of presumed transformation or metamorphosis, the burden of proof should lie in particular with the transformationists. In the absence of compelling proof, it is reasonable to accept the rocks as they are and not as they might have been.

Furthermore, I think the data of Ferguson and Edgar (1978), which they cite, were not weighed heavily enough in their considerations. The transformation hypothesis requires that all the blairmorites have been originally leucitite, an ultrapotassic rock of distinctive chemistry. Rb is known to substitute for K in leucite but does not substitute readily for Na in analcime. Therefore analcime formed by alteration of leucite will likely inherit a high Rb content from the leucite. On the other hand, analcime formed from a nepheline syenite magma will probably have far less Rb. Even if we do not know the exact distribution coefficents, a reported two-hundredfold difference in Rb content between the fresh primary analcime in the Crowsnest Formation (23 ppm) and the secondary analcime in Italy (4000 ppm) is significant. If both analcimes were formed from alteration of leucite from an ultrapotassic magma, then, surely, both should have high levels of Rb. Therefore, I cannot agree with Karlsson and Clayton that either their data or all the available data collectively favor a secondary origin. The secondary analcime hypothesis can only be accepted by overlooking certain key information: the systematic thermal alteration of the analcime (indicating the presence of analcime in the hot volcanic pile), the low Rb and high Fe contents of the analcime (unlikely to have been inherited by transformation from leucite), the coexistence of analcime and K-rich feldspar (confirmed by experimental phase petrology), and the lack of any evidence of any unreplaced leucite (as occurs in the Italian localities).

Paradoxically, it is not the fresh nature of the Crowsnest analcime that is good evidence for its primary origin, but rather its pervasive and locally incomplete alteration. This question of the thermal discoloration and decomposition of the analcime in the Crowsnest volcanics has yet to be addressed by any of the writers who support a leucite transformation hypothesis. The alteration is different from that of leucite. The textures are clear and definitive: they indicate that analcime was present in the volcanics while the rocks were still hot enough to decompose the analcime. I believe that this textural evidence has primacy over permissive indirect evidence and indicates that the Crowsnest analcime is a genuine igneous phase.

If, however, one is still not convinced that the Crowsnest analcime is primary, then it might be worthwhile studying the feldspar in the upper part of the Blairmore Formation, where it lies directly under the Blackstone Formation (without intervening Crowsnest material) to see if the Blackstone sea was capable of penetrating into the underlying material and transforming it at low temperatures (subgreenschist metamorphism). I would predict a negative result from such a study. Further work on distribution coefficients for analcime and coexisting sanidine in alkaline magmas also appears indicated.

Everyone who has done fieldwork on the Crowsnest rocks (from Dawson in 1885 to Ferguson and Edgar in 1978) has concluded that the analcime is likely to have been primary. Only those who have studied limited aspects of the material in the laboratory doubt this conclusion. I think there is a message here. Narrowly based laboratory work, although it may be an important source of data, is no substitute for combined field and laboratory studies and careful textural analysis. The Crowsnest material continues to intrigue new generations of geologists, as it has for the past century, and we probably have not heard the last of these fascinating rocks. To all interested workers, I recommend a trip to the area: the scenery in the foothills of the Canadian Rockies is spectacular, and the garnet, analcime, and sanidine are all worth collecting. Specific details of important locations can be found in Pearce (1967).

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