

Analcime phenocrysts in igneous rocks: Primary or secondary?—Reply

HARALDUR R. KARLSSON

Department of Geosciences and Department of Chemistry and Biochemistry, Texas Tech University, Box 41053, Lubbock, Texas 79409, U.S.A.

ROBERT N. CLAYTON

Enrico Fermi Institute, Department of Chemistry and Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, U.S.A.

INTRODUCTION

In the preceding discussion Pearce (1993) questioned our recent conclusion (Karlsson and Clayton, 1991) of a secondary rather than a primary origin of analcime from the Crowsnest Formation. His objections are based on field and textural observations, phase-relation considerations, and trace-element and Sr isotope data. We feel compelled to point out that much of the evidence presented by Pearce (1993) has not been previously published except in abstract form, so it seems hardly surprising that it was not considered by Karlsson and Clayton (1991). We welcome these new data but show that they fail to support arguments for a primary analcime and, indeed, some of them are indicative of secondary processes. We consider Pearce's arguments in the order in which he presented them.

FIELD AND TEXTURAL OBSERVATIONS

Pearce (1993) wrote, "Everyone who has done field-work on the Crowsnest rocks . . . 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." However, Ferguson and Edgar (1978), who studied the same area, stated "Neither the field relationships nor the petrography negate the possibility of the analcime being formed originally from leucite." Clearly, not every worker is as impressed by the implications of the field relations as Pearce is.

Pearce (1993) also points out that the analcime occurs in a variety of different colors, including brown, red, orange, and green. The brown analcime, he asserted, is the unaltered original mineral whereas the other colored varieties are alteration products. Ferguson and Edgar (1978), however, suggested that the color variation may be due to nothing more than the presence or absence of various inclusions. Another piece of evidence, which according to Pearce is consistent with the brown analcime being heated from the outside in, comes from measurements purported to show that the rims have less H₂O than the interiors. According to Pearce (1970) "a crystal . . . was cut up, and the outer zone found (by loss on ignition) to have 10% less water than the lighter core" (p. 52). We find this observation puzzling in light of the rapid self-diffusion rate of H₂O in analcime. For example, the measured diffusion coefficients are 1.97×10^{-13} cm²/s and 0003-004X/93/0102-0230\$02.00

1.57×10^{-11} cm²/s at 46 and 100 °C, respectively (Dyer and Molyneux, 1968). Using diffusion rates in conjunction with the equation $x^2 = 2Dt$, where x is grain radius in cm, D is the diffusion coefficient and t is time in seconds, we can estimate how rapidly the analcime crystals would reach equilibrium. The largest Crowsnest analcime, 2.5 cm in diameter, would thus homogenize in about 100 000 yr at 46 °C and in 1600 yr at 100 °C. The observed gradient in H₂O concentration, if true, must therefore be a secondary effect reflecting conditions in the last tens to hundreds of thousands of years and not in 100 m.y., when any igneous analcime would have to have been formed.

THE SMOKING GUN

Pearce considers the alteration or decomposition of analcime to be the smoking gun. He points to a particular volcanic bomb, 25 cm long sample PN-27A, where the analcime phenocrysts are fresh toward the center of the bomb, becoming progressively more altered toward the bomb's surface. The occurrence of charred analcimes in this particular bomb and the progressively greater alteration toward the bomb's surface do not exclude leucite to analcime transformation. At Roccamonfina Volcano, Italy—to date, one of few localities where primary leucite is observed to be partially or wholly converted to analcime—the analcime and partially transformed leucite occur in pumices that can reach 40 cm in diameter. The pumice clasts are invariably altered from outside in, and only the cores in the larger clasts are visibly unaltered (Luhr and Giannetti, 1987). There is evidence of widespread low-temperature alteration in the Crowsnest volcanics (Ferguson and Edgar, 1978) and it is thus possible that the analcime is secondary after leucite and that the progressive alteration noted by Pearce reflects additional or even contemporaneous low-temperature processes.

SR ISOTOPES AND THE TRANSFORMING SOLUTION

Pearce commented that we "appear to have overlooked the Sr isotope data." We apologize for overlooking an abstract from the early 1970s (Pearce et al., 1971), although, in our defense, we note that later workers such as Ferguson and Edgar (1978) also made no mention of these data. Pearce (1993) lists revised initial ⁸⁷Sr/⁸⁶Sr ratios for 12 minerals and rocks from Crowsnest, with ra-

tios ranging from 0.7027 to 0.7046, consistent with a mantle origin. Pearce contends that mantlelike Sr isotope values indicate that the analcime is primary. However, this is clearly not the case. If analcime had formed from leucite it would have inherited $^{87}\text{Sr}/^{86}\text{Sr}$ from one of two sources: the preexisting leucite or the altering fluid. The leucite would be expected to have mantlelike $^{87}\text{Sr}/^{86}\text{Sr}$, as would any alteration phases that obtained their Sr from the leucite. Meteoric H_2O would have been low in Sr and would have taken on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the rocks and not, as Pearce insists, the other way around. It is well known, for example, that rivers and groundwater derive their Sr isotope signature from the rocks with which they have interacted (e.g., Faure, 1986). In addition, the Sr isotope data given by Pearce (1993) show evidence of isotopic disequilibrium. For example, the analcime phenocrysts in the blairmorite samples PN-15 and PN-27 differ in initial $^{87}\text{Sr}/^{86}\text{Sr}$ values by as much as 0.0019 from their respective matrices. The Sr isotope data thus argue strongly for exchange after deposition, further corroborating our O isotope data (Karlsson and Clayton, 1991). The O isotope evidence for the feldspars shows that at least some of the rocks were exposed to fluids, probably of meteoric origin.

Albitization of sanidine shows that Na was mobilized, which led us to argue that Na was derived locally within the formation (Karlsson and Clayton, 1991). Pearce objected to a Na-bearing fluid on the grounds that "the freshest sanidine . . . occurs in the analcime-bearing rocks." However, according to his own description of sanidine in the smoking gun sample (PN-27A), which is a "typical occurrence of blairmorite" (Pearce, 1970, p. 61), "The sanidine is clear except for minor albitized patches" (p. 62). The albitization of sanidine is an indication of Na mobilization and is consistent with the leucite-analcime transformation at the same time. Pearce also argued that if these rocks originally contained leucite, then fluid flowing through these rocks would have been K-rich rather than Na-rich. However, he described the Crowsnest rocks as having "relatively normal but rather sodic" compositions. If, as Pearce suggested, a Na-rich solution is required, one need look no further than the carbonatite tuff layers, which, according to Pearce, appear "to be the source material for much of the alteration in the formation." These tuff layers are presently predominantly Ca-bearing, but may initially have been Na-bearing, similar to carbonatite ashes of East African Rift Valley, in which case the carbonatite could have been a source of Na. Studies of Oldoinyo Lengai volcano show that freshly erupted carbonatite is mostly a mixture of sodium and calcium carbonate. However, nearby prehistoric carbonatitic tuffs consist of limestone from which Na has been leached (Dawson, 1964a, 1964b; Hay, 1978). The Sr isotope data indicate that the carbonatite may have been a source of Sr for the altering fluids. The fact remains, however, that Na was mobilized in all the rocks. Another possibility is that the Na was derived locally within the rocks. All that the leucite to analcime trans-

formation requires is a redistribution of the preexisting K and Na locally within the rock.

PHASE RELATIONS

Pearce (1993) stated that the available experimental data "shows that analcime is a legitimate igneous phase." It is true that analcime occurs on the liquidus in simple experimental systems that do not include important elements such as Mg, Fe, Ca, F, or Cl, as has repeatedly been pointed out (Luhr and Carmichael, 1981; Luhr and Kyser, 1989; Karlsson and Clayton, 1991). Whether these simple systems can be applied directly to more complicated natural systems needs further study. At present experimental data are permissive, but they cannot be used as positive evidence either for or against primary analcime.

TRACE ELEMENTS

Pearce felt that we did not give the trace-element data of Ferguson and Edgar (1978) enough credence. We simply reiterate what we stated in our paper (Karlsson and Clayton, 1991). Without knowledge of distribution coefficients for leucite and analcime or the trace-element concentration in the host rock, it is inappropriate to compare the concentration of elements such as Rb in minerals occurring in different localities, nor is there anything magically igneous about low Rb concentrations in analcime. For example, Wood et al. (1976) reported that hydrothermal analcime from eastern Iceland contains only 5 ppm Rb. Similarly, leucites with Rb values as low as 25 ppm have also been reported (see e.g., Edgar, 1984).

DISCUSSION

The absence of leucite in the Crowsnest Formation cannot be used as proof that the analcime could not have formed from leucite, as was implied by Pearce (1970). As we discussed in Karlsson and Clayton (1991), there is abundant experimental evidence, apparently ignored by Pearce, suggesting that the leucite to analcime transformation can occur very rapidly even on a laboratory time scale (Gupta and Fyfe, 1975; Taylor and MacKenzie, 1975). The Crowsnest rocks have had 100 m.y. to complete the transformation of leucite to analcime.

Pearce gave the impression that our conclusion was based solely on O isotope data and stated that "the O isotope data of Karlsson and Clayton (1991) are permissive of either primary analcime (with isotopic exchange with meteoric H_2O) or secondary analcime. The O isotope data do not prove either case." To the contrary, our suggestion that the Crowsnest analcime might be secondary was based on a body of data, rather than O isotope data alone. All that the O isotope data tell us is that the Crowsnest rocks have interacted with fluids. For example, we wrote that O isotope values "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" (Karlsson and Clayton, 1991, p. 189). "The figure demonstrates that the

origin of igneous analcime cannot be uniquely determined solely on the basis of O isotopes" (p. 191, caption of Fig. 1). "The O isotope results indicate that analcime phenocrysts in the Crowsnest Formation have either suffered subsolidus O isotope exchange or formed from the transformation of leucite . . ." (p. 193). "Our results show that . . . analcime samples have either undergone subsolidus O isotopic exchange or formed from preexisting leucite . . ." (p. 198). The lack of hydrous igneous minerals in the rocks suggests that the Crowsnest magmas were relatively dry. Thus the leucite replacement hypothesis seems a more viable explanation than the igneous analcime hypothesis.

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REFERENCES CITED

- Dawson, J.B. (1964a) Carbonatite volcanic ashes in northern Tanganyika. *Bulletin of Volcanology*, 27, 1–11.
- (1964b) Carbonate tuff cones in northern Tanganyika. *Geological Magazine*, 101, 129–137.
- Dyer, A., and Molyneux, A. (1968) The mobility of water in zeolites. I. Self-diffusion of water in analcime. *Journal of Inorganic Nuclear Chemistry*, 30, 2831–2840.
- Edgar, A.D. (1984) Chemistry, occurrence and paragenesis of feldspathoids: A review. In W.L. Brown, Ed., *Feldspars and feldspathoids*, p. 501–532. Reidel, Dordrecht.
- Gupta, A.K., and Fyfe, W.S. (1975) Leucite survival: The alteration to analcime. *Canadian Mineralogist*, 13, 361–363.
- Faure, G. (1986) *Principles of isotope geology* (2nd edition), 589 p. Wiley, New York.
- Ferguson, L.J., and Edgar, A.D. (1978) The petrogenesis of and origin of the analcime in the volcanic rocks of the Crowsnest Formation, Alberta. *Canadian Journal of Earth Sciences*, 15, 69–77.
- Hay, R.L. (1978) Melilite-carbonatite tuffs in the Laetoli beds of Tanzania. *Contributions to Mineralogy and Petrology*, 67, 357–367.
- Karlsson, H.R., and Clayton, R.N. (1991) Analcime phenocrysts in igneous rocks: Primary or secondary? *American Mineralogist*, 76, 189–199.
- Luhr, J.F., and Carmichael, I.S.E. (1981) The Colima volcanic complex, Mexico. II. Late-Quaternary cinder cones. *Contributions to Mineralogy and Petrology*, 76, 127–147.
- Luhr, J.F., and Giannetti, B. (1987) The brown leucitic tuff of Roccamonfina Volcano (Roman Region, Italy). *Contributions to Mineralogy and Petrology*, 95, 420–436.
- Luhr, J.F., and Kyser, T.K. (1989) Primary igneous analcime: The Colima minettes. *American Mineralogist*, 74, 216–223.
- Pearce, T.H. (1970) The analcime-bearing volcanic rocks of the Crowsnest Formation, Alberta. *Canadian Journal of Earth Sciences*, 7, 46–66.
- (1993) Primary or secondary analcime—Discussion. *American Mineralogist*, 78, 225–229.
- Pearce, T.H., Jones, L.M., and Walker, R.L. (1971) Strontium isotope composition of alkalic rocks, Crowsnest Pass, Alberta (abs.) *Geological Association of Canada 1971 Annual Meeting*, Sudbury, Ontario, Canada.
- Taylor, D., and MacKenzie, W.S. (1975) A contribution to the pseudo-leucite problem. *Contributions to Mineralogy and Petrology*, 49, 321–333.
- Wood, D.A., Gibson, I.L., and Thompson, R.N. (1976) Elemental mobility during zeolite facies metamorphism of the Tertiary basalts of eastern Iceland. *Contributions to Mineralogy and Petrology*, 55, 241–254.

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