

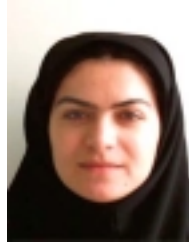
Reappraisal of magmatic origin for euhedral analcimes in volcanic rocks

Roghieh Akbar Ashrafi

(Presenter)

Geological Survey of Iran (GSI), Meraj St., Azadi Sq., Tehran, Iran

Email: Rashrafi@khayam.ut.ac.ir Tell: +98 21 6459281



Jamshid Hassanzadeh,

Department of Geology, University of Tehran, PO Box 14155-6455, Phone: 61112985

Email: jamshidh@khayam.ut.ac.ir Fax: +98 21 6491623



Ali Mohammad Ghazi

Georgia Department of Natural Resources, 2 Martin Luther King Jr., Suite 1154

Atlanta, GA 30334

Email: geoamg@langate.gsu.edu

Abstract

Analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) occurs in various modes including hydrothermal, replacement, metamorphic and diagenetic. For the genesis of euhedral analcimes that occur as micro- to mega-phenocrysts in silica-undersaturated lavas, two different views exist: magmatic and hydrothermal replacement of leucites. Experimental data indicate that analcime is not stable in high T and low P. Other data supporting subsolidus origin of euhedral analcime include oxygen and hydrogen isotopes. Such data on lavas from Alberta indicate that analcimes have been equilibrated with meteoric water. Radiometric analcime ages younger

than the host lavas for a tephrite-phonolite suite in Iran are presented as an independent argument against primary igneous view.

1. Introduction

Analcime occurs as euhedral trapezohedrons embedded in aphanitic -and in some cases truly vitric- groundmass of silica-deficient volcanic rocks such as basanites, tephrites, phonolites, lamprophyres and blairmorites. Igneous origin of analcime phenocrysts has long been discussed. Prior to the lab experiments in mid 1970s, views were skewed more towards primary or magmatic origin, but after the P-T conditions for the coexisting analcime-silicate melt were experimentally constrained, ideas shifted towards secondary origin or subsolidus ion-exchange replacement of leucite. Nevertheless the debate is not over yet. In this paper we assess the historical dispute, and then provide radiometric ages on Iranian analcimes in support of the secondary origin.

2. Review of pros and cons

Certain features give analcime phenocrysts the appearance of leucite for which igneous origin is undoubted. These are: enclosure of euhedral crystals in aphanitic and sometimes glassy matrix, radial trains of inclusions of igneous microlites, and absence of alterations in the accompanying olivines and pyroxenes. These kinds of textural relationships have lead to the primary magmatic view for such analcimes.

Pearce (1967 and 1970) has heavily studied the analcime-bearing volcanic rocks of the Crowsnest Formation, Alberta, Canada and advocates igneous origin. For his view he specifically stresses on unaltered analcimes in a blairmorite bomb which are brown in hand specimen and clear honey color, isotropic and inclusion-free in thin section. His opinion is mainly based on: 1) Analcime color: Pearce (1993) believes that analcime formed after leucite is typically white as reported by Luhr and Giannetti (1987) for partly to completely transformed leucites in Roman Region tuffs of Italy. Pearce (1993) considers brown analcimes of Crowsnest and red analcimes of Lupata Gorge (Woolley and Symes, 1976) as primary. We argue that color cannot be taken as definitive criteria for primary analcime because as it will be shown later, brown and honey colors are common for analcime pseudomorphous after leucite in similar rock types from Iran. 2) Fe contents: Crowsnest analcimes contain 1-2% Fe_2O_3 . According to Pearce (1970) the iron is in the crystal structure. He uses this as a distinction between primary and secondary analcimes (Pearce, 1993). As we show in the following, analcime as a replacement for leucite in Iran could also contain high structural Fe (Fig. 1). 3) Isotropy: Pearce (1970) observes that only brown analcime which he considers as primary is isotropic in thin section. According to him anisotropic and twined analcimes are the altered ones. We tend to disagree also with this criterion proposed by Pearce (1970 & 1993), as the Iranian analcimes described below are either isotropic or anisotropic in thin section.

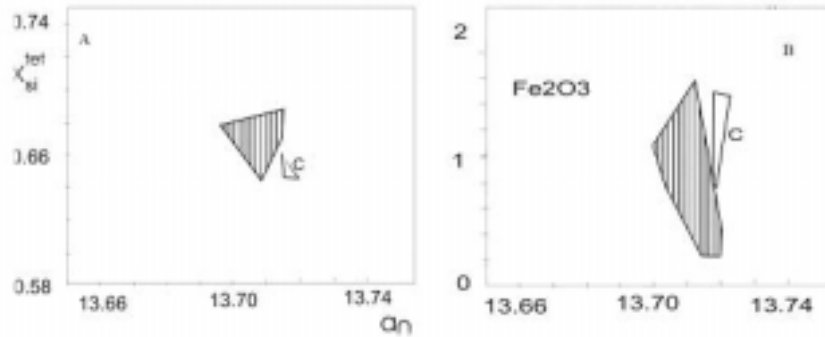


Fig. 1- Comparison of analcime pseudomorphous after leucite in the Paleogene volcanic rocks of Iran and isotropic analcimes of Crowsnest Formation of Alberta on **A)** X_{Si}^{tet} vs. cell constant (a_0) and **B)** Fe_2O_3 vs. cell constant (a_0). As it is obvious, the secondary analcimes of Iran are similar to the Crowsnest analcimes that Pearce (1993) maintains them as primary.

3. Experimental petrology

Experiments in the albite-orthoclase-nepheline-kalsilite-water system by Roux and Hamilton (1976) have revealed that analcime can coexist with silicate melt only in $P = 5$ to 13 kbars and $T = 600$ to 640 and very high H_2O pressures. These conditions are too far from those of eruptive environments. Phases accompanying analcime in most rocks are anhydrous. Olivines and clinopyroxenes are the dominant mafic minerals. Analcime-bearing rocks of Iran –in the following section- lack biotite and amphibole indicating derivation from dry magmas. Hydrous nature of analcime imposes a severe petrogenetic problem especially when it makes a significant percentage of a volcanic rock.

4. Analcime-bearing volcanics in Iran

Analcime-bearing lavas are common in the upper parts of the widespread Paleogene shoshonitic volcanics of Iran. Regional aspects of this volcanism have been treated by Aftabi and Atapour (2000).

4.1. Azerbaijan Province: Many occurrences ranging in composition from basanites to phonolites and rarer blaimorites have been reported from the Azarbaijan region of NW Iran by Comin-Chiaramonti et al. (1979), Lescuyer and Riou (1976), Riou et al. (1981) and Didon and Gemain (1976). A conspicuous 4-10 X 500 m lens of analcinite was also reported by Comin-Chiaramonti (1977) in eastern Azerbaijan. The analcinite cuts coarse volcanoclastic deposits and consists of 50 to 70% of clear and isotropic analcime with composition: $(Na_{0.91}K_{0.09})(Al_{1.03}Fe_{0.5}^{3+}Si_{1.92})O_6 \cdot H_2O$. The original assemblage consisted leucite, alkali feldspar, plagioclase, clinopyroxene and rare olivine.

4.2. Alborz: Farther east from Azerbaijan, in the western Alborz Mountains well-known occurrences of basanites and tephrites of Taleghan Ranges have been described by

Stalder (1971) and Annells et al. (1975). Analcime micro- and mega-phenocrysts are brown to honey color in hand specimen and like leucites contain circular concentric trails of inclusions. They are often isotropic in thin section although anisotropic and twined ones are also present.

4.3. Central Iran: Analcime tephrites have been reported from several localities including Torud Ranges (Hushmandzadeh et al., 1978), Davazdah Emam Mountains (Amidi et al, 1984), Anarak area (Sharkovski et al., 1984), and Qaleh Khargooshi, west of Aghda (Amidi and Michel, 1985; Carr et al., 1996).

Nain-Bazman volcanic belt: This zone is the SE segment of the famous Tertiary Urumieh-Dokhtar continental arc. Analcime-bearing shoshonites are ubiquitous and have been reported from Shahr-e babak area (Hassanzadeh, 1993), Bardsir Ranges (Aftabi and Atapour, 2000), and Bam area (Aghanabati, 1995).

4.4. Subrecent analcime basanites: Analcime is also present as microphenocrysts in post-collisional volcanics of Iran. Ashrafi (2003) has studied the Pleistocene olivine basanites of the Little Damavand in central Alborz. Excluding scarce phogopite, analcime is the only hydrous phase in these lavas and is enclosed in glassy matrix as euhedral sub-millimeter crystals (Fig. 2A). Analcime is clear and isotropic in thin section and frequently includes circular trains of microlites. Expansion cracks are common around analcime (Fig. 2B) and are attributed to hydration-induced expansion. According to Karlsson and Clayton (1991) leucite-analcime transformation involves about ~10% increase in volume. The flow in Little Damavand belongs to a cinder cone, and is partly overlain by a carbonate cemented trachyandesitic ash deposit.

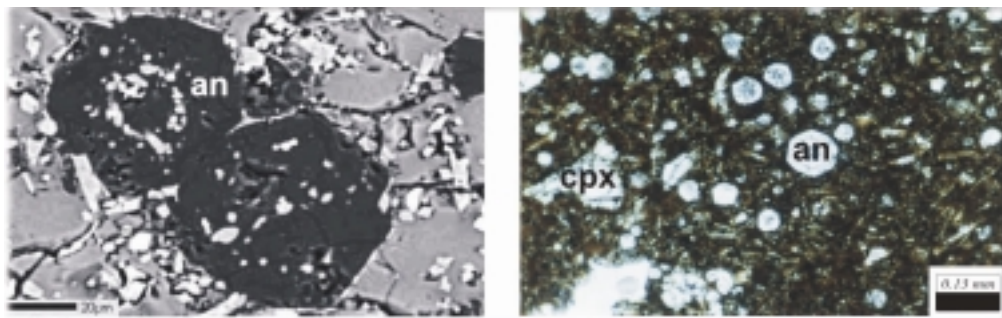


Fig. 2- Two photomicrographs from the Little Damavand olivine basanites (Ashrafi, 2003). **A)** General view showing euhedral analcime (an) microphenocrysts in a fresh dark brown glassy matrix. Clinopyroxene (cpx) is also present. Analcime is isotropic. Some crystals are clear and others contain inclusions. Scale bar equals 0.13 mm. Non-crossed polarizers. **B)** SEM image of the same section showing expansion cracks around two euhedral analcimes. Note circular pattern of inclusions in one and haphazard distribution in the other. Scale bar equals 20 μm.

5. Radiometric dating of analcimes

One way of resolving the debate on primary or secondary origin of analcime seems to be radiometric dating of the phenocrysts and comparing the results with the eruption age of the host volcanic rock. This approach has been employed by Hassanzadeh (1993) on the Hezar alkali volcanic complex, north of Shahr-e Babak in Kerman Province of SE Iran. The Hezar complex overlies Eocene calc-alkaline volcanics and sediments. Hezar tephrites lack biotite and amphibole but contain groundmass K-feldspar. Most also contain analcime which is presumably pseudomorphous after leucite but the potassium contents are extremely low (Table 1). Analcime is clear and isotropic in thin section. Some analcimes contain round trails of inclusions.

Table 1- Radiometric dating of analcimes

Locality	Damavand								Shahr-e Babak								Locality	Azerbaijan Province			Colima	Colima
Sample	LDMV/11		BMA	DJ 3b-2	DJ 3b-13	DJ 3b-14	DJ 3b-17	SH 1-83	JZ 1-47	Sample	AZ151W	AZ173 M	AZ80	SAY - 104	Sample	SAY - 104						
	Cone	Edge																				
SiO ₂	61.40	59.13	59.46	58.19	54.00	54.59	58.83	54.28	54.12	SiO ₂	51.28	54.09	55.3	55.28	SiO ₂	55.66						
TiO ₂	0.22	0.25	0.33	0.06	0.00	0.01	0.13	0.06	0.02	AZ03	23.48	22.44	23.28	21.84	AZ03	21.59						
Al ₂ O ₃	24.66	23.38	23.46	23.88	23.34	23.93	23.95	22.98	22.23	Fe ₂ O ₃	1.56	0.46	0.42	0.98	Fe ₂ O ₃	1.17						
FeO	0.63	0.58	0.84	0.21	0.61	0.30	0.34	0.02	0.60	MgO	0.21	0.09	0.12		CaO	0.23						
MnO	0.09	0.04	0.00	0.00	0.01	0.00	0.00	0.04	0.03	CaO	0.20	0.43	0.54	0.26	Na ₂ O	12.40						
MgO	0.04	0.02	0.02	0.00	0.30	0.00	0.00	0.06	0.07	Na ₂ O	12.78	13.87	11.88	11.58	K ₂ O	0.30						
CaO	0.27	0.27	0.55	0.09	0.23	0.46	0.15	0.51	1.22	K ₂ O	1.92	0.33	0.16	0.38	SiO	0.12						
Na ₂ O	5.23	10.62	10.68	9.13	12.51	13.21	8.95	13.27	12.18	H ₂ O+	9.20											
K ₂ O	0.05	0.12	0.20	0.04	0.51	0.07	0.00	0.06	0.14													
BaO	0.07	0.11	0.10	0.00	0.00	0.00	0.00	0.06	0.00													
Total	83.65	93.75	94.66	81.72	81.60	81.60	91.33	91.27	90.92	Total	99.73	81.49	91.27	99.52	Total	81.48						
	Number of cations per 8 oxygens									Number of cations per 90 oxygens												
Si	2.12	2.06	2.05	2.08	1.99	2.01	2.09	2.06	2.01	Si	1.93	2.00	2.02	2.07	Si	2.05						
Ti	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	Al	1.04	0.98	1.00	0.93	Al	0.94						
Al	1.00	0.98	0.97	1.01	1.01	0.99	1.01	1.00	0.97	Fe	0.04	0.01	0.01	0.03	Fe	0.04						
Fe	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.00	0.02	Mg	0.01	0.00	0.01		Ca	0.01						
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	Ca	0.01	0.02	0.02	0.01	Na	0.99						
Mg	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	Na	0.00	0.98	0.83	0.84	K	0.01						
Ca	0.01	0.01	0.02	0.00	0.01	0.02	0.01	0.02	0.05	K	0.00	0.02	0.01	0.02	Sr	0.01						
Na	0.42	0.75	0.73	0.63	0.89	0.94	0.58	0.95	0.88													
K	0.00	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.01													
Raj	0.00	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.01													
SUM	3.59	3.83	3.83	3.74	3.99	3.97	3.88	3.88	3.95	SUM	4.04	4.01	4.02	3.89	SUM	3.95						
References	This study									References	Conis-Charamzai (1979)			Luhr and Kyser (1993)	Luhr and Carmichael (1981)							

Apparent ages from three single crystal analcime analyses of sample JZ3a range from 19.9-23.2 with average 21.3 ± 1.7 Ma. Eight laser fusions of the groundmass K-feldspar crystal aggregates separated from a 80-100 mesh fraction of the same sample (JZ3a) gave apparent ages of 17.6-28.8 Ma. The average apparent age is 22.8 ± 3.2 Ma (Table 2). From a +30 mesh fraction of the same sample (JZ3a), groundmass fragments principally consist of K-feldspar and subordinate Ti-magnetite were selected and laser fused. Analyses gave apparent age of 23.2-26.3 Ma with an average of 25.3 ± 1.1 Ma (Table 2). Although results of the three sets of experiments on JZ3a are fairly close to one

another, they seem to represent a date younger than the eruption age because a more robust, but older age was obtained for an overlying phonolite flow (FT3) discussed below.

A stratigraphically younger subdivision of the Paleogene upper unit that rests on top of the JZ3a analcime tephrite contains nepheline phonolite flows. Separates of nepheline and fresh sanidine phenocrysts were selected for $^{40}\text{Ar}/^{39}\text{Ar}$ age determinations (sample FT3). Apparent ages from 15 single sanidine crystal fusions yield apparent ages of 28.3-30.8 Ma with an average of 29.8 ± 0.6 Ma (Table 2). Eight high-K nepheline single crystal fusions from the same sample (FT3) give apparent ages of 27.4-29.1 Ma with a weighted mean of 28.4 ± 0.6 Ma. The near one million year difference between the ages yielded by sanidine and nepheline from sample FT3 is likely to be the result of slight sericitization of nepheline.

A three point Rb-Sr isochron analysis of the same phonolite (FT3) gave an age of 28.4 ± 1 Ma (Table 2). We take the sanidine Ar-Ar date of 29.8 ± 1 Ma to be the eruptive age of the nepheline phonolite flow because of its consistency with the Rb-Sr date. Based on this postulate, the younger dates obtained for the underlying JZ3a analcime tephrite provides another evidence for subsolidus origin of Shahr-e Babak analcimes.

Table 2- Younger radiometric ages of euhedral analcime phenocrysts relative to the eruptive age of the host lava

Rock unit	Rock types & sample no.	Radiometric ages (Ma)
Oligocene Hezar volcanic complex, SE Iran	Nepheline phonolites (sample FT3)	Rb-Sr 3-point isochron: 28 ± 1 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ sanidine: 29.8 ± 0.6 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ slightly sericitized nepheline: 28.4 ± 0.6 Ma
	Analcime tephrites (sample JZ3a)	$^{40}\text{Ar}/^{39}\text{Ar}$ analcime: 21.3 ± 1.7 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ groundmass K-feldspar: 22.8 ± 3.2 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ groundmass aggregate: 25.3 ± 1.1 Ma

6. Conclusions

Petrographic criteria and high structural iron set forth by Pearce (1993) for magmatic analcime have been observed to hold in case of Iranian analcimes-bearing volcanics for which secondary origin is indisputable. Radiometric datings of analcime and the host volcanic rock shown by an example from Iran seems to be a resolving approach and is suggested to be attempted for Crowsnest and Colima analcimes.

Acknowledgments

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Biography:

Roghieh Akbar Ashrafi: She got her B.S degree in Geology at Zanzan University and M.Sc. degree in Petrology at University of Tehran. The areas of her interests are: Geochemistry, Crystallography, Hydrology.