ISERDAR

International Science and Engineering Reviews: Development, Analysis and Research

Breakdown of Amphibole in Disequilibrium Conditions: an Experimental Approach

Rahim Dabiri [1*], Abdollah Yazdi [2], Nasser Ashrafi [3], Mohammad Elyas Moslempour [4], Keivan Shiaian [5], Reza Arjmandzadeh[6], Alaaddin, Vural[7]

[1] Department of Geology, Mashhad Branch, Islamic Azad University, Mashhad, Iran, r.dabiri@mshdiau.ac.ir, ORCID No: 0000-0003-4043-3153*

[2] Department of Geology, Kahnooj Branch, Islamic Azad University, Kahnooj, Iran, ORCID No: 0000-0002-6096-4739

[3] Department of Geology, Payame Noor University,Tehran, Iran, ORCID No: 0000-0003-2700-6560

[4] Department of Geology, Zahedan Branch, Islamic Azad University, Zahedan, Iran, ORCID No: 0000-0003-3418-4226

[5] Department of Geology, Tabas Branch, Islamic Azad University, Tabas, Iran, ORCID No: 0000-0003-1278-8344

[6] Department of Geology, Payame Noor University,Tehran, Iran, ORCID No: 0000-0001-6482-4760

[7] Department of Geological Engineering, Ankara University,Ankara, Türkiye, ORCID No: 0000-0002-0446-828X
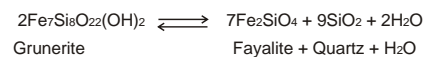
ARTICLE INFO

ABSTRACT

Evidences of amphibole and biotite breakdown can be seen in some volcanic rocks of the Tertiary and quaternary periods of Iran. This paper, investigates the breakdown of amphiboles in disequilibrium conditions. By investigation andesites of Quaternary pyroxenes northeast of Warzghan in northwest Iran, we obtained the combined temperature-pressure conditions of the amphibole crystals. Geothermometry and geobarometry based on amphibole single-phase compositions indicate that most of the amphibole crystals are not in equilibrium with hydrous melts containing ~64-69 wt% SiO_2. In the pyroxene andesites of the region, some amphiboles have been breakdown. Investigations showed that the arrival of new and hot magma pulse caused the magma cell to migrate from deep levels (22.5 km depth and 7.5 kbar pressure) to shallower depths (21 km depth and 7 kbar pressure). This increase in temperature and decrease in pressure destroyed the stability conditions of amphibole and created the conditions for the growth of augite.
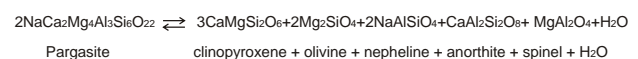
1. Introduction

Fundamentally, evidences of amphiboles and biotites breakdown can be observed in many volcanic rocks of the Tertiary and quaternary periods of Iran [1]. In most of these cases the primary amphibole crystals are still seen relatively intact [2]. In these rocks, amphibole or biotite have lost their stability and turned into anhydrous minerals (such as pyroxene), feldspar and metallic minerals [3-4]. In Figure 1 (d,e,f), we see the breakdown of a pargasite crystal. The border of this breakdown and transformations is defined by a reactive margin, which eventually grew an augite crystal on this phenomenon. In this paper, the causes of this special phenomenon and its application to temperature and pressure changes in the magma cell are discussed and investigated.

2. Discussion

The breakdown of amphibole produces different products depending on its composition. For example, the breakdown of Grunerite with the formula $Fe_7Si_8O_{22}(OH)_2$ can be shown by the following reaction [5].

$$2Fe_7Si_8O_{22}(OH)_2 \rightleftharpoons 7Fe_2SiO_4 + 9SiO_2 + 2H_2O$$
$$\text{Grunerite} \qquad \text{Fayalite + Quartz + } H_2O$$

They also show the breakdown of Pargasite with the following reaction [6].

$$2NaCa_2Mg_4Al_3Si_6O_{22} \rightleftharpoons 3CaMgSi_2O_6 + 2Mg_2SiO_4 + 2NaAlSiO_4 + CaAl_2Si_2O_8 + MgAl_2O_4 + H_2O$$
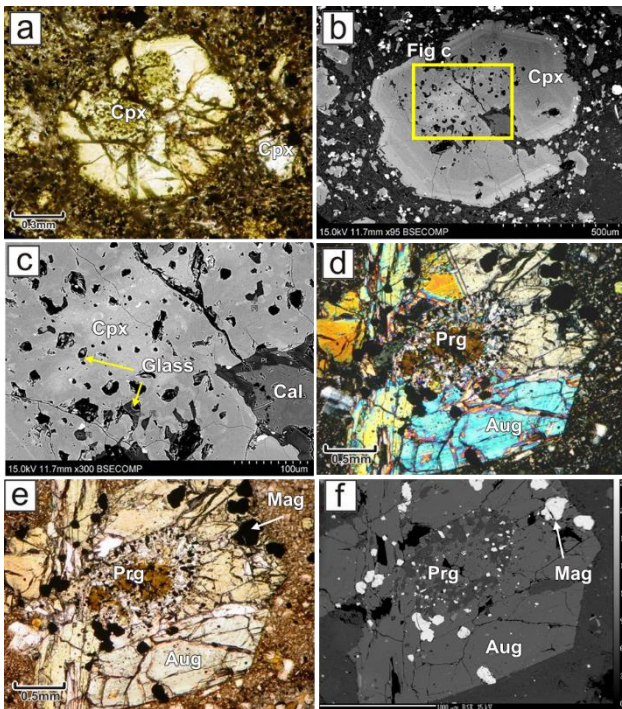$$\text{Pargasite} \qquad \text{clinopyroxene + olivine + nepheline + anorthite + spinel + } H_2O$$

Fig 1. Images of clinopyroxenes in intermediate rocks of the region. (a) Image of a clinopyroxene crystal (Cpx) with sieve texture and embayed margins (b,c) BSE images of image a showing sieve texture, embayed margins and fluctuating chemical zoning in more detail. In picture c, the empty spaces of the sieve tissue are filled by volcanic glass. (d,e,f) Break down of pargasite mineral (Prg) into a set of minerals (such as pyroxene, feldspar and metal minerals) and overgrowth of an augite crystal (Aug) on pargasite (Prg)) (images a, e are in PPL transmitted light, d is in XPL transmitted light, and images b, c, f are of Backscatter type)

Basically, amphiboles are very sensitive to changes in water vapor pressure [7-8]. In other words, changes in water vapor pressure (PH$_2$O) are factors affecting the breakdown of amphiboles. In addition to the role of water vapor pressure, amphibole breakdown is subject to the two factors of heat and lithostatic pressure [9-10]. The results of the laboratory work in the temperature and pressure coordinate device are shown in Figure 2. The slope of these curves is always positive due to the positivity of Δs (entropy) and Δv (volume). As shown in the diagram of Figure 2, decreasing the amount of water vapor pressure limits the stability field of pargasite, and on the contrary, increasing the amount of water vapor pressure expands the range of stability of pargasite. Also, with increasing temperature, pargasite loses its stability and transforms into other ferromenesine minerals [11-12]. At high water vapor pressures (XH$_2$O=1), the curve has an almost vertical slope and the role of lithostatic pressure reaches its lowest level [13-14]. (Maksimov, 2000, 2009). In other words, in the case of PH$_2$O=Ptotal, pargasite breakdown is more sensitive to temperature changes than to lithostatic pressure changes. Therefore, under constant pressure conditions, with increasing temperature, the univariate breakdown

curve is interrupted and amphibole turns into a set of anhydrous minerals (path 1) (Figure 2). The rise in temperature at constant pressure can be occurred by the entry of hot and fresh magmas into the magma cell.

In addition, research shows that an amphibole may breakdown at constant temperature and variable pressure [15-16] (Path 2). For example, if the magma contains amphibole or biotite at relatively high depths, with the sudden transfer of magma to shallower levels (closer to the surface of the earth), the said minerals will breakdown. In such conditions, the temperature remains almost constant and the pressure suddenly drops significantly (path 2). This decrease in pressure causes the mineral to break the single-variable amphibole breakdown curve and turn into anhydrous minerals such as clinopyroxene, olivine, feldspar (plagioclase and alkali feldspar) and spinel. This change of conditions is usually seen in volcanic environments where magma suddenly reaches the earth's surface as a result of finding its way through tension zones. In this way, it is easy to imagine that the breakdown of amphiboles in the earth occurs as a result of the rapid passage of magma to higher levels or, in fact, a sudden decrease in pressure at a constant temperature (Isothermal Decompression) [17]. In the meantime, the phase of the released fluids together with the previous fluid phases (in equilibrium with the primary magma) accelerated the transfer of cations (especially the transfer of alkaline cations) and caused the formation of magmatic residues very rich in alkali feldspar (series Shoshonite). These fluids cause alkaline metasomatism in intervening environments [15]. In such conditions, some primary plagioclase is surrounded by fluid with alkali feldspars.

The third state is when the role of temperature and pressure is applied simultaneously [18]. In other words, it is possible that hot magmas enter the magma cell, causing the temperature of the complex to rise and its rise to high levels. In such conditions, the temperature increases and the pressure decreases, and the univariate curve of amphibole breakdown may be interrupted (path 3).

Now the question arises under what conditions the studied pargasites breakdownd. Did temperature changes at constant pressure (path 1) cause the breakdown, or pressure changes at constant temperature (path 2) or a combination of these two (path 3) caused this phenomenon. To investigate this issue, we will calculate the temperature and pressure of amphibole and pyroxene formation under study. Due to the fact that equilibrium investigations show the imbalance of crystals and mesostasis of pyroxene andesite rocks, we are only allowed to use thermobarometric methods based on crystal compositions only in this part.

Table 1 shows the results of calculating the temperature and pressure of amphibole and pyroxene formation based on different thermobarometric methods. The average pressure obtained for the studied amphibole according to the methods of Hammarstrom and Zen (1986), Hollister at al. (1987), Johnson and Rutherford (1989) and Schmidt (1992) is equal to 7.5 kbar [19-22]. Also, according to the

method of [23,18], the formation temperature of this amphibole (including the pressure of 7.5 kbar) is about 1043 and 1020 C, respectively (Table 1 and Figure 3). Also, according to the method of [24] (temperature and pressure measurement only based on the composition of clinopyroxene), the formation pressure of this clinopyroxene is about 7 kbar and its temperature is 1071 C (Table 1). The plot of these values in the pargasite stability chart shows that the breakdown path of this mineral follows path 3. Allen and Broettcher [18] believe that water-saturated magmas will cut the stability curve of amphibole by ascending to shallow levels and this mineral will become unstable [25].
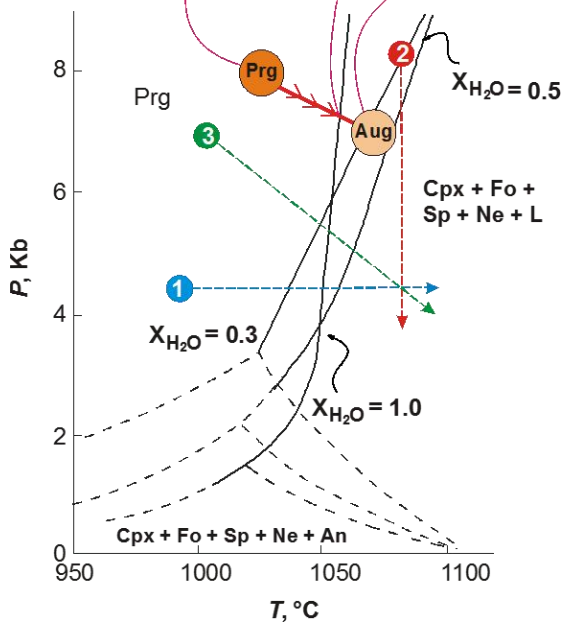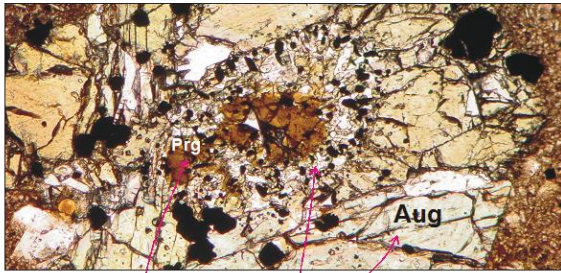

Fig 2- (a) Breakdown of a pargasite into an anhydrous minerals and the overgrowth of an augite on it (b) P-T diagram of the stability range of pargasite (Prg) based on experimental work [14]. By reducing the amount of XH_2O from 1 to 0.3, the range of pargasite stability becomes more limited. Path 1 shows an increase in temperature at a constant pressure, path 2 shows a decrease in pressure at a constant temperature, and path 3 shows a decrease in pressure with an increase in temperature. Pargasites (Prg) present in the pyroxene andesites of the region have breakdownd as a result of pressure reduction along with temperature increase and have turned into augite (Aug) type clinopyroxene. The boundary of this change and transformations is determined by the reactive margin between these two minerals, including an amalgam of different minerals (clinopyroxene, olivine, spinel, feldspar and opaque minerals).
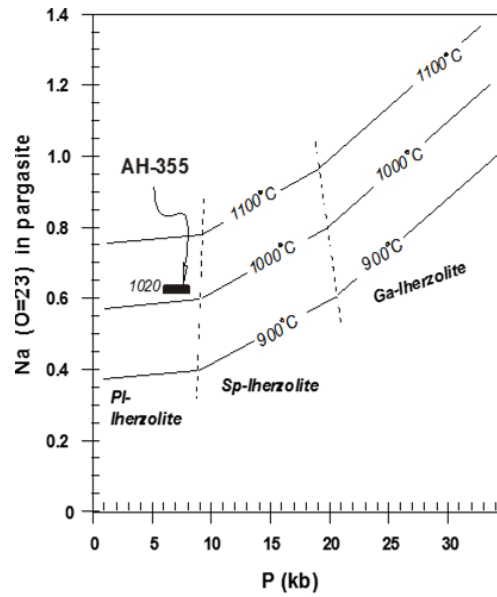

Figure 3- Thermometric diagram of pargasite based on changes of sodium cation in pargasite against pressure changes (after [15]). Based on the calculations, in the Ah-355 sample, the amount of Na available was 0.63 and the prevailing pressure was between 6.3 and 8.2 kbar (on average 7.5 kbar). Therefore, the temperature determined for the formation of pargasite is around 1020 C.

3. Conclusion:

With the things stated above, we can conclude that at the time of amphibole (pargasite) formation, magma had a lower temperature and higher pressure, and then as a result of an accident, its temperature increased and pressure decreased.

According to the texture of other minerals in the sample and region, it is believed that when the hot magma entered the magma cell, its temperature increased and as a result of the pressures on the magma cell, the roof cover of the magma cell was broken and the gases in the magma cell were released. Degassing) and the pressure has dropped rapidly. It is also possible that the arrival of new and hot magma pulses caused the magma cell to migrate from deep levels (depth of 22.5 km and pressure of 7.5 kbar) to shallower depths (depth of 21 km and pressure of 7 kbar). This increase in temperature and decrease in pressure destroyed the stability conditions of amphibole and created the conditions for the growth of augite (Figures 1 and 2). As far as this mineral can grow euhedrally on pargasite. The border of this change and transformations in the presented diagram can be defined by the reaction margin between these two minerals (Figure 2). In other words, the mixture of different minerals (including plagioclase, clinopyroxene and opaque minerals) between these two minerals (amphibole and clinopyroxene) can be considered as an indicator of the time of magma migration and disequilibrium conditions (pressure 7.2 kbar and temperature 1050 C). The confirmation of this is also evidenced by the growth of alkali feldspars on certain plagioclase samples.

Table 1- Electron microprobe analysis results for Figure 1 (Sample Ah-355) (Explanation that for pyroxene and amphibole thermobarometry, methods based on the composition of the mineral were used. For amphibole thermometry, two methods were used (one based on only the mineral composition and the other based on amphibole-plagioclase) and the amphibole formation pressure is considered as an average (around 7.5Kbar). Sources used for thermobarometry are specified for each case. For the formulas used, you can refer to the mentioned references)

Mineral	Px	Amp	Pl	P-T	Cpx	reference
Sample No	Ah-355	Ah-355	Ah-355	P (Kbar)	7.0	Putrika, 2008
Rock Type	PA	PA	PA	T (°C)	1071	Putrika, 2008
SiO$_2$	49.95	40.67	53.61	P-T	Amp	reference
TiO$_2$	0.74	2.40	0.07	P (Kbar)	7.6	Hammarstrom & Zen ,1986
Al$_2$O$_3$	3.07	13.34	29.94	P (Kbar)	8.2	Hollister et al. 1987
FeO	7.81	11.00	0.39	P (Kbar)	6.3	Johnson & Rutherford 1989
MnO	0.44	0.12	0.00	P (Kbar)	7.9	Schmidt,1992
MgO	15.23	14.37	0.00	T (°C)	1045	Holland and Blundy,1994
CaO	21.53	12.26	10.57	T (°C)	1020	Niida and Green,1999
Na$_2$O	0.44	2.21	5.05			
K$_2$O		1.35	0.10			
Sum	99.21	97.72	99.76			

References

[1] Allen, J. C., & Boettcher, A. L. (1983). The stability of amphibole in andesite and basalt at high pressures. American Mineralogist, 68(3-4), 307-314.

[2] Bailey, D.K., (1969): The stability of acmite in the presence of H20. Am. J. Sci., Schairer, 267(A), 1-16.

[3] Bonechi, B., Perinelli, C., Gaeta, M., Tecchiato, V., & Fabbrizio, A. (2020). Amphibole growth from a primitive alkaline basalt at 0.8 GPa: Time-dependent compositional evolution, growth rate and competition with clinopyroxene. Lithos, 354, 105272.

[4] Dabiri, R., Akbari-Mogaddam, M., & Ghaffari, M. (2018). Geochemical evolution and petrogenesis of the eocene Kashmar granitoid rocks, NE Iran: implications for fractional crystallization and crustal contamination processes. Iranian Journal of Earth Sciences, 10(1), 68-77.

[5] Davidson, J., Turner, S., Handley, H., Macpherson, C. Dosseto, A. (2007): Amphibole. "sponge" in arc crust? Geology, 35(9), 787-790.

[6] Deer, W. A., Howie, R. A., & Zussman, J. (Eds.). (1997). Rock-forming minerals: disilicates and ring silicates, volume 1B. Geological Society of London.

[7] D'Mello, N. G., Zellmer, G. F., Negrini, M., Kereszturi, G., Procter, J., Stewart, R., ... & Iizuka, Y. (2021). Deciphering magma storage and ascent processes of Taranaki, New Zealand, from the complexity of amphibole breakdown textures. Lithos, 398, 106264.

[8] Ghasempour, M. R., Mehdipour Ghazi, J., Biabangard, H., & Dabiri, R. (2014). Petrogenetic Evolution of Plio-Quaternary Mafic Lavas in Nehbandan (East Iran). Iranian Journal of Earth Sciences, 6(2), 133-141.

[9] Hammarstrom, J. M., & Zen, E. A. (1986). Aluminum in hornblende: an empirical igneous geobarometer. American mineralogist, 71(11-12), 1297-1313.

[10] Holland, T., & Blundy, J. (1994). Non-ideal interactions in calcic amphiboles and their bearing on amphibole-plagioclase thermometry. Contributions to mineralogy and petrology, 116, 433-447.

[11] Hollister, L. S., Grissom, G. C., Peters, E. K., Stowell, H. H., & Sisson, V. B. (1987). Confirmation of the empirical correlation of Al in hornblende with pressure of solidification of calc-alkaline plutons. American mineralogist, 72(3-4), 231-239.

[12] Johnson, M. C., & Rutherford, M. J. (1989). Experimental calibration of the aluminum-in-hornblende geobarometer with application to Long Valley caldera (California) volcanic rocks. Geology, 17(9), 837-841.

[13] Juriček, M. P., & Keppler, H. (2023). Amphibole stability, water storage in the mantle, and the nature of the lithosphere-asthenosphere boundary. Earth and Planetary Science Letters, 608, 118082.

[14] Maksimov, A.P., (2000): The Water Influence on the Temperature of the Amphibole Stability in the Melts, Experiment in Geosciences, 9 (1), 41–42.

[15] Maksimov, A.P., (2009): The water influence on the temperature of the amphibole stability in the melts , . Journal of Volcanology and Seimologym 3 (1), 27-33.

[16] Niida, K., & Green, D. H. (1999). Stability and chemical composition of pargasitic amphibole in MORB pyrolite under upper mantle conditions. Contributions to Mineralogy and Petrology, 135(1), 18-40.

[17] Ousta, S., Ashja-Ardalan, A., Yazdi, A., Dabiri, R., & Arian, M. A. (2024). Petrogenesis and tectonic implications of Miocene dikes in the southeast of Bam: Constraints on the development of active continental margin. Geopersia, 14(1), 89-111.

[18] Putirka, K.D. (2008) Thermometers and Barometers for Volcanic Systems. Reviews in Mineralogy and Geochemistry, 69, 61-120.

[19] Ridolfi, F., Renzulli, A., & Puerini, M. (2009). The feeding system of calc-alkaline volcanoes as inferred from new amphibole-thermobarometric formulations: reconciling petrological and geophysical evidence.

[20] Rutherford, M. J., & Hill, P. M. (1993). Magma ascent rates from amphibole breakdown: an experimental study applied to the 1980–1986 Mount St. Helens eruptions. Journal of Geophysical Research: Solid Earth, 98(B11), 19667-19685.

[21] Sabzehi, M (2005): Breakdown of amphiboles and biotites in magmas and its petrological significance, The 24th Earth Sciences Conference, Tehran, Iran.

[22] Sajeev, K., Windley, B. F., Connolly, J. A. D., & Kon, Y. (2009). Retrogressed eclogite (20 kbar, 1020 C) from the Neoproterozoic Palghat–Cauvery suture zone, southern India. Precambrian Research, 171(1-4), 23-36.

[23] Schmidt, M.W., (1992): Amphibole composition in tonalite as a function of pressure: an experimental calibration of the Al-in-hornblende barometer. Contrib Mineral Petrol, 110, 304-310.

[24] Schorn, S., Rogowitz, A., & Hauzenberger, C. A. (2023). Partial melting of amphibole–clinozoisite eclogite at the pressure maximum (eclogite type locality, Eastern Alps, Austria). European Journal of Mineralogy, 35(5), 715-735.

[25] Tracy R. J., Frost, B. R. (1991). Phase equilibria and thermobarometry of calcareous, ultramafic and mafic rocks.

[26] Wallace, P., De Angelis, S. H., Larsen, J., Caricchi, L., & Lavallée, Y. (2024). Amphibole breakdown rim textures as archivists of pre-eruptive magmatic processes (No. EGU24-16546). Copernicus Meetings.2014