# ZEOLITES IN AMYGDALOIDAL BASALTS FROM TONNGE AREA, TIGYAING TOWNSHIP, SAGAING REGION, MYANMAR

Myo Min Tun<sup>1</sup>, Thet Tun<sup>2</sup>, Thet Naing<sup>3</sup>

## Abstract

Tonnge basaltic field is situated 100 km north of Mandalay in Tigyaing Township, Sagaing Region of Myanmar. It is regarded as an intraplate Quaternary basaltic field and located to the north of well-known Singu-Kabwet basaltic lava field of Central Myanmar. In this study, zeolites filling in the amygdales of the olivine basalts from Tonnge area have been reported and studied by field observation, transmitted light microscopy and X-ray diffraction analysis. The zeolite group minerals are identified as natrolite, phillipsite, mordenite, laumontite, analcime, and epistilbite. Non-zeolite mineral phases in the amygdaloidal infillings are recognized as smectite, quartz (as amorphous silica), and carbonates. Zeolites and associated minerals are interpreted to be developed possibly as a consequence of late-stage hydrothermal circulation. Moderately to weakly alkaline hydrothermal solutions are responsible for the formation of zeolites in the basalts. Due to the occurrence of different zeolite minerals, it can be deduced that a change in fluid composition occurred as temperature dropped during their formation.

Keywords: Tonnge basalt, Amygdaloidal, zeolites, hydrothermal, alkaline

# Introduction

Zeolites are crystalline, microporous, hydrous alumina-silicates of alkaline or alkaline earth metals. Framework structure of zeolites consists of [SKO] and [AlO] tetrahedra, which cornershare to form open structures. Such tetrahedra are linked to each other by sharing every O with adjacent tetrahedron to form interconnected cages and channels containing mobile water molecules and alkali and/or alkaline earth cations (Breck, 1974; Barrer, 1982; Gottardi and Galli, 1985; Szoztak, 1998). Zeolites form at low pressures, temperatures, and alkaline pH in the presence of H<sub>2</sub>O and possess channels and voids in their structures.

Natural zeolites occur in the rocks of different mineralogical and chemical composition, age and geological environments. They are developed during aqueous fluids reaction with rocks in a variety of geological environments (Breck, 1974; Gottardi and Galli, 1985). Their formation and distribution depend on three main factors (Bargar & Keith, 1995; Chipera and Apps, 2001; Sheppard and Hay, 2001; Utada, 2001); (a) the composition of host rocks, (b) variation in temperature and pressure and (c) the chemistry of pore water. Two main origins were recognized (Iijima, 1980; Gottardi & Galli, 1985; Hay & Sheppard, 2001): (1) those formed under diagenesis to very low-grade metamorphism, resulted from leaching of glass-containing volcanic lavas and tufts by alkaline aqueous solution and (2) those of hydrothermal genesis. Zeolites occurring in volcanic terrains are developed either during burial metamorphism (Neuhoff et al., 1999), hydrothermal alteration (Walker, 1960) or diagenetic processes influenced by the high heat flow in the active geothermal systems (Weisenberger and Selbekk, 2008).

Zeolites are widely used in several applications such as catalysts, adsorbents and ion exchangers (Breck, 1974; Booker et al, 1996; Dixit and Prasada, 1998; Misaelides, 2011; Loiola et al., 2012). Previous studies reported the occurrences of zeolites in late stage pegmatite veins (Orlandi and Scortecci, 1985, in hydrothermal ore veins (Deer et al., 2004), as alteration products along fault planes (Vincent and Ehlig, 1988), in hydrothermal fractures and veins of granites and

<sup>&</sup>lt;sup>1</sup>Associate Professor, Department of Geology, Kyaukse University, Kyaukse, Myanmar

<sup>&</sup>lt;sup>2</sup> Professor and Head, Department of Geology, Kyaukse University, Kyaukse, Myanmar

<sup>&</sup>lt;sup>3</sup> Professor and Head, Department of Geology, Pathein University, Pathein, Myanmar

gneisses (Weisenberger and Bucher, 2010, and in hydrothermal alteration of epithermal highsulfidation system (Tun et al., 2017).

Tonnge basaltic field is situated 100 km north of Mandalay in Tigyaing Township, Sagaing Region, Myanmar (Figure 1) and is regarded as an intraplate Quaternary basaltic field (Tun et al., 2019). It is located to the north of well-known Singu-Kwbwet basaltic lava field of central Myanmar. This study reports natural zeolites filling in the amygdales of intraplate alkali olivine basalts from Tonnge area and investigates the mineralogical characteristics of zeolites and other associated minerals.



Figure 1 Location map of the Tonnge area, Tigyaing Township, Sagaing Region, Myanmar.

# Geology of the Tonnge Area

Basaltic field in the Tonnge area is roughly circular in outline (Figure 2) and consisting of basaltic lava flows. Eruption seems to be occurred from a central vent in the northeastern part of the Tonge Hill and further spread out horizontally to the south-southwest direction. The lavas rest unconformably upon the clastic sediments of Irrawaddy Formation (Upper Miocene-Pliocene). Thus, the age of the basaltic lava field is considered to be post-Pliocene.

The lava flows has an average thickness of less than 5 m (Figure 3a). The fresh surface of the basalts is bluish to dark grey in color (Figure 3b). Their surfaces are often coated by reddish brown iron oxides. The flows are characterized by vesicular nature (Figure 3c) in the upper part whereas columnar in the lower section (Figure 3d). Vertical columns are 4- to 6-sided and 0.3 to 0.5 m across in diameter. Prismatic jointing is common. Dyke-like intrusion is observed in the central-eastern part. In this area, basaltic lava exhibits vesiculation features containing abundant amygdaloidal infillings.



Figure 2 Geological Map of the Tonnge area, Tigyaing Township, Sagaing Region (after Theingi, 2018 and Tun et al, 2019).



Figure 3 Nature of exposure of Tonnge basalts (a) Basaltic lava flow in the western part of the area (b) An exposure of dark grey olivine basalt at the quarry in the central portion of the research area (c) Vesicular basalt in the southern part of the Tonnge area (d) Basalt column in the southeastern part of the study area.

## **Materials and Methods**

Geological fieldworks primarily focusing on the collection of representative samples of natural zeolites-bearing basalts from the Tonnge area have been made. Samples containing zeolites and other secondary minerals filling in amygdales were taken from rock exposures in the quarries. Petrographical and microscopic studies were carried out for the identification of mineral species from the collected samples. A transmitted light polarizing microscope was used to examine the optical properties of zeolites. X-Ray Diffraction (XRD) patterns of zeolites were recorded with a Rigaku RINT-2100 Diffractometer using Cu-K $\alpha$  radiation at 40 kV and 20 mA. Count data were gathered from 2°- 65° two theta ranges operated at 2°/minute scanning rate. Mineral identification used the powder diffraction file (PDF-2) of International Centre for Diffraction Data. Nomenclature used for the description of the zeolite group minerals follows that of Combs et al. (1998).

# **Results and Discussion**

## **Field Occurrences of Zeolites**

A good exposure of zeolite occurrence was observed in a quarry located to the west of Tonnge village. In this locality, zeolites occur in amygdales or cavities of the amygdaloidal olivine basalts. The olivine basalts that usually show a reddish brown weathering surface (Figure 4a, 4b & 4d). Fresh olivine basalts are bluish to dark gray with zeolites developed as void-filling (Figure 4a). Figure 2 shows macroscopic characteristics of zeolites commonly observed in the field. The occurrence and distribution of zeolites and other secondary associated minerals in the amygdales of the basalts are non-uniform and discontinuous in nature. Zeolites generally occur as minerals outlining the cavities and sometimes they completely fill them. They are perfectly rounded (Fig. 4a), elliptical (Fig. 4b and 4d) and irregular in shape (Fig. 4c), and their sizes range from 1–10 cm in diameter (Fig. 4a to 4d).



Figure 4 Outcrops nature of zeolite infillings in Tonnge basalt (a) small and rounded amygdales filled by zeolites (b) elongated cavities filled by zeolites and other secondary minerals in the amygdaloidal basalt (c) Large irregular void filled by zeolites (natrolite and mordenite) (d) Large and elongate cavity filled by zeolites (natrolite and phillipsite). Ntr-Natrolite; Mor-Mordenite; Php-Phillipsite.

Vesicles are developed when dissolved gases are escaped during the ascent of lava as a result of pressure drop, forming gas bubbles and leaving the cavities in the upper part of the lava flow. Those vesicles are filled with secondary minerals due to near-surface circulation of meteoric water. Some large amygdales are observed (Figure 4c). Veins development is not observed. Druzy amygdales, having a partial filling, exhibit various types of zeolite minerals. A fibrous zeolite phases displaying a silky luster occup the outer cavity wall whilst a fibrous interior or granular zeolite phases having a glassy luster occur as an interior padding. Zeolytic phases and other associated minerals such as calcite and smectite in the amygdaloidal basalts were considered to be deposited sequentially from the outer wall to the center of amygdales. The spatial distribution of zeolites is likely to be controlled by the chemistry of host rock, its porosity, and local hydrological and hydrothermal conditions.

## Petrography

The basalts from Tonnge area are porphyritic, holocrystalline and consist mainly of phenocrysts of olivine, plagioclase  $\pm$  clinopyroxene (Figure 5a and 5b). Olivine is the dominant mineral in the studied samples. The groundmass is intergranular and consists predominantly of plagioclase microlites with subordinate olivine, clinopyroxene, and opaque minerals (titanomagnetite and ilmenite). Parallel and sub-parallel arrangement of plagioclase microlites developing trachytic texture (Figure 5a) is commonly observed in the basalt samples. Glomeroporphyritic texture (Figure 5b) is also observed in the basalt sample by the clustered olivine phenocrysts in the fine-grained plagioclase laths. Absence of quartz and presence of fairly abundant olivine suggest the rocks as alkali olivine basalts.



**Figure 5** (a) Phenocrysts and microphenocrysts of olivine set in the trachytic plagioclase microlites (b) Glomeroporphyritic texture showing a cluster of olivine phenocrysts enclosed by fine-grained groundmass of plagioclase, olivine and pyroxene. Ol-Olivine; Pl-Plagioclase.

Zeolites are white with silky luster and show a predominance of fibrous aggregates, acicular and radial aggregates (Fig.6a-6d). Most zeolites are relatively coarse-grained and easily identifiable. However, they sometimes occur as fine-grained aggregates and are identified by petrographic microscopy and XRD analyses. Figure 4 illustrates the main microscopic features of the zeolites and associated mineral phases. The common zeolite mineral is natrolite and others include phillipsite, mordenite, laumontite, analcime and epistilbite.



**Figure 6** Photomicrographs of zeolites in amygdaloidal basalt of the Tonnge area in thin-section (a and b) fan-shape zeolite (natrolite) enclosing calcite in the cavity of olivine basalt (under XN) (c) Mordenite enclosed by other radial aggregate zeolite in the ellipsoidal amygdale (under XN). (c) Radial and fibrous zeolite (mordenite) completely filling the perfectly rounded cavity in olivine basalt (under PPL). Mineral abbreviations as in Figure 4.

## **X-Ray Diffraction Analysis**

Qualitative XRD analysis enables the identification of the mineral species of zeolite. Figure 7 and Figure 8 illustrate representative zeolites diffraction patterns and associated phases. XRD analysis identifies the zeolite species, including natrolite, as the dominant phase of zeolite, followed by laumontite, phillipsite, analcime, epistilbite and mordenite. Other secondary mineral associated with zeolite was smectite.

Results from the X-Ray Diffraction analysis (Figure 7 and 8) indicate that laumontite has the characteristic peaks having the d-spacings of 9.42Å, 4.16Å and 3.03Å. Phillipsite has characteristic peaks with d-spacings of 7.20 to 7.23 Å, 5.07 Å and 4.16Å. Natrolite is identified in the X-Ray diffractograms by the diffraction peaks with basal spacing of 6.55 Å, 5.89 Å, 4.69 Å, 4.60 Å, and 4.36 Å. Analcime has characteristic peaks with d-spacings of 5.63Å, 3.44Å and 2.93Å. The presence of epistilbite was evident by the XRD pattern exhibiting d-spacings of 3.91Å and 3.76Å. Mordenite is identified by its characteristic diffraction peak with basal spacing of 3.22Å in the X-Ray diffractograms.



Figure 7 Diffraction pattern of zeolite mineral assemblage and associated phase in amygdaloidal basalt of Tonnge area. It shows an assemblage of natrolite, phillipsite, mordenite, laumontite, analcime and epistilbite. The main zeolytic phases are natrolite, phillipsite and mordenite. Non-zeolite mineral is nontronite.

In addition to zeolite minerals, the XRD pattern also shows the presence of a certain amount of nontronite (smectite) as non-zeolite mineral having its main diffraction peak occurring at 15.06 or 15.06 Å (Figure 7 and 8), provides an evidence for the alteration of pre-existing minerals. Several zeolytic phases were identified in this study which could be organized into five structural groups according to Meier's classification (1968). The heulandite group was represented by laumontite and mordenite. Clinoptilolite group was represented by epistilbite. The analcime group is represented by analcime. The natrolite group was made up of natrolite. Phillipsite belongs to the phillipsite group.



**Figure 8** Diffraction pattern of zeolite mineral assemblage and associated phase in amygdaloidal basalt of Tonnge area. It shows an assemblage of natrolite, phillipsite, mordenite, laumontite, analcime and epistilbite. The main zeolytic phases are natrolite, phillipsite and mordenite. Non-zeolite mineral is nontronite.

#### **Formation of Zeolites**

Tonnge basalt is particularly well-known for its characteristic intraplate character and amygdaloidal texture. The distribution of zeolites in the basalt has been controlled by a combination of factors such as temperature, pressure, hot aqueous fluid circulation and rock's chemical composition (Walker, 1960). The zeolites and associated secondary minerals were deposited from the outer wall to the center of amygdales in the basalts.

Chemical elements necessary for the formation of these mineral phases were released directly as a result of hydrothermal devitrification. Zeolites were probably formed from fluids, which penetrated the vesicles and fractures, but the origin of the fluid remains unknown and yet to be studied. No sequential zoning of zeolites was observed in this study. Non-zeolite and smectite group mineral nontronite was probably formed by basalt devitrification as a result of hydration, although ferromagnesian mineral phases in the basalts may also have been responsible for its formation. Hence, the existence of nontronite along with very well-developed zeolite crystals such as analcime, and phillipsite indicated that nontronite was deposited prior to fibrous zeolites, and suggest low temperature (<100  $^{\circ}$ C) hydrothermal alteration (Deer et al., 2004).

Phillipsite formation is usually triggered by host basalt low-temperature hydrothermal alteration (~ 90 °C). Ca- and K-rich fluids changed their composition as the temperature decreased (Chipera and Apps, 2001). Depletion of these elements in the fluid during phillipsite formation promoted the introduction of Na-rich zeolites such as calc-sodic analcime, chabazite and natrolite (Cochemé et al., 1994), at lower temperatures (Chipera and Apps, 2001). It was experimentally confirmed that chabazite is stable up to 100 °C, whereas analcime is stable in the temperature range between 100 and 200 °C (Hay and Sheppard, 2001). Chipera and Apps (2001) stated that decreased in Si activity reduced the analcime stability field and promoted natrolite development after analcime and chabazite. This suggested that zeolites formed in the edges of basalt cavities are at higher temperature and lower Si activity during the early stage of crystallization, whereas zeolite species in the central cavity were developed under lower temperature condition and are more aluminous in composition.

Formation of laumontite and stilbite could be attributed to the nature of the hydrothermal fluids associated with pluton emplacement, which were more likely enriched in elements such as Ca, Ba, and Sr produced by a late event, taking into account that they usually appear to be developed as filling fractures in basalts.

## **Conclusions and Recommendation**

Formation of zeolites and associated secondary minerals filling amygdales in basaltic rocks from Tonnge area has been documented in this study. Zeolites deposited in vesicles were the result of a hydrothermal process, having a variety of species and this was due to reduced Si activity in the fluid. The variable amounts of silica, alumina and alkali and alkaline-earth cations required for zeolite formation could be resulted either from primary igneous fenocrystal dissolution or the plagioclase alteration reaction that release calcium in the rock matrix. Due to the occurrence of different zeolite minerals, it can be deduced that a change in fluid composition occurred as temperature dropped. Secondary mineral smectite represented the first crystallized species lining the outer part of the cavities. Na-rich zeolites such as analcime, and phillipsite were the first zeolites that became crystallized, followed by acicular-fibrous natrolite and Ca-rich zeolites. The Si activity decreased during alteration and temperature increased to 200 °C thereby allowing analcime formation followed by that of natrolite. Laumontite and stilbite formation could be attributed to the presence of Ca, Ba, and Sr-rich hydrothermal fluids produced by a late event.

It is strongly recommended that SEM-EDS or EPMA analysis of zeolites should be carried out in order to identify the chemical composition of each mineral species, and to interpret the chemical variation among them. It would help understand the sequence of mineral deposition, origin and evolution of these zeolite group minerals in the amygdaloidal olivine basalts of Tonnge area.

# Acknowledgements

The authors would like to give special thanks to Dr Aung Khin Myint, Rector of Kyaukse University, for his permission to carry out this research. We want to extend our thanks to Dr Su Su Win, Pro-rector of Kyaukse University for her kind support for the present work. We would like to acknowledge the Head of the Tonnge Village, Tigyaing Township (Sagaing Region) for his kind support during field investigation in the research area.

#### References

Bargar, K.E. and Keith, T.E.C. (1995) Calcium zeolites in rhyolitic drill cores from Yellowstone national park, Wyoming. In D.W. Minga, F.A. Mumpton (eds), "*Natural Zeolites*," International Committee on Natural Zeolites, *Brockport*, New York, pp. 69-86.

Barrer, R. M. (1982) Hydrothermal chemistry of zeolites," Academic Press, New York, 360p.

- Booker, N. A. Cooney, E.L. Priestley, A.J. (1996) Ammonia removal from sewage using natural Australian zeolite," *Water Sci Technol*, Vol. 34, pp. 17-24.
- Breck, D.W. (1974) Zeolite Molecular Sieves: Structure, Chemistry and Use, John Wiley, New York, 313p.
- Chipera, S.J. and Apps, J.A. (2001) Geochemical stability of natural zeolites" In: D.L. Bish, D. W. Ming (eds), "Natural Zeolites: Occurence, Properties, Applications," *Reviews in Mineralogy and Geochemistry*, Mineralogical Society of America, Vol. 45, pp. 117-161.
- Cochemé, J., Aguirre, L., Bevins, R. and Robinson, D. (1994) Zeolitization processes in basic lavas of the Baucarit Formation, Northwestern Mexico, *Rev Soc Geol Chile*, Vol. 21, pp. 217-231.
- Coombs, D.S., Alberti, A., Armbruster, T., Artioli, G., Colella, C., Galli, E., Grice, J.D., Liebau, F., Mandarino, J.A., Minato, H., Nickel, E.H., Passaglia, E., Peacor, D.R., Quartieri, S., Rinaldi, R., Ross, M., Sheppard, R.A., Tillmanns, E. and Vezzalini, G. (1998) Recommend-ed nomenclature for zeolite minerals: Report of the Subcommittee on Zeolites of the Mineralogical Assiciation, Commision on New Minerals and Mineral Names, *European Journal of Mineralogy*, Vol. 10, pp. 1037-1081.
- Deer, W.A., Howie, R.A., Wise, W.S., and Zussman, J. (2004) An Introduction to Rock-Forming Minerals," Longmans, The Geological Society, London, 696p.
- Dixit, L. and Prasada, T.S.R. (1998) New approach to acid catalysis and hydrocarbon zeolite interactions," *Stud Surf Sci Catal*, Vol. 113, pp. 313-319.
- Gottardi, G. and Galli, E. (1985) Natural Zeolites. Springer-Verlag, Berlin, Germany, 409p.
- Hay, R. and Sheppard, R. (2001) Occurrence of zeolites in sedimentary rocks: An overview" In: D.L. Bish, D.W. Ming (eds), "Natural Zeolites: Occurence, Properties, Applications," *Reviews in Mineralogy and Geochemistry*, Mineralogical Society of America and the Geochemical Society, Vol. 45, pp. 217-234.
- Iijima, A. (1980) Geology of natural zeolites and zeolitic rocks. Pure and Applied Chemistry, Vol. 52, pp. 2115-2130.
- Loiola, A.R., Andrade, J.C.R.A., Sasaki, J.M., and da Silva, L.R.D. (2012) Structural analysis of zeolite NaA synthesized by a cost-effective hydrothermal method using kaolin and its use as water softener," J Coll Int Sci, Vol. 367, pp. 34-39.
- Meier, W.M. (1968) Zeolite structures In: R Szostak (eds), "Molecular Sieves," *Blackie Academic and Professional*, London, pp. 10-27.
- Misaelides, P. (2011) Application of natural zeolites in environmental remediation: A short review," *Micropor. Mesopor. Mat.*, Vol. 144, pp. 15-18.
- Neuhoff, P.S. Fridriksson, T. Arnórsson, S. (1999) Porosity evolution and mineral paragenesis during low-grade metamorphism of basaltic lavas at Teigarhorn, Eastern Iceland," *Am J Sci*, Vol. 299, pp. 467-501.

Orlandi, P. and Scortecci, P.B. (1985) Minerals of the Elba pegmatites, Mineral Rec, Vol. 16, pp. 353-364.

- Szoztak, R. (1998) Molecular sieves, *Blackie Academic and Professional*, London, 359p.
- Sheppard, R.A. and Hay, R.L. (2001) Formation of zeolites in open hydrologic systems" In D.L. Bish, D.W. Ming (eds) "Natural Zeolites: Occurrence, Properties, Applications," *Reviews in Mineralogy and Geochemistry*, Mineralogical Society of America and the Geochemical Society, Vol. 45, pp. 261-276.
- Theingi, M. (2018) Petrology and Tectonic Significance of Basaltic Rocks from Tonnge Area, Sagaing Region. MSc Thesis (unpublished), University of Mandalay, Mandalay, Myanmar.
- Tun, M.M., Yonezu, K., and Watanabe, K. (2017) Laumontite Mineralization in the Cijulang High-Sulfidation Epithermal Deposit, West Java, Indonesia," In the Proceedings of International Symposium on Earth Science and Technology, Japan, pp.690-693.
- Tun, M. M., Theingi, M., Khaing, S.Y., Naing, T., Sann, Z.O. and Thin, A.K. (2019) Petrology and Geochemistry of Basalts from Tonnge Area, Tigyaing Township, Sagaing Region, Myanmar, *Open Journal of Geology*, 2019, Vol. 9, No.9, pp. 516-526.
- Utada, M. (2001) Zeolites in hydrothermally altered rocks In D.L. Bish and D.W. Ming (eds). "Natural zeolites: Occurrence, Properties, Applications," *Reviews in Mineralogy and Geochemistry*, Mineralogical Society of America and the Geochemical Society, Vol. 45, pp. 305-319.
- Vincent, M.W. and Ehlig, P.L. (1988) Laumontite mineralization in rocks exposed north of San Andreas Fault at Cajon Pass, southern California, *Geophys. Res. Let.*, Vol. 15, pp. 977-980.
- Walker, G.P.L. (1960) Zeolite zones and dike distribution in relation to the structure of the basalts of eastern Iceland, *J Geol*, Vol. 68, pp. 515-528..
- Weisenberger, T. and Selbekk, R.S. (2008) Multi-stage zeolite facies mineralization in the Hvalfjördur area, Iceland," Int. J. Earth Sci., Vol. 98, pp. 985-999.
- Weisenberger, T. and Bucher, K. (2010) Zeolites in fissures of granites and gneisses of the Central Alps," *J Metam Geol*, Vol. 28, pp. 825-847.