Techno-Science Research Journal 4 (2016) 40-48

Content list available at ITC

Techno-Science Research Journal

Journal Homepage : www.itc.edu.kh

Techno-Science Research Journal

MINERALOGICAL CHARACTERISTICS OF THE SIDOMULYO ZEOLITE AND THE KEDUNGBEDAH BENTONITE, GUNUNGKIDUL REGENCY AND BOYOLALI REGENCY, RESPECTIVELY, INDONESIA AND THEIR UTILIZATIONS AS HEAVY METAL ADSORBENTS

Bunchoeun PICH[1], Anita YULIYANTI[2], I Wayan WARMADA[2], Arifudin IDRUS[2], Anastasia Dewi TITISARI[2], and Tetsuro YONEDA[3`]

[1,2]Department of Geological Engineering, Faculty of Engineering, Gadjah Mada University, Yogyakarta, Indonesia
[3]Division of Solid Waste, Resources and Geo-environmental Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, Japan

ABSTRACT

The Sidomulyo zeolitic and Kedungbedah bentonitic tuffs are respectively located in the Gunungkidul and the Boyolali regencies, Indonesia. The study of their mineralogical characteristics was primarily done. The petrographical analysis indicates that the Sidomulyo zeolitic or Kedungbedah bentonitic tuffs is composed of volcanic glass, quartz, plagioclase, and altered minerals. The XRD investigation reveals that the zeolite tuff contains clinoptilolite, mordenite, montmorillonite, plagioclase, quartz, and orthoclase whereas the bentonitic tuff contains montmorillonite, clinoptilolite, illite, dickite, and quartz. The SEM observation of zeolitic tuff displays the presence of clinoptilolite in tabular structure and mordenite in fibrous structure and that of bentonitic tuff mostly presents montmorillonite in webby structure. The activated ion-exchange capacity of the Sidomulyo zeolitic and Kedungbedah bentonitic tuffs are 65.30 mgr.eq.Na_2O/100 gram zeolite and 37.6 mg.eq.Na_2O/100 gram. The zeolitic tuff dominantly contains clinoptilolite whereas the bentonitic tuff mostly consists of montmorillonite. Due to their porous structure, the zeolite and bentonite are effectively used as heavy-metal adsorbents: 10g of zeolite in a solution of 250ml can adsorb about 9.80ppm of Cu(II), 10.5ppm of Cr(VI), and 11ppm of Ni(II) and 2.5g of bentonite of a solution of 25ml can adsorb 98% of Cu, 97.2% of Co, 96.8% of Ni, 98.3% of Zn.

Keywords: *zeolitic tuff, bentonitic tuff, adsorbent, heavy metal*

INTRODUCTION

In general, zeolite and bentonite are in the same group of silicate minerals, excepted that zeolite is a mineral of the tectosilicates (framework silicates) and that bentonite, often used synonymously with montmorillonite (Eslinger and Pevear, 1988), is one of the phyllosilicates (sheet or layer silicates). In other words, "zeolite" is a large group of minerals composed of hydrated aluminum silicates of alkali metals and alkaline earth metals, whereas "bentonite" is a rock formed of highly colloidal and plastic clays composed mainly of montmorillonite which is a clay mineral of smectite group. From these definitions, their general formulae can be defined: (Na_2, K_2, Ca, Ba).[(Al, Si)O_2]$_n$. $x$$H_2O$ for zeolite mineral (Deer *et al.*, 1992) and (Na, Ca)$_{0.33}$(Al, Mg)$_2$$Si_4O_{10}(OH)_2$. $(H_2O)n$ for bentonite/ montmorillonite mineral (Papke, 1990).

Due to the usefulness of this zeolite- or bentonite-bearing rock in commercialization, many researches on characteristics of zeolite and bentonite have been widely conducted nearly in most of their deposits in Indonesia (Titisari, 2004; Titisari, 2006; Idrus, 2007). The studies of their characteristics were carried out by means of mineralogical analyses (XRD, SEM, petrological analysis, petrographical analysis), chemical analyses (XRF, ASS), physical property analysis, and so forth. Among these, XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscope) investigations are mostly and preferably used in mineral type analyses. Obviously, the Sidomulyo zeolite and the Kedungbedah bentonite were also characterized under petrographical analysis, XRD investigation, and SEM observation for characteristics study in order to interpret the mineral types and contents consisting in the rock-forming zeolites and bentonites as well as their roles as adsorbents of heavy metals ions containing in wastewater.

Study area

The previous studies (Titisari, 2004; Titisari, 2006; Idrus, 2007) revealed that natural zeolites are abundant at the Sidomulyo area (Fig.1), Gedangsari district, Gunungkidul regency, Yogyakart special province, whereas natural bentonites are often found in the Kedungbedah area (Fig.1), Wonosegoro district, Boyolali regency, central Java, Indonesia. Therefore, these are the selected areas at which zeolitic tuffs (natural zeolites) and bentonitic ones (natural bentonites) from the surface were respectively collected for characteristics study.

Regional Geologies

Sidomulyo Area

Located in the northwestern part of the Southern Mountain, Sidomulyo (Fig. 3) is an area belonging to the Kebobutak Formation which is composed of interbedding sandstone, vitreous tuff and zeolitic green stone layers which are the Late Oligocene – Lower Miocene in age (Soeria-Atmadja *et al.*, 1991). This area is comprised of Oligocene-Miocene volcano-clastic sediments whose layers relatively dip towards the south (van Bemmelen, 1970). The zeolitic tuff unit is a member of the Kebobutak Formation which is covered conformably by the Semilir Formation characterized by dacitic breccia, dacitic pumice tuffaceous and white tuff (Marks, 1957).

Kedungbedah Area

Located in the western part of the Kendeng Anticlinorium, Kedungbedah (Fig. 4) is an area belonging to the Kerek Formation whose lower part consists of interbedding of argillaceous marl, marl, claystone, and intercalation of calcareous tuff sandstone, tuffaceous sandstone, and calcarenite; whose middle part is found interbedding of claystone and pyroclastic rocks; and whose upper part is the clastic limestone. This area is among the faults which are the boundary of the unit lithology on different formations: the Pelang Formation is covered conformably by the Kalibeng Formation and is overlaid conformably by the Kerek Formation (Genevraye and Samuel, 1972).

METHODOLOGY

Several natural zeolite samples from the Sidomulyo area, Gedangsari district, Gunungkidul regency, Yogyakarta special province along with several natural bentonite ones from the Kedungbedah area, Wonosegoro district, Boyolali regency, central Java, Indonesia were analyzed in terms of 3 kinds of mineralogical characteristics, namely petrographical analysis, XRD investigation, and SEM observation. These Sidomulyo zeolitic tuffs and the Kedungbedah bentonitic tuffs were investigated by the XRD equipment at the Geochemistry Laboratory, Geological Engineering Department, Faculty of Engineering, Gadjah Mada University, Indonesia. Also, they were observed by SEM equipment at the Quarter Geology Laboratory, Geology Survey Center, Bandung, Indonesia. Meanwhile, the petrographical analysis was determined at the Geological Engineering Department, Faculty of Engineering, Gadjah Mada University, Indonesia. Besides, these tuffs were analyzed for CEC in the Chemical Engineering Department, Faculty of Engineering, Gadjah Mada University, but the activation was done at the Geological Engineering Department, Faculty of Engineering, Gadjah Mada University, Indonesia. The results of the analyses are beneficial in indentifying the major types of minerals forming the zeolitic and bentonitic tuffs and in interpreting their utilization as adsorbents of heavy metals from wastewater

CHARACTERISTICS

Physical Characteristics

The Sidomulyo zeolitic tuff (Fig. 2) is predominantly composed of zeolite mineral and tuff. It is green in color, clastic-textural, coarse-fine, and grain-sized (Idrus, 2006), whereas the Kedungbedah bentonitic tuff (Fig. 2) abundantly contains montmorillonite mineral and tuff. It is grayish-white in color, conchoidal-fractural, earthy-plastic when moistened, argillaceous-odorous when breathed upon (Titisari, 2006). In terms of physical property, the natural/initial ion exchange capacity of the Sidomulyo zeolitic tuff and the Kedungbedah bentonitic tuff are 44.40 mgr.eq. Na_2O/100 gram zeolite and 28.99 mgr.eq.Na_2O/100 gram bentonite and are then increased to 65.3 mgr.eq.Na_2O/100 gram zeolite and 37.6 mgr.eq.Na_2O/100 gram bentonite, respectively during 1 hour at the heating temperature of 250 ºC for zeolite and 300 ºC for bentonite.

Petrographical Analysis

The photomicrograph of the Sidomulyo zeolite resulted from petrographical analysis indicate the type of zeolite mineral characterized by the alteration of volcanic glass in a clastic texture with the presence of zeolite, montmorillonite, plagioclase, and quartz as shown in Fig. 5, and some other altered minerals such as orthoclase, chlorite, magnetite, and sericite. In the same way, the Kedungbedah bentonite photomicrograph depicts the clay mineral (montmorillonite) from the alteration of a number of volcanic glass with the content of zeolite, plagioclase, quartz, and other opaque minerals (Fig. 5).

XRD Investigation

The XRD analysis results show that the Sidomulyo zeolitic tuff bears several types of abundant minerals namely clinoptilolite, mordenite, montmorillonite, quartz, plagioclase (albite), and orthoclase (Fig. 6). The Kedungbedah bentonitic tuff displays the content of montmorillonite, clinoptilolite, dickite, quartz, and illite (Fig. 6) (Titisari, 2006).

SEM Observation

In addition to the XRD analysis for more clear definition of mineral types, the Sidomulyo zeolites and the Kedungbedah bentonites were observed by SEM analysis. Its result exhibits the structural characteristics of the zeolite and bentonite. From the photomicrograph of the Sidomulyo zeolite (Fig. 7), the tabular structure of clinoptilolite, the fibrous structure of mordenite, the webby structure of montmorillonite can be clearly recognized and identified. Regarding the Kedungbedah bentonite, the photomicrograph exposes the webby structure of montmorillonite, the blade structure of clinoptilolite, the sheet structure of dickite, and the hairy structure of illite (Fig. 7) (Titisari, 2006). Also, volcanic glass altered to zeolite and clay minerals can be detected in the photomicrographs of the rocks.

DISCUSSION

The petrographical analysis indicates that the Sidomulyo zeolitic tuff or the Kedungbedah bentonitic tuff is composed of volcanic glass, quartz, plagioclase, and altered minerals. The altered minerals are derived from volcanic glasses which can be identified as zeolite minerals and bentonite (montmorillonite) minerals. From the XRD investigation, the zeolite-bearing rock contains clinoptilolite, mordenite, montmorillonite, plagioclase, quartz, and orthoclase whereas the bentonite-bearing rock contains montmorillonite, clinoptilolite, illite, quartz, and plagioclase. The SEM observation displays the presence of clinoptilolite and mordenite in the zeolitic tuff and the presence of montmorillonite, clinoptilolite, illite, and volcanic glass in the bentonitic tuff. It is summarized that the zeolitic tuff predominantly contains volcanic glass and clinoptilolite ($Na_4,K_4.[Al_8Si_{24}O_{72}].24H_2O$) and the bentonitic tuff abundantly contains volcanic glass and montmorillonite ($Na_{0.33}[Al, Mg]_2Si_4O_{10}(OH)_2 . (H_2O)n$). The clinoptilolite is one of the zeolite types which are rich in K^+ and Na^+ cations (Hay, 1977). Also, montmorillonite is one of the smectite types of clay mineral which is rich in Na^+ cation for the Wyoming type, called swelling bentonite (Eslinger and Pevear, 1988). The initial/natural ion exchange capacity of the Sidomulyo zeolitic tuff is 44.4 mgr.eq.Na_2O/100 gram zeolite and that of the Kedungbedah bentonitic tuff is 28.99 mgr.eq.Na_2O/100 gram bentonite which are then increased to 65.3 mgr.eq.Na_2O/100 gram zeolite and 37.6 mgr.eq.Na_2O/100 gram bentonite, respectively after activation. The Na^+ ionic radius of the clinoptilolite and the montmorillonite and the K^+ ionic radius of the synthetic zeolite could be easily substituted by the ions of heavy metals containing in wastewater such as Cu, Zn, Cr, Cd, Fe, Pb, etc. This is supported by the work about the utilization of zeolite as fertilizer (Idrus *et al.*, 2006; Titisari *et al.*, 2006) and the utilization of bentonite for healing (anti-diarrhea) (Titisari *et al.*, 2007). The batch adsorption experiment has been carried out to study about adsorption capacity of zeolite and bentonite with their roles as adsorbents. For instance, the previous study (Prasetya, 2006) shows that 10 g of zeolite (-20+30 mesh) can adsorb about 9.80 ppm of Cu (II), 10.5 ppm of Cr (VI), and 11 ppm of Ni (II) in solution of 250 ml and another study on bentonite (Vega, 2005) indicates the percentages of four heavy metals of equally 0.001 M and 0.005 M concentration in the same solution of 25 ml and pH of 2.5 adsorbed by bentonite, i.e. 98 % of Cu, 97.2 % of Co, 96.8 % of Ni, 98.3 % of Zn and 90.1 % of Cu, 62.7% of Co, 59.8 % of Ni, 63.6 % of Zn, respectively. The adsorption capacity of zeolite and bentonite can express in heavy metal concentration or in percentage of heavy metals adsorbed on them; it is various depending on the parameters or the variables which could be a range of amount of zeolite or bentonite, particle size of zeolite or bentonite, metal concentration in solution, pH in sorption rate, percentage mixture of zeolite and bentonite, or solution of heavy metal.

CONCLUSIONS

The petrographical analysis, XRD analysis, and SEM analysis show the majority of clinoptilolite containing in the Sidomulyo zeolitic tuff and the abundance of montmorillonite in the Kedungbedah bentonitic tuff; both of which consist of volcanic glass or volcanic ash with evidence of plagioclase, orthoclase, and quartz which can be interpreted as their precursors. The Sidomulyo zeolite-bearing rock also display the content of mordenite and montmorillonite and the Kedungbedah bentonite-bearing rock exhibit the content of clinoptilolite, and illite. The activated ion exchange capacity of the Sidomulyo zeolitic tuff and the Kedungbedah bentonitic tuff are 65.3 mgr.eq.Na_2O/100 gram and 37.6 mgr.eq.Na_2O/100 gram, respectively. Considering the pore structure, the clinoptilolite (zeolite) which is multi-porous has higher adsorption capacity in terms of speed and effectiveness than the montmorillonite (bentonite). The zeolite and bentonite are widely known as the good adsorbents due to their characteristics in adsorbing or removing heavy metal ions from wastewater.

ACKNOWLEDGEMENTS

The authors are thankful to the Japanese International Cooperation Agency (JICA) who funded the ASEAN University Network/Southeast Asia Engineering Education Development Network (AUN/SEED-Net) Program.

REFERENCES

Anindita, S., 2005, *Geology of Kedungbedah Area, Boyolali Regency, Central Java, Indonesia*, Report of Geological Mapping, Geological Engineering Department, Faculty of Engineering, Gadjah Mada University, Yogyakarta, unpublished.

Deer, W. A., Howie, R. A., and Zussman, J., 1992, *An Introduction to the Rock-Forming Mineral*, 2nd ed., John Wiley & Sons, Inc., 605 Third Avenue, New York, NY 10158.

Eslinger, E. and Pevear, D., 1988, *Clay Minerals for Petroleum Geologists and Engineers*, Society of Economic Paleontologists and Mineralogists, USA

Genevraye, P., de and Samuel, L., 1972, *Geology of the Kendeng Zone (Central and East Java)*, Proceedings of the First Indonesian Petroleum Association Annual Convention, Jakarta

Hay, R.L., 1977, *Geology of Zeolites in Sedimentary Rocks*, Mumpton, F.A. (editor), Mineralogical Society of America, Short Course Notes, v.4, pp. 53-64.

Idrus, A., Titisari, A.D., Sudiyo, R., and Soekrisno, R., 2006, *Development of A Zeolites-Based Industry Through and Integrated Study on Characterization Quality Improvement and Utilization as Additive Fertilizer Materials of Natural Zeolite Deposits from Yogyakarta, Indonesia*, Proceedings of Final Report of Hi-Link Project Research, Gadjah Mada University, Yogyakarta, Indonesia.

Idrus, A., Titisari, A.D., and Kurniawan, A.P., 2007, *Characteristics, Quality Improvement and Exploitation of Zeolitic Tuff of the Sidomulyo Area, Gunung Kidul Regency, Yogyakarta Special Province*, Proceedings of Joint Convention Bali 2007, The 32nd HAGI and The 36th IAGI Annual Convention and Exhibition, Bali, Indonesia.

Marks, P., 1957, *Stratigraphic Lexicon of Indonesia*, Publikasi Keilmuan no 31, Seri Geologi, Pusat Djawatan Geologi, Kementrian Perekonomian R.I. Bandung, 233 p.

Papke, Keith G., 1990, *montmorillonite*, http://en.wikipedia.org/wiki/Bentonite [accessed: 20/11/2007]

Prasetya, A., Purnomo, C.W., and Rifai, A., 2006, *In-Situ Heavy Metal Contained Wastewater Remediation of Small and Medium Scale Industries (SMIs) Using Natural Zeolite and Modified Fly Ash Compound*, Proceedings of Final Report of Hi-Link Project Research, Gadjah Mada University, Yogyakarta, Indonesia.

Soeria-Atmadja, R., Maury, R.C., Bellon, H., Pringgoprawiro, H. Polve, M., and Priadi, B., 1991, *The Tertiary Magmatic Belt in Java*, Proceedings of Symposium in the Dynamic of Subduction and Its Products, Research and Development Center of Geo-technology, Indonesia Institute of Science (LIPI), Bandung, pp. 98-121.

Titisari, A.D., Idrus, A., and Widiasmoro, 2004, *Characteristics, Measured Resources and Quality of Bantengwareng Zeolitic Tuff at Gedangsari Area of Gunungkidul Regency as Agriculture Products Absorbent and Fertilizer*, Research Report on SP-4 Program at Geological Engineering Department, Gadjah Mada University, unpublished, p. 41.

Titisari, A.D., Idrus, A., and Widiasmoro, 2006, *Mineralogical Characteristics of the Sampang Zeolitic Tuff, Gunungkidul-Indonesia, and its Utilization as Fertilizer*, The 4th International Workshop on Earth Science and Technology, 4-5 December 2006, Kyushu University, Japan.

Titisari, A.D., and Widiasmoro, 2006, *Mineralogical Characteristics of the Kedungbedah Bentonite, Boyolali, Indonesia*, Proceedings of The 8th Field Wise Seminar on Geological Engineering Field and The 3rd International Symposium & Exhibition on Earth Resources and Geological Engineering Education, Gadjah Mada University, Yogyakarta, Indonesia, pp. 309-315.

Titisari, A.D., Widiasmoro, and Idrus, A., 2007, *The Characteristics and Quality of Kedungbedah Bentonite at Wonosegoro Area, Boyolali Regency, Central Java and its Utilization for Healing (Anti-Diarrhea)*, Proceedings of Joint Convention Bali 2007, The 32nd HAGI and The 36th IAGI Annual Convention and Exhibition, Bali, Indonesia.

van Bemmelen, R.W., 1970, *The Geology of Indonesia: General Geology of Indonesia and Adjacent Archipelagoes*, 2nd ed., Vol. 1A, Martinus Nijhoff, The Haque, 732 p.

Vega, J.L., Ayala, J., Loredo, J., and Garcia Iglesias, J., 2005, *Bentonite as Adsorbent of Heavy Metals Ions from Mine Waste Leachates: Experimental Data*, 9th International Mine Water Association Congress (IMWAC), Oviedo, Spain, pp. 603-609

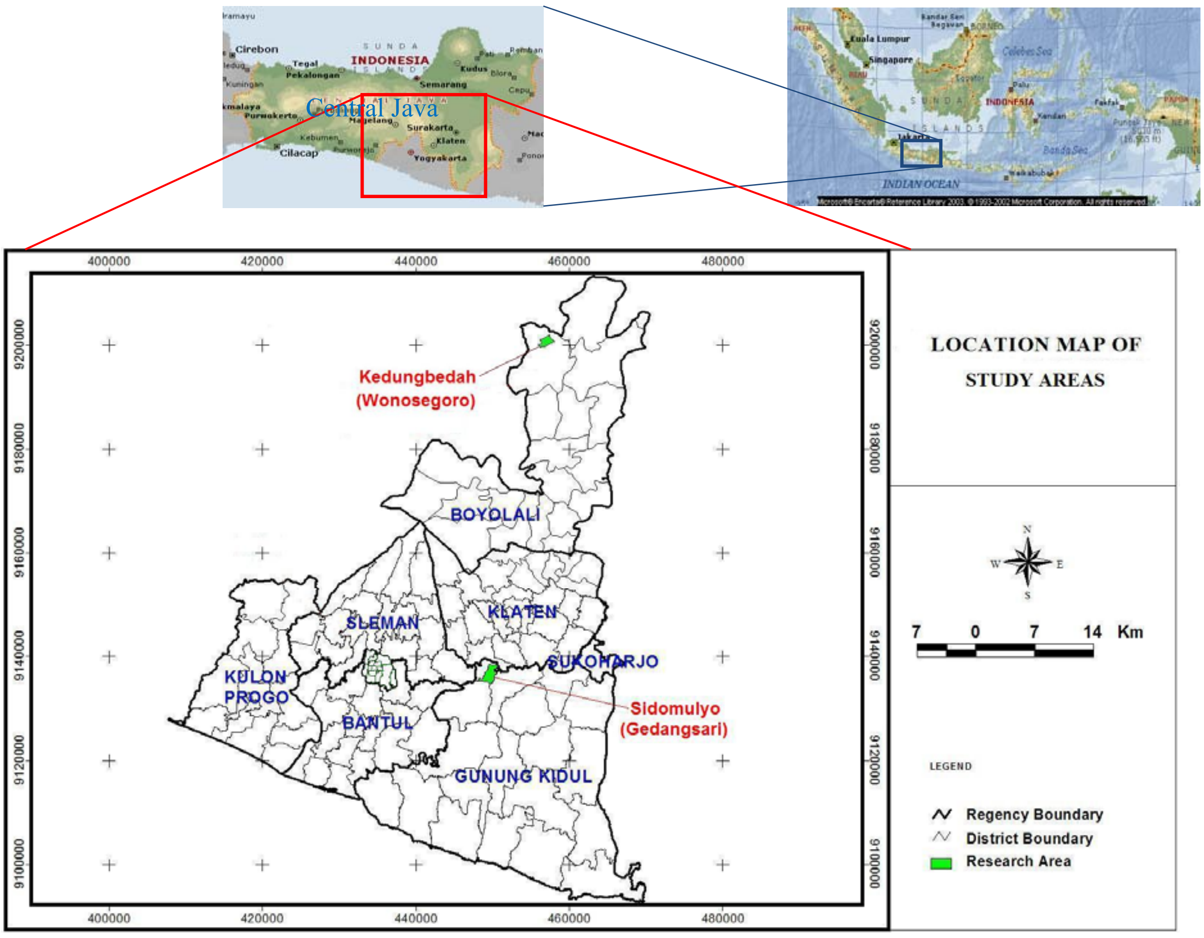


Figure 1. Location map of the Sidomulyo and Kedungbedah areas, Java Island, Indonesia

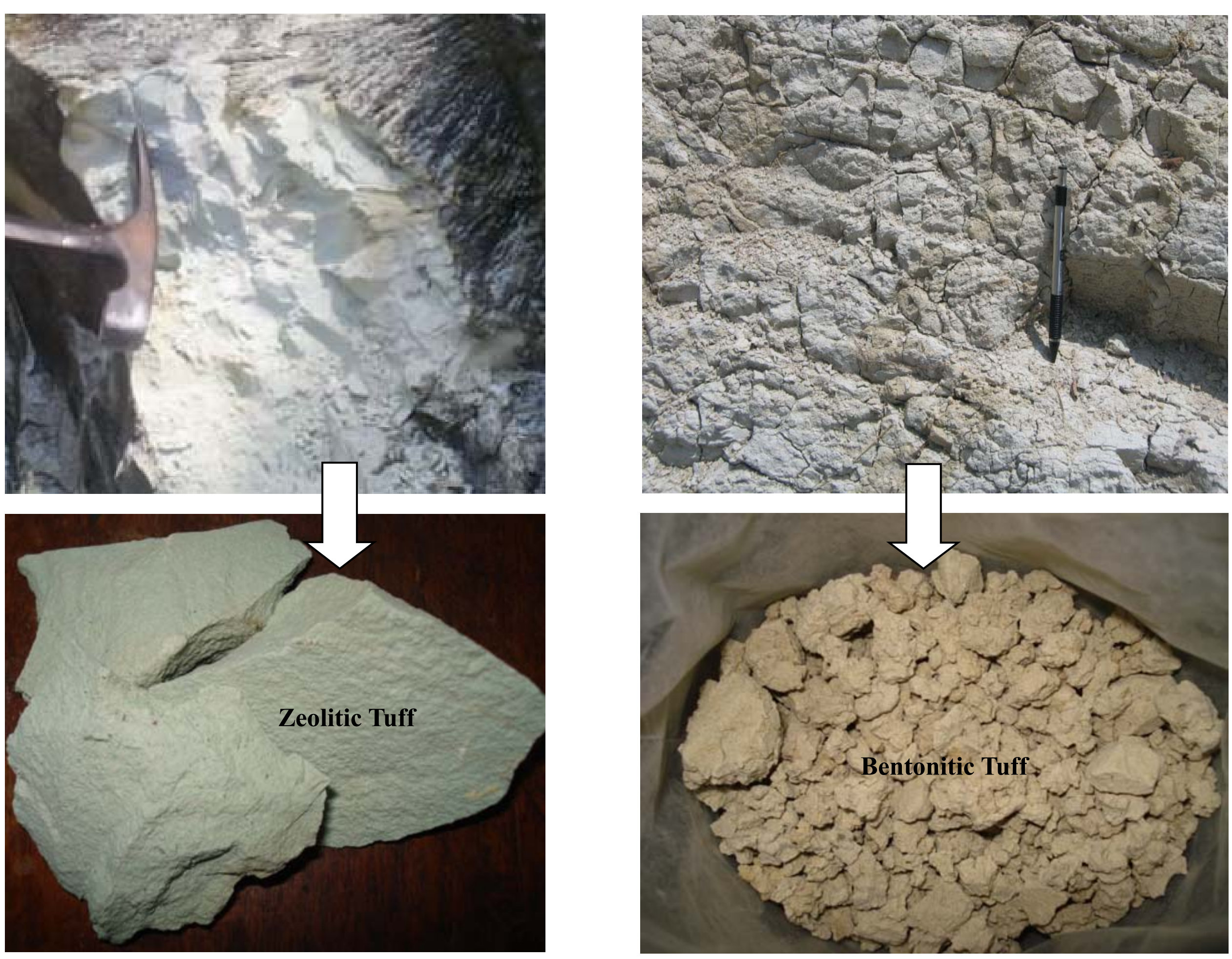


Figure 2. The surficial zeolitic and bentonitic tuff at the Sidomulyo area (Gunungkidul regency) and the Kedungbedah area (Boyolali regency), respectively, Java island

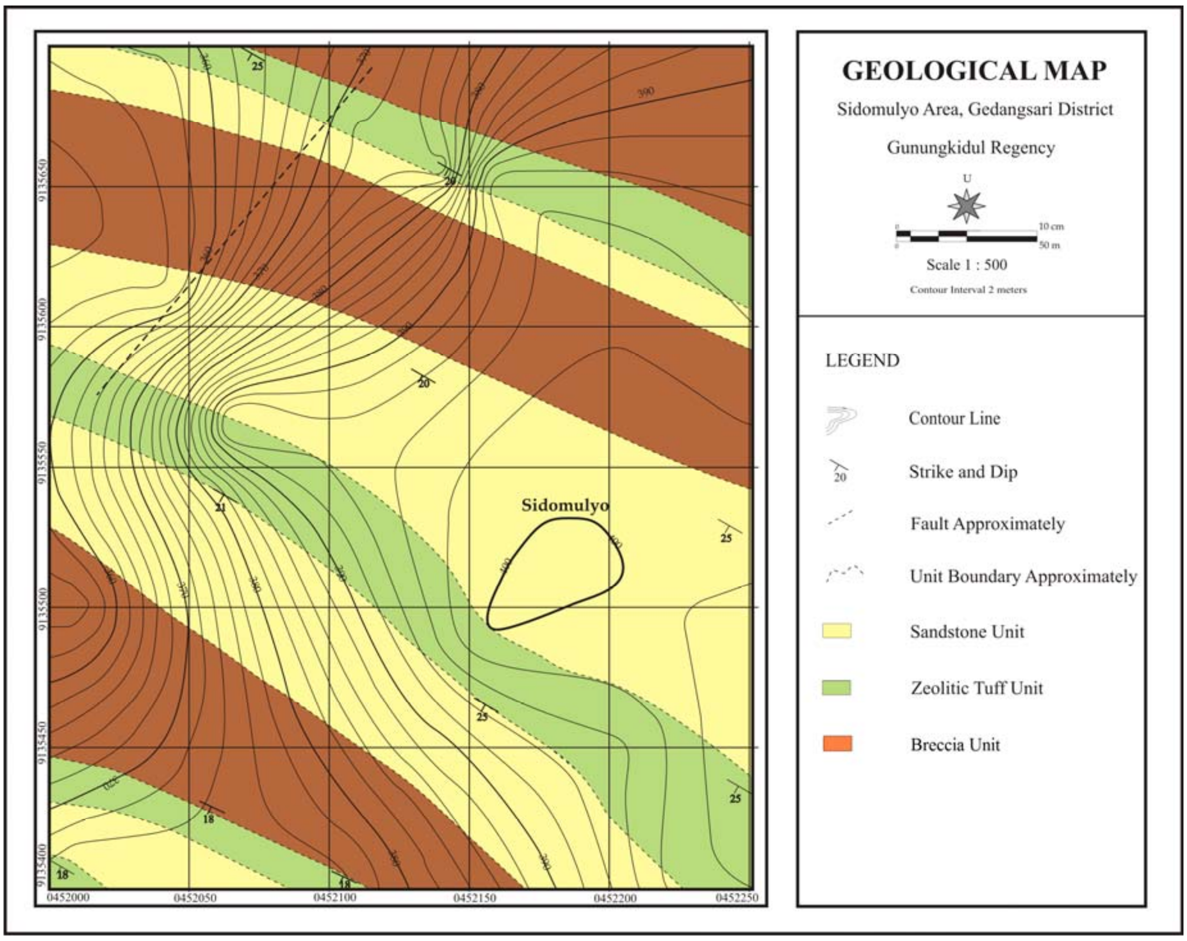


Figure 3. Detailed geological map of Sidomulyo area, Gunungkidul regency, Yogyakarta special province, Indonesia (modified from Idrus *et al.*, 2006; Idrus *et al.*, 2007)

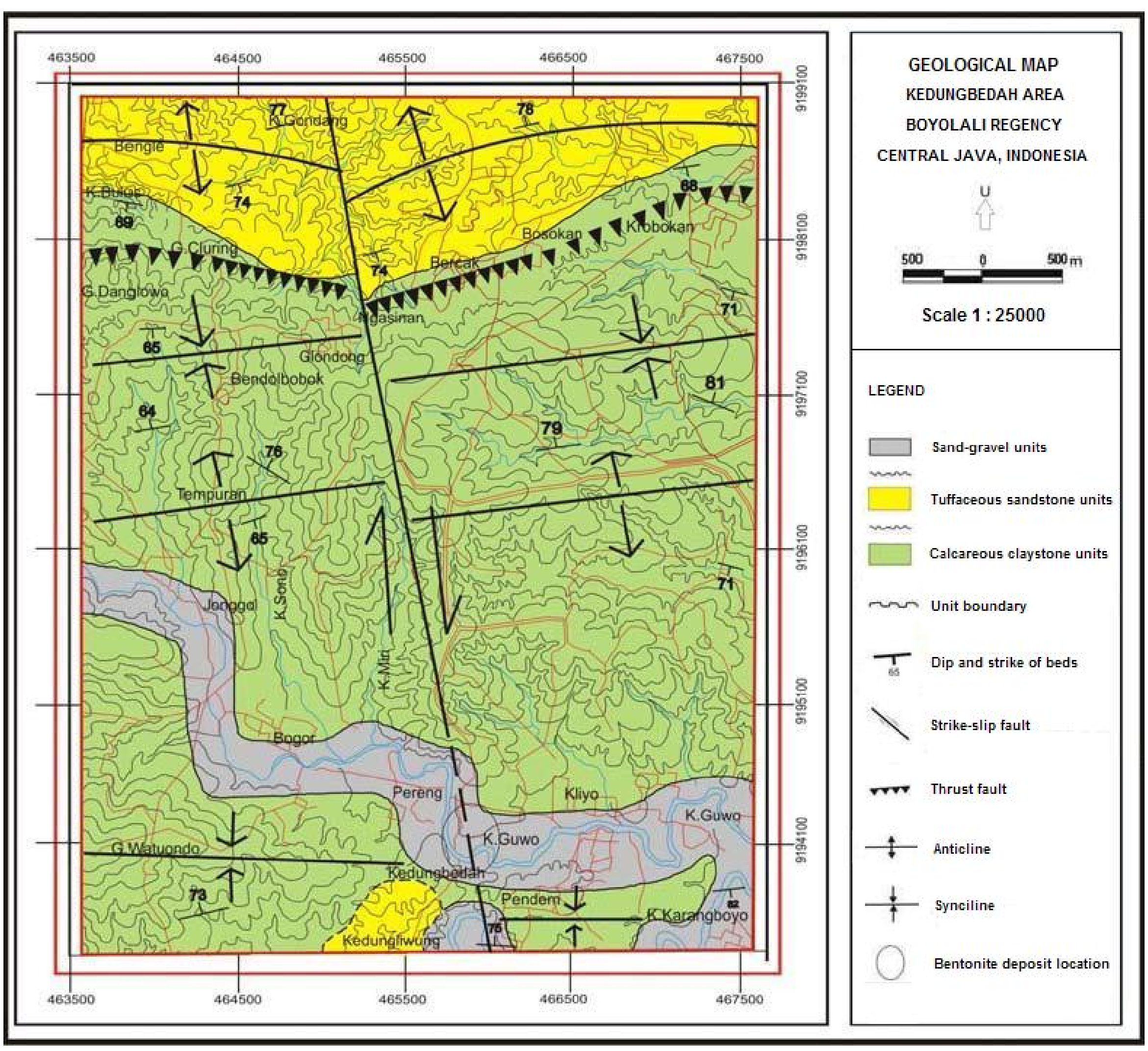


Figure 4. Geological map of Kedungbedah area, Boyolali regency, central Java, Indonesia (modified from Anindita, 2005)

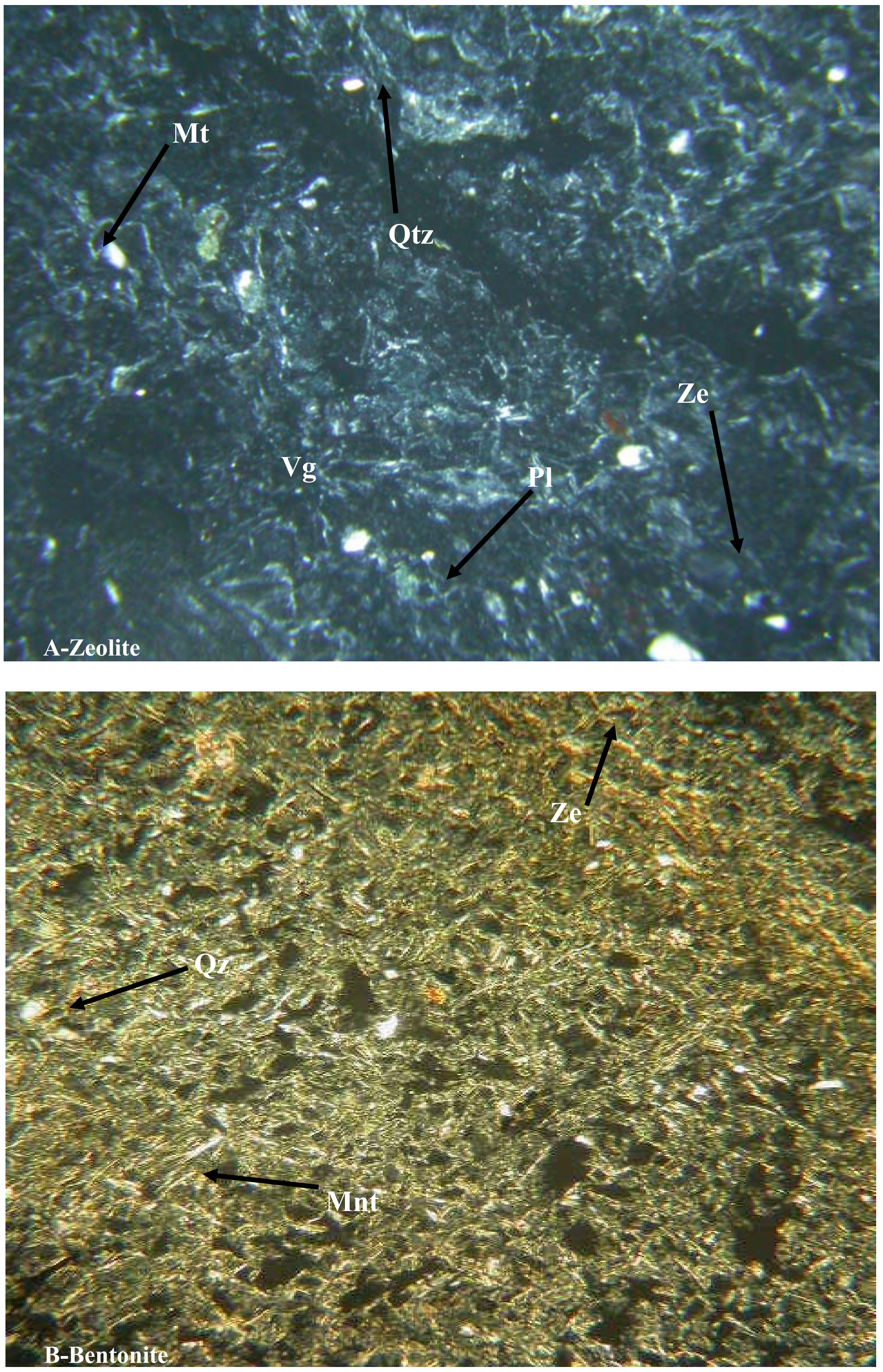


Figure 5. The petrography results of (A) the representative Sidomulyo zeolitic tuff showing the existence of zeolite (Ze), and montmorillonite (Mnt), plagioclase (Pl), quartz (Qtz), and volcanic glass (Vg) (Idrus *et al*., 2006; Idrus *et al*., 2007), and the representative Kedungbedah bentonitic tuff indicating the montmorillonite (Mnt), zeolite (Ze), and quartz (Qtz) (Titisari *et al*., 2006; Titisari *et al*., 2007)

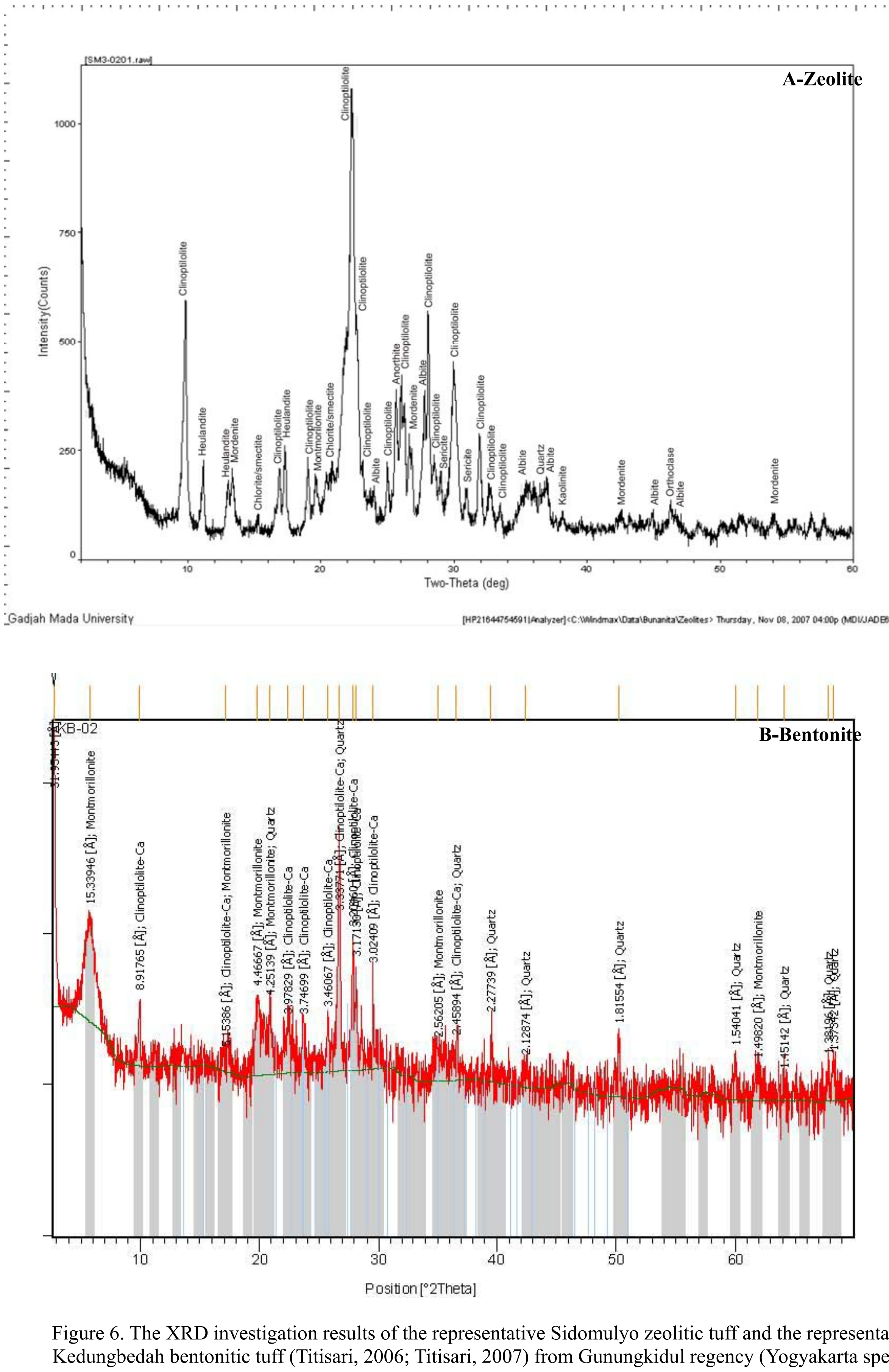
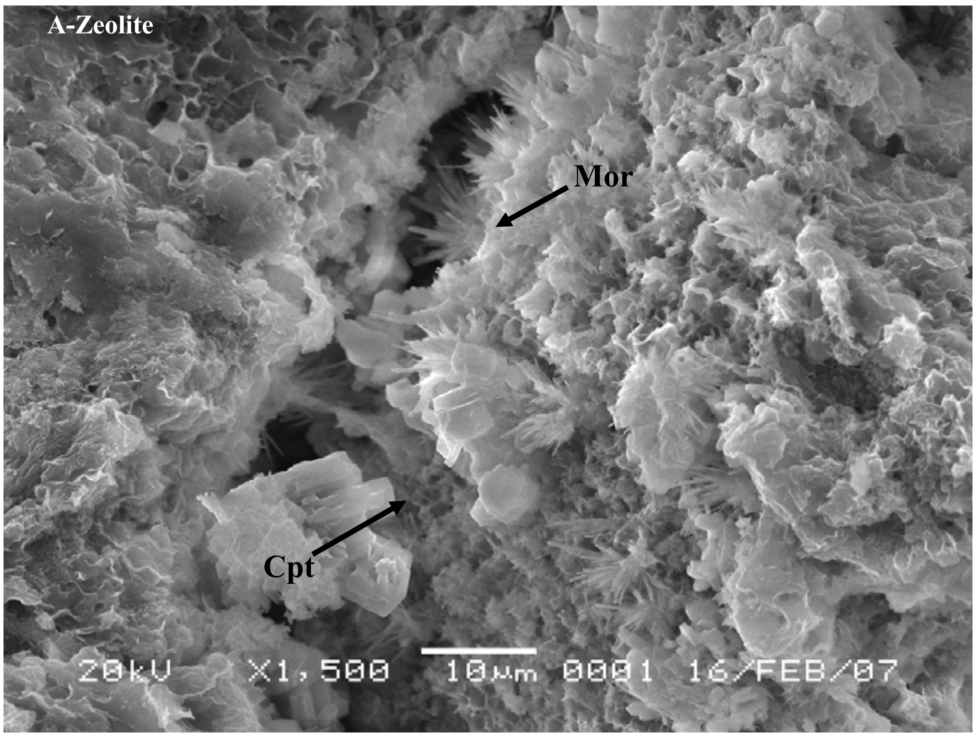


Figure 6. The XRD investigation results of the representative Sidomulyo zeolitic tuff and the representative Kedungbedah bentonitic tuff (Titisari, 2006; Titisari, 2007) from Gunungkidul regency (Yogyakarta special province) and Boyolali regency (central Java), respectively, Indonesia



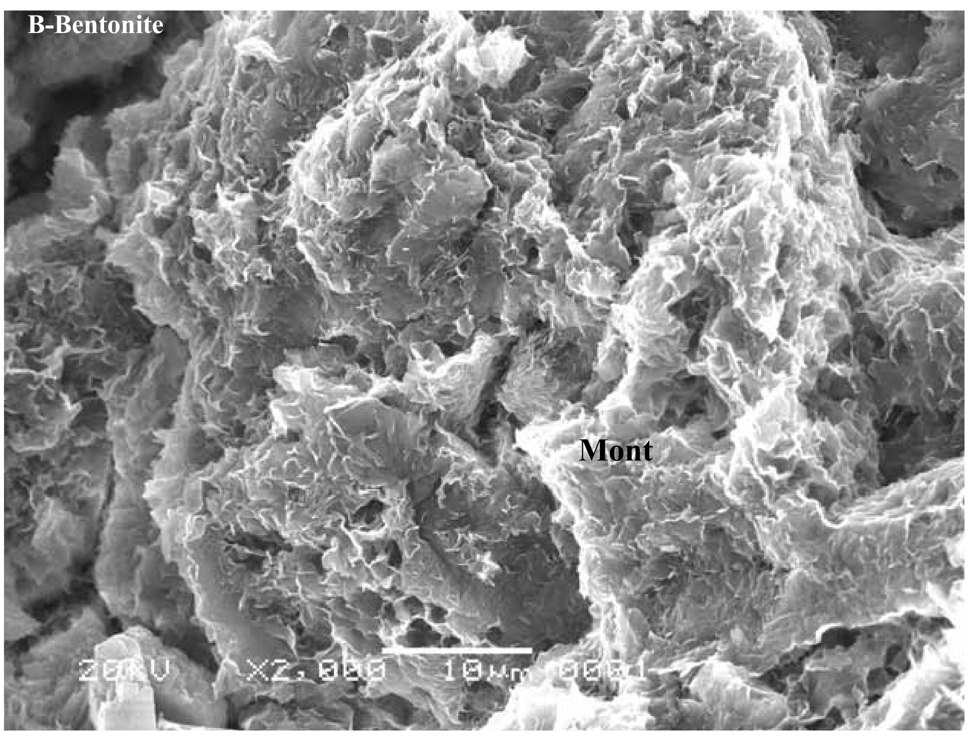


Figure 7. The SEM photomicrograph result of (A) the representative Sidomulyo zeolitic tuff, showing the presence of abundant zeolite minerals including clinoptilolite (Cpt) in tabular structure and mordenite (Mor) in fibrous structure (Idrus *et* al., 2006; Idrus *et al*., 2007), and (B) the representative Kedungbedah bentonitic tuff exhibiting the dominance of montmorillonite (Mnt) with its webby structure and other volcanic glasses (Titisari *et al*., 2006; Titisari *et al*., 2007)