

SYNTHESIS OF ZEOLITIC MATERIALS FROM VOLCANIC ASH IN PRESENCE AND ABSENCE OF CETYLTRIMETHYLAMMONIUM BROMIDE

Vilma Mayerling SANHUEZA NÚÑEZ* and Leonardo Daniel BENNUN TORRES

Universidad de Concepción. Edmundo Larenas s/n, Concepción 3, Chile

*Autor de correspondencia: vsanhuez@udec.cl

(Recibido marzo 2014; aceptado enero 2015)

Key words: zeolites, phillipsite, chabazite, analcime, ash, synthesis

ABSTRACT

Zeolitic materials as Na-phillipsite, Na-K-phillipsite-like zeolites and the mixtures of zeolites (phillipsite+analcime and phillipsite+chabazite+analcime) were synthesized from volcanic ash, either in presence and absence of cetiltrimetilamonium bromide (CTAB). The ash sample used in the laboratory experiments contains 75.36 % SiO₂ and 14.11 % Al₂O₃, abundances. The reaction time as well as the influence of CTAB were studied in the zeolitic materials crystallization. The experiments were carried out under hydrothermal conditions, autogenic pressure and temperature of 150 °C, as well as reaction time from 8 to 116 h. Products from this hydrothermal treatment were identified by X-ray diffraction (XRD) and characterized by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS). Of the zeolitic materials obtained the Na-K-phillipsite-like zeolite was found to be the most effective for the retention of cations Pb²⁺, Zn²⁺, and Ba²⁺.

Palabras clave: zeolitas, phillipsita, chabazita, analcima, ceniza, síntesis

RESUMEN

Materiales zeolíticos tipos Na-phillipsita, Na-K-phillipsita y mezclas de zeolitas (phillipsita+analcima y phillipsita+chabazita+analcima) fueron sintetizados a partir de ceniza volcánica, en presencia y ausencia de bromuro de cetiltrimetilamonio (BCTA). La muestra de ceniza usada en los experimentos de laboratorio posee un 75.36 % de SiO₂ y 14.11 % de Al₂O₃. El tiempo de reacción y la influencia del BCTA fueron los parámetros estudiados en la cristalización de los materiales zeolíticos. Los experimentos se llevaron a cabo bajo condiciones hidrotermales, a presión autógena y una temperatura de 150 °C, así como tiempos de reacción de 8 a 116 h. Los productos de este tratamiento hidrotermal fueron identificados por difracción de rayos-X (DRX) y caracterizados por microscopía electrónica de barrido con espectrometría dispersiva de rayos-X (MEB-EDRX). La zeolita Na-K-phillipsita resultó ser la más efectiva para la retención de los cationes Pb²⁺, Zn²⁺ y Ba²⁺.

INTRODUCTION

Zeolites are microporous aluminosilicate crystalline materials with well-defined pore structures and compositions. Because of their properties such as thermal stability, adsorption, catalytic activity, acidity, cation exchange and molecular sieves, zeolites have important applications in refining processes at the petrochemical industry, as well as gas separation, water purification at mining industry and environmental catalysis (Zhang *et al.* 2011, Izidoro *et al.* 2012).

Most zeolites are synthesized from commercial materials (Martucci *et al.* 2009, Tanaka *et al.* 2009, Trejda *et al.* 2010, Morales-Pacheco 2011, Xue *et al.* 2012). Many of them have been synthesized, at a given temperature and crystallization time, from gels containing $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Some sources of silicon are: Na-silicate HS-40 (Sig and Seung 2004, Chen *et al.* 2009), Na-silicate, Cab-O-Sil M-5 fused silica (Rivallan *et al.* 2010), fumed silica (Xu *et al.* 2010), UltraSil silica TMA- SiO_2 and Cab-O-Sil TMA- SiO_2 (Shvets *et al.* 2008). On the other hand, some of the sources of aluminum that have been employed are: Na-aluminate (Anuwattana and Khummongkol 2009, Gupta *et al.* 2009) and Al-isopropylate (Tosheva *et al.* 2005). Surfactants of different chain lengths have been used as templates. Among them, the following can be mentioned: $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}-\text{OH}/\text{Cl}$, $\text{C}_{12}\text{H}_{25}(\text{CH}_3)_3\text{N}-\text{OH}/\text{Cl}$, $\text{C}_{14}\text{H}_{29}(\text{CH}_3)_3\text{N}-\text{Br}$, $\text{C}_{16}\text{TMA}-\text{OH}$ and $\text{C}_8\text{TMA}-\text{Br}$ (Han *et al.* 2009, Sakthivel *et al.* 2009).

Ashes generated by thermoelectric plants are another starting material that has been widely used to synthesize zeolites. In fact different zeolites such as NaA, NaPl, analcime, gmelite and phillipsite, have been synthesized from fly ash (Moriyama *et al.* 2005, Terzano *et al.* 2005, Tanaka *et al.* 2008, Walek *et al.* 2008, Font *et al.* 2009, Kumar *et al.* 2009, Ríos *et al.* 2009, Goni *et al.* 2010), lignite and rice husk ash (Ahmaruzzaman 2010).

On the contrary experiments oriented to synthesize zeolites by means of natural products as starting materials are relatively scarce. The chemical synthesis of zeolites is subject to disturbance caused by the impurities present in these materials. Some natural raw materials that have been used are kaolin (Sanhueza *et al.* 1999, Mignoni *et al.* 2008, Miao *et al.* 2009), bentonite (Boukadir *et al.* 2002, Hongchao *et al.* 2010), pumice (Sanhueza *et al.* 2006), diatomite (Sanhueza *et al.* 2003, 2004, 2006, 2011 and Chilean patents 2004, 2006, 2009, 2010), and perlite glass (Christidis and Papantoni 2008).

Other raw materials for obtaining zeolites are natural zeolitic rocks hydrothermally treated (Watanabe *et al.* 2005). Phillipsite and chabazite were obtained from trachytic glass by hydrothermal conversion at 200 °C (De Gennaro *et al.* 1999). Wilkin and Barnes (2000) used Na-clinoptilolite zeolite as a starting material to synthesize analcime zeolite. Phillipsite and merlinoite zeolites have been synthesized by chemical reaction between an obsidian and NaOH or KOH solutions at hydrothermal conditions, autogenic pressure and temperatures between 150 °C and 200 °C (Kawano and Tomita 1997).

The products from Chaitén volcano (eruption occurred on May 2, 2008) including its ash are vitrophyric and mostly rhyolitic in composition, constituting a natural low cost source of silicon and aluminium (Lara 2009). The Chaitén volcano is located in the southern area of the Southern Volcanic Zone of the Andes-Chile at 42°50'S.

Fortunately in this kind of events, not all is disaster and always there is something positive that can be rescued from. This fact motivated us to evaluate the possibility of investigating the reactivity of ash as a raw material thrown by the Chaitén volcano eruption in the formation of zeolites and/or zeolitic materials.

MATERIALS

The volcanic ash comes from the Chaitén (2008) volcanic eruption. The chemical composition of the ash was determined by X-ray fluorescence (XRF; **Table I**), and it was used to carry out the experiments. The volcanic ash (molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 9.1$)

TABLE I. MAJOR ELEMENTS COMPOSITION (NORMALIZED TO 100 %, VOLATILE FREE) OF THE VOLCANIC ASH

Oxide	Volcanic ash (wt %)
SiO_2	75.36
TiO_2	0.17
Al_2O_3	14.11
Fe_2O_3	1.73
MnO	0.06
MgO	0.28
CaO	1.63
Na_2O	3.95
K_2O	3.07
P_2O_5	0.01
Total	100.37

was collected at the bottom of the Chaitén volcano. Minerals found correspond mainly to anorthite and quartz, followed by minor amounts of rutile, anatase, amphibole, chlorite and ilmenite, which probably come from the volcanic ash. With the aim of converting the volcanic ash into zeolite or zeolitic materials, several experiments were done.

Zeolites preparation

The volcanic ash sample was dried at room temperature, ground and the grain size employed in the synthesis was less than 200 mesh. The experiments (**Tables II and III**) were carried out in Parr steel autoclave reactor (150 cc of capacity) in static conditions under hydrothermal conditions, autogene pressure, temperature of 150 °C, with high and low concentrations of cetyltrimetilamonium bromide (**Table II**). The runs 1, 2, 3, 4 and 5 were prepared with high CTAB concentration. The aim of runs 6, 7, 8, 9 and 10 was to investigate whether phillipsite-like zeolite and zeolitic materials would be formed by introducing half CTAB (low concentration of cetyltrimetilamonium bromide). The runs in **Table III** were prepared without CTAB.

TABLE II. EXPERIMENTAL CONDITIONS AND REACTION PRODUCTS RELATED TO THE CHEMICAL REACTION BETWEEN THE VOLCANIC ASH WITH LOW AND HIGH CTAB CONCENTRATIONS AND A 0.3 M NaOH SOLUTION

RUN	Volcanic ash (g)	CTAB (g)	Time (h)	Reaction products
1	1.00	0.44 (high)	15	(An + Qz)
2	1.00	0.44	20	(An + Qz)
3	1.00	0.44	25	PHI + (An + Qz)
4	1.00	0.44	96	PHI, ANA + (An + Qz)
5	1.00	0.44	116	ANA, PHI + (An + Qz)
6	1.00	0.22 (low)	15	(An + Qz)
7	1.00	0.22	20	PHI, Ha
8	1.00	0.22	25	PHI, ANA + (An + Qz)
9	1.00	0.22	96	ANA, PHI + (Qz)
10	1.00	0.22	116	ANA, scarce PHI + (Qz)

PHI = phillipsite, ANA = analcime, Ha: Halloysite, An = anorthite, Qz = quartz. (An+Qz) = coming from the ashes, CTAB = cetyltrimetilamonium bromide

Once the run was completed and the system cooled down, the products were washed off with abundant distilled water (Milli-Q water 18.2 MΩ/cm resistivity), filtered using Advantec 5C filter paper and dried at 120 °C for 15 h. The calcination of samples prepared with template agent were carried

TABLE III. EXPERIMENTAL CONDITIONS AND REACTION PRODUCTS RELATED TO THE CHEMICAL REACTION BETWEEN THE VOLCANIC ASH AND A 0.3 M NaOH SOLUTION

RUN	Volcanic ash (g)	Time(h)	Reaction products
1	1.00	8	(An + Qz)
2	1.00	15	PHI + (An + Qz)
3	1.00	21	PHI, CHA, ANA
4	1.00	33	PHI, CHA, ANA
5	1.00	48	PHI, ANA

PHI = phillipsite, ANA = analcime, CHA = chabazite, An = anorthite, Qz = quartz. (An+Qz) = coming from the ashes.

out in air at 600 °C for 6 h. The heating rate of the furnace was 1.5°/min.

The retention capacity of the zeolitic materials was determined through aqueous solutions of Pb (NO₃)₂, ZnCl₂ and BaCl₂. 100 mL were taken of each solution containing 400 ppm of the cation to be analyzed. 0.1 g of zeolitic material was added in polyvinylchloride bottles at room temperature under continuous stirring until equilibrium. Then the samples were filtered and the solutions were stored at 4 °C for later analysis.

Characterization

The major elemental components of volcanic ash were determined using a Rigaku X-ray fluorescence spectrometer. Mineralogy was determined by a Qemscan with Tescan System Vega LSH. The zeolites were identified through a D4 Endeavor X-ray Diffraction equipment, Cu-α1 radiation ($\lambda = 1.5406 \text{ \AA}$) at 30 kV and 15 mA was employed. The morphology of the zeolites was determined by means of a JEOL JMS 6380 LV with EDS. Before mounting, the samples were ultrasonically dispersed in a 40 % solution of water/ethanol. Metal concentrations were analyzed using a Hitachi Z-8100 Polarized Zeeman Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Fifteen experiments were carried out (**Tables II and III**). In both cases products are the result of a chemical reaction between the volcanic ash and a NaOH 0.3M solution at 150 °C temperature reaction whether in presence or in absence of CTAB, respectively. Phillipsite-like zeolite crystallized at 25 h of reaction time (**Fig. 1**). If the concentration of CTAB halved the crystallization time for phillipsite-like zeolite decreases to 20 h of reaction (**Fig. 2**).

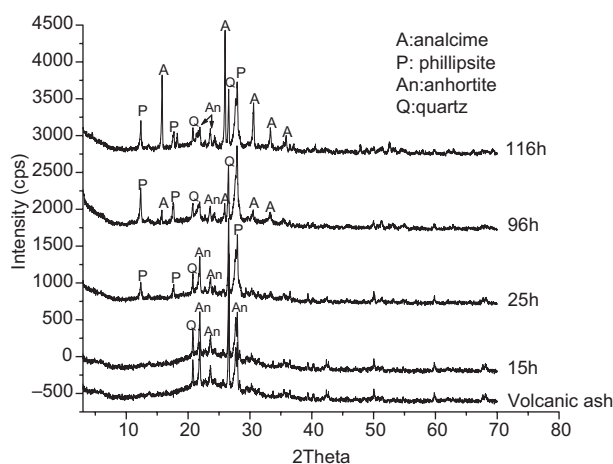


Fig. 1. XRD patterns of the phillipsite-type zeolite and zeolitic mixture (analcime + phillipsite) at reaction time of 25 and 96 h, respectively. Synthesized by the chemical reaction between the volcanic ash and a solution of 0.3M NaOH. The samples were synthesized with high CTAB concentration

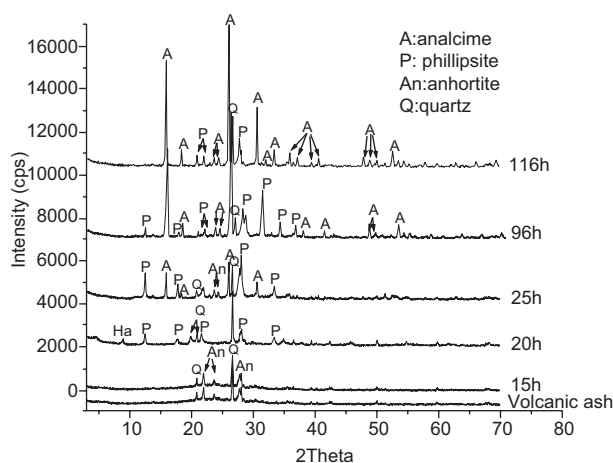


Fig. 2. XRD patterns of phillipsite zeolite and the zeolitic mixture (phillipsite + analcime) synthesized by the chemical reaction between the volcanic ash and a solution of 0.3 M NaOH. The samples synthesized with low CTAB concentration. Anorthite and quartz come from the volcanic ash

Within a 25 h time of reaction (**Fig. 2**) and a low concentration of CTAB, two phases crystallize (PHI, ANA), whereas if the CTAB concentration increases, then a 96 h time of reaction would be needed to reach the same phases (PHI, ANA; **Fig. 1**)

The XRD pattern of the sample synthesized without CTAB shows high intensity peaks that correspond to the phillipsite-like zeolite (**Fig. 3**, 15 h). On the other hand, the patterns of the samples obtained at the same reaction time (15 h) with low and high CTAB concentrations (**Figs. 1** and **2**) show only quartz and

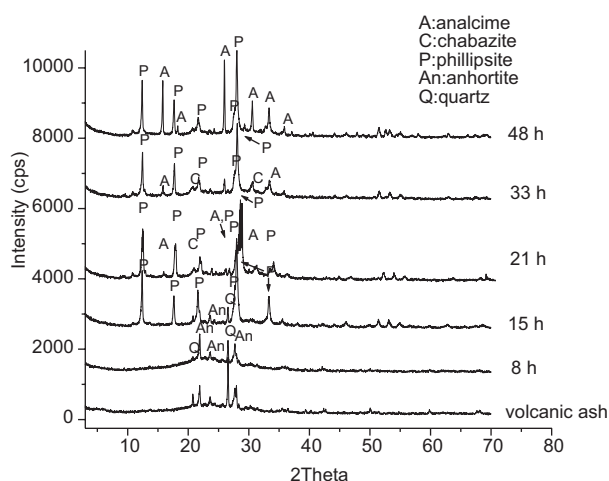


Fig. 3. XRD patterns of the zeolite and zeolitic material (analcime + chabazite + phillipsite) synthesized by the chemical reaction between the volcanic ash and a solution of 0.3 M NaOH, in absence of CTAB at different reaction times. Anorthite and quartz come from the volcanic ashes

anorthite coming from the volcanic ash. An extra peak at 20 h appeared in the pattern (**Fig. 2**) indicating that another phase, most probably halloysite, was forming together the phillipsite-like zeolite.

In **figure 3** no crystallization is observed during the first 8 h of reaction. Two new zeolite-like are added to the reaction (21 and 33 h) chabazite and analcime-like phases. Similar mixtures of natural zeolites phillipsite + chabazite and phillipsite + chabazite + analcime have been reported by Dwairi *et al.* (2009) in Tall Amir and Tall Juhira, two important volcanoes located in southern Jordan.

The study ended after 48 h of reaction where the mixtures of zeolites phillipsite + analcime prevail.

The results of the kinetics experiments to measure the retention of metal ions from aqueous solutions as a function of time are shown in **figure 4a, b, c** and **d**. Differences in the sequences of selectivity of cations by the zeolitic materials are expected due to differences in composition. In **figure 4a** selectivity sequence is $\text{Ba}^{2+} > \text{Zn}^{2+} > \text{Pb}^{2+}$, in about an hour and then reaches equilibrium. In **figure 4b** the sequence selectivity is $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ba}^{2+}$, it takes about 2 h to reach equilibrium. Sequence selectivity in **figure 4c** is $\text{Zn}^{2+} > \text{Pb}^{2+} > \text{Ba}^{2+}$, with a period of approximately 2 h to reach equilibrium. And finally **figure 4d** shows the preference of cations in descending order: Pb, Ba and Zn. The Na-K-phillipsite-like zeolite was the most effective with a 60 % retention for Pb^{2+} , 56 % for Zn^{2+} and 43 % for Ba^{2+} . The retention of cations by the ash is very low. 3.6 % for Zn^{2+} , 3.9 % for Ba^{2+} and 4.6 % for Pb^{2+} .

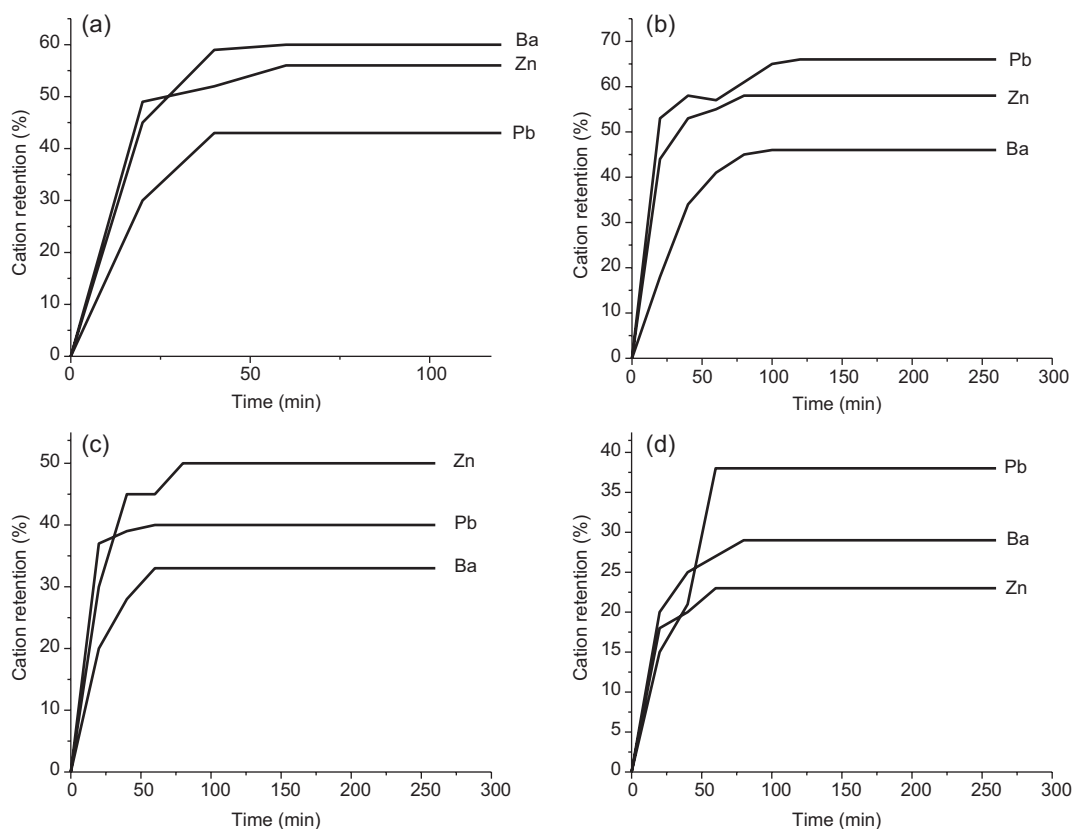


Fig. 4. Retention (%) of Pb, Zn and Ba cations by: (a) Na-phillipsite, (b) Na-K-phillipsite-like zeolite, (c) phillipsite + chabazite + analcime and (d) phillipsite + analcime

Under SEM examination, the volcanic ash shows evidence of angular glassy shards (**Fig. 5**). In **figure 6a**, it is possible to observe Na-phillipsite-like zeolite ($\text{Si}/\text{Al} = 1.6$). In **figure 6b**, trapezohedron crystals of analcime and groups of prismatic crystals of phillipsite are observed. In **figure 6c**, analcime appears as

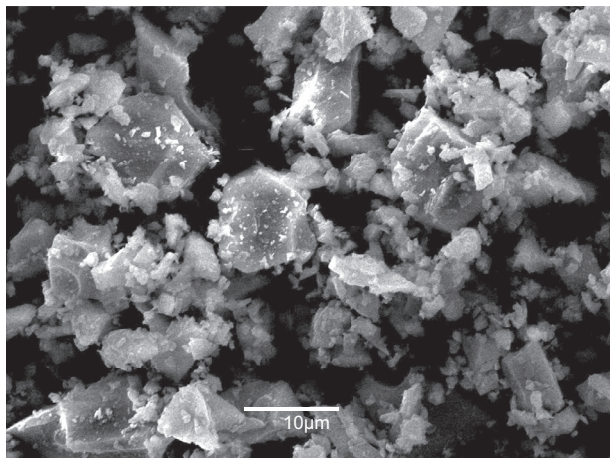


Fig. 5. SEM image of volcanic ash from the eruption of Chaitén Volcano

the most abundant zeolite. All the above experiments were performed with high concentrations of cetyltrimethylammonium bromide. When the previous experiments were carried out with low cetyltrimethylammonium bromide, concentration clearly decreases the crystallization time of analcime. The transformation of a zeolite phase into another by dissolution–recrystallization is frequently observed during hydrothermal syntheses, this transformation is known as metastability. In this case it shows the formation of analcime at expense of phillipsite-like zeolite (**Fig. 6d**) at a reaction time of 25 h. Photographic evidence not previously reported. Presumably temperature of 150 °C is lost structural water phillipsite-like zeolite lattice destabilizing its evolving into the more stable cubic phase thermodynamically. In presence or in absence of CTAB the morphology of the phillipsite is the same. Phillipsite exhibits a well defined morphology called sword blade (**Figs. 6a** and **7a**). In **figure 6f** analcime crystals finalizing the process of crystallization can be observed.

Highly crystalline Na-K-PHI-like zeolite with a $\text{Si}/\text{Al} = 3.1$ ratio crystallizes at 15 h of reaction (**Fig. 7a**). After 21 h a mixture of phillipsite and chabazite is

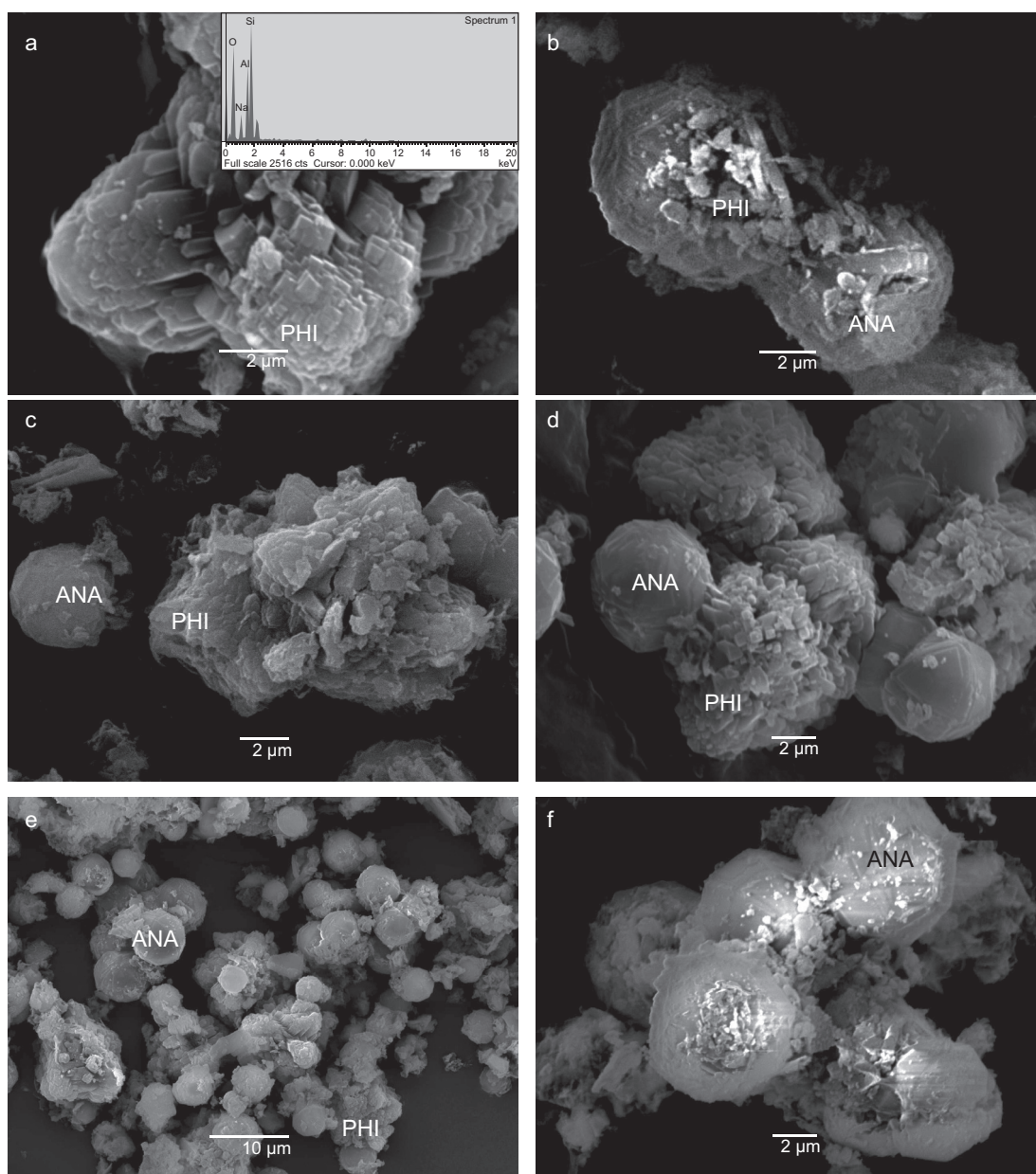


Fig. 6. SEM images of the products corresponding to the chemical reaction between volcanic ash and a NaOH 0.3M solution, at 150 °C and reaction times of: 25 h (**a** and **d**), 96 h (**b** and **e**) and 116 h (**c** and **f**). Images **a**, **b** and **c** show the materials prepared with a high CTAB concentration. Images **d**, **e** and **f** show the materials prepared with a low CTAB concentration. ANA: analcime, PHI: phillipsite

obtained (**Fig. 7b**). Increasing the reaction time to 33 h, analcime is added to the phillipsite and chabazite (**Fig. 7c**). This suggests that the crystallization sequence is phillipsite → chabazite → analcime. De Gennaro *et al.* (1999) obtained similar results from synthetic monocationic glasses. However, they obtained the chabazite → phillipsite → analcime sequence at 200 °C and not at 150 °C, like in our experiments. Probably, the difference in the reaction

temperature caused the change of the crystallization sequence. Following the methodology of De Gennaro *et al.* (1999) a temperature of 200 °C and 48 h of reaction time are required to crystallize the phillipsite. In our case, the phillipsite crystallization took place at 150 °C and in just 15 h of reaction time.

Höller and Wirsching (1988) reported the synthesis of chabazite with different morphologies using volcanic glasses as starting materials. Among

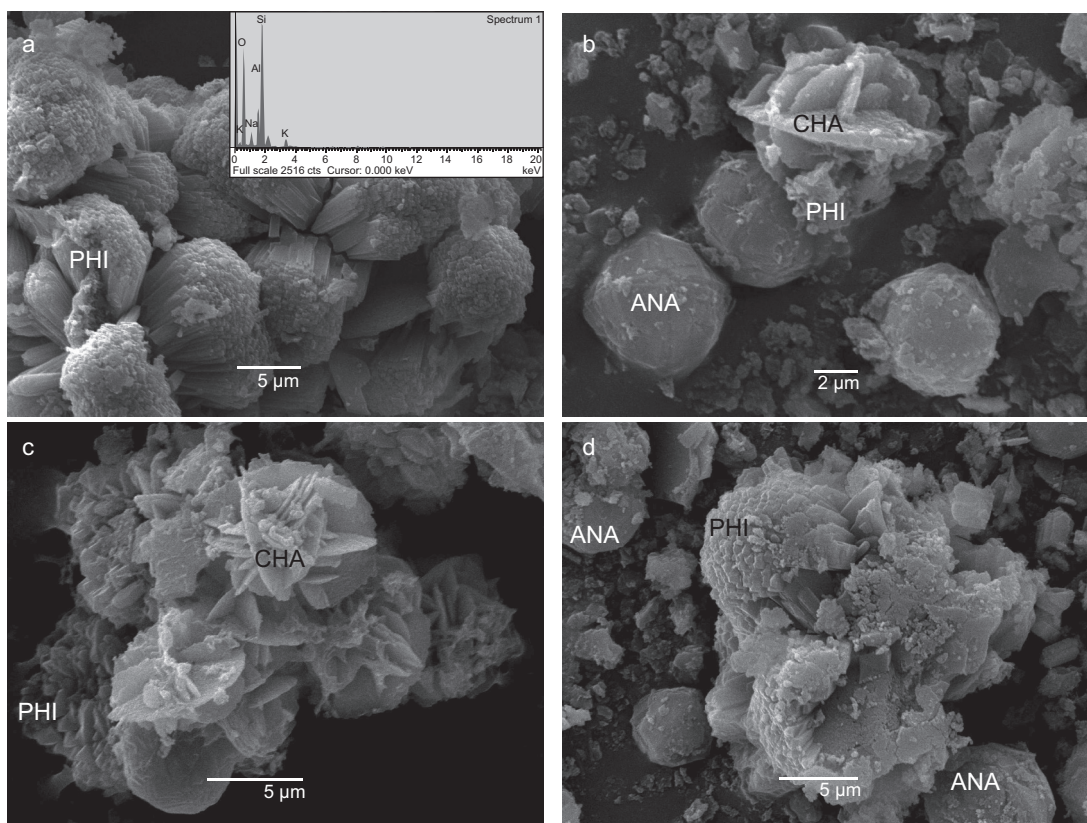


Fig. 7. SEM images of the products corresponding to the chemical reaction between volcanic ash and a NaOH 0.3M solution, in absence of CTAB. ANA: analcime, CHA: chabazite and PHI: phillipsite

the products they obtained at 200 °C and 20 days of reaction time, there was a mixture of chabazite + phillipsite + analcime. However they did not specify the crystallization sequence of the members of this mixture.

On the other hand, Ibrahim (2004) reports the following paragenetic sequence: smectite@phillipsite@chabazite@natrolite@analcime@calcite. The zeolites were synthesized using volcanic glass granules transformed into palagonite as starting material by the action of percolating waters in a closed hydrothermal system. The paragenetic sequence is similar to the one we obtained in the sense that the chabazite crystallization took place after the crystallization of phillipsite.

CONCLUSIONS

It is possible to synthesize a single phillipsite-like zeolite and zeolitic mixtures (phillipsite + analcime and phillipsite + chabazite + analcime) by chemical reactions between the Chaitén volcanic ash and a NaOH 0.3 M solution at 150 °C, under hydrothermal

conditions, autogenic pressure and either in presence or absence of the template agent CTAB. The Na-K-phillipsite-like zeolite was the most effective to retain cations with about a 60 % retention for Pb^{2+} , 56 % for Zn^{2+} and 43 % for Ba^{2+} .

Obtaining phillipsite-like zeolite at 150 °C and 15 h of reaction time would represent an economical advantage if the process could be carried out at industrial level. This would contribute to mitigate the socioeconomic damages produced by the Chaitén (2008) volcanic ash. In the light of the results obtained it is possible to postulate that zeolites could be also synthesized from others SiO_2 , Al_2O_3 and K_2O rich volcanic products like rhyolitic domes and silicic pyroclastic deposits.

ACKNOWLEDGMENTS

This paper was possible thanks to the collaboration of the Instituto GEA. We also give our thanks to the Vicerrectoría de Investigación y Desarrollo of the Universidad de Concepción (Chile). The authors are grateful to Dr. Andrés Tassara and

Priscilla Riveros who donated the Chaitén volcano ash samples analyzed, also to Mónica Uribe for her help in the identification of the synthesized minerals by XRD and to Julio Pugin and Hugo Pacheco for their assistance in the SEM characterization of the synthesized zeolites.

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