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Thermochimica Acta 269/270 (1995) 443–452

thermochimica
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Zeolitization of glasses: a calorimetric study [☆]

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Received 16 September 1994; accepted 7 February 1995

Abstract

The construction of calorimetric ampoules for work in hydrothermal conditions makes it possible to investigate the enthalpy of mineral crystallization. The potential of the equipment is demonstrated for the case of zeolite synthesis from glasses. Two synthetic Na- and Na–K-glasses, and dacite pumice were used as starting materials. Aqueous solutions of 2 N and 6 N NaOH and KOH were prepared. The crystallization was performed in a Kalve calorimeter DAC-1A at 95°C.

Three peaks are observed in the e.m.f. curves due to: wetting of the glass, glass hydration and dissolution, and crystallization of zeolites. Their position versus time and their intensity depend on the experimental conditions.

The described calorimetric equipment is very useful for the low-temperature hydrothermal synthesis of zeolite minerals under isothermal conditions and provides a means of controlling the crystallization process.

Keywords: Crystallization; Glass; Kalve calorimeter; Zeolite

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1. Introduction

The zeolitization of volcanic glasses is a regional process leading to the formation of huge zeolite deposits [1, 2]. This process can be successfully studied by hydrothermal modelling [3–6]. The experimental zeolite synthesis is usually troubled by the absence of an effective fitback with the autoclave. This makes it necessary to carry out

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[☆] Presented at the 6th European Symposium on Thermal Analysis and Calorimetry, Grado, Italy, 11–16 September 1994.

SSDI 0040-6031(95)02353-4

numerous experiments of differing duration in order to clarify the character and sequence of the processes involved in the glass zeolitization. In fact, neither geological observations nor hydrothermal investigations provide information on the heat effects of the process.

A preliminary communication has shown that the calorimetric method is effective in studying the process of zeolitization [7]. In the present work, calorimetric equipment for low-temperature hydrothermal synthesis is described and quantitative data on the thermal effects of zeolitization are discussed.

2. Materials and experimental methods

Two glasses, $Na_2O \cdot Al_2O_3 \cdot 3.9SiO_2$ and $0.6K_2O \cdot 0.5Na_2O \cdot Al_2O_3 \cdot 4.3SiO_2$ were prepared as starting materials by melting quartz sand, γ-Al_2O_3, Na_2CO_3 and K_2CO_3 at 1300°C and by subsequent water hardening. In some cases, dacite pumice from the Ksudach volcano, Kamchatka (Russia), of composition $0.54Na_2O \cdot 0.08K_2O \cdot 0.39CaO \cdot 0.23MgO \cdot 0.21Fe_2O_3 \cdot Al_2O_3 \cdot 9.32SiO_2 \cdot 1.46H_2O$ was used. The glasses were crushed and fractions less than 0.1 mm in size were used. Aqueous solutions of 2 N and 6 N NaOH and KOH were prepared. The solid-to-liquid ratio in the experiments was 1:5.3. The experimental conditions are specified in Table 1.

The crystallization was performed at 95°C in a Kalve differential calorimeter DAC 1A (Russia) in ampoules specially constructed for hydrothermal synthesis (Fig. 1). The solution was placed in a titanium ampoule, while the glassy material was in a small Ni basket over the solution. Another ampoule, with the same solution but with an empty basket was lowered into the second socket of the device. After reaching isothermal conditions, the baskets were carefully immersed in the solutions and registration of the heat effect started. The heat effects of zeolitization were determined from the shape of the electromotive force (e.m.f.) curves versus time. The end of the process was assumed when the recorder pen reached the base line.

Then, the ampoules were removed and the reaction products were washed with distilled water and dried at room temperature. An electrical calibration of the device was used in the present case. The calibration coefficient was determined before each

Table 1
Experimental conditions and results for the calorimetric study of zeolite crystallization

Experimental conditions and results	Solid materials			
	Na glass 1	Na glass 2	Na–K glass 3	Pumice 4
Concentration of solution	6 N	2 N	2 N	2 N
Solution	NaOH	NaOH	NaOH	(Na,K)OH (Na:K = 2:1)
Synthesized minerals	Hydroxylsodalite	Zeolite Na-P	Phillipsite	Phillipsite
Reaction enthalpy/J g^{-1}	−277.0	−325.6	−209.2	−202.8

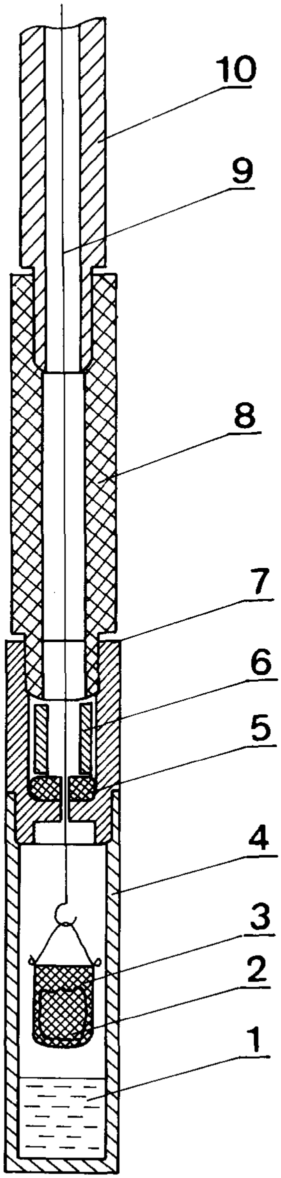

Fig. 1. The scheme of the calorimetric ampoule: 1, solution; 2, sample; 3, basket of nickel net; 4, titanium ampoule; 5, resin gland; 6, sleeve; 7, ampoule shutter; 8, teflon connector; 9, nickel wire; 10, titanium tube.

experiment within an error of 0.2–0.3%. All experiments were repeated, the observed reproducibility being ± 1.5–2%.

The synthesized minerals (Table 1) were identified by X-ray powder diffractometer with filtered Co Kα radiation. The X-ray data for the samples were compared with the

PDF-2 DATA JCPDS-ICDD. The samples were also investigated by a Philips SEM 515 scanning electron microscope.

In addition, in separate experiments the samples were analysed by X-ray diffraction and electron microscopy at different stages of zeolitization (data not given in Table 1).

3. Results and discussion

The experimental conditions, the reaction enthalpy and the mineral composition of the synthesized samples are shown in Table 1, while the experimental e.m.f. curves are given in Fig. 2.

3.1. Synthesized samples

Hydroxylsodalite, zeolite Na-P and phillipsite were synthesized. An increase in the alkalinity favours the formation of hydroxylsodalite. The phillipsite-group minerals were found to crystallize in 2 N NaOH solutions: zeolite Na-P in the Na-system and phillipsite in the Na–K-system. This correlates well with previously published results [6, 8].

Hydroxylsodalite was observed as complex intergrowths of plate crystals, often forming spheroidal aggregates (Fig. 3).

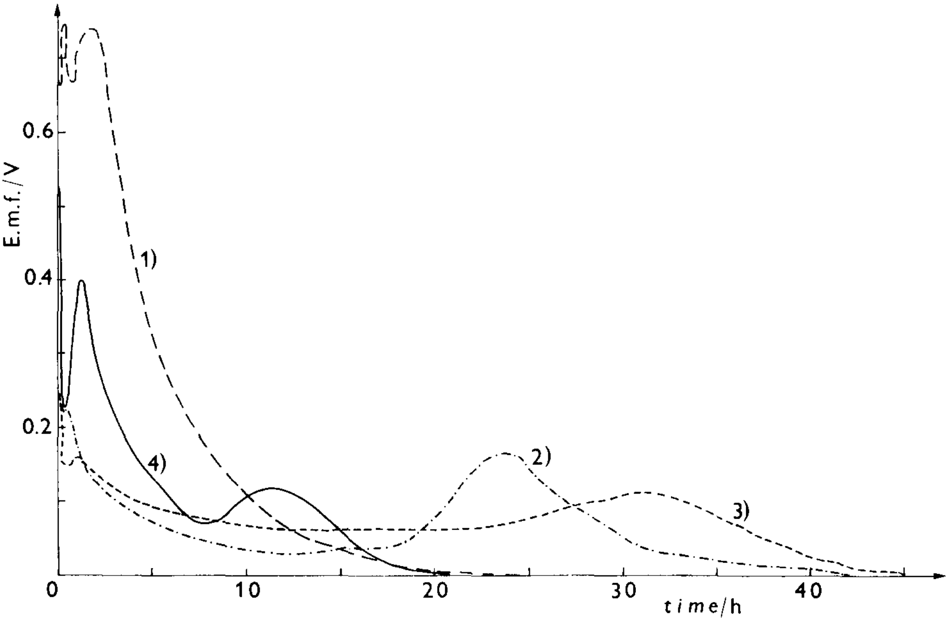

Fig. 2. E.m.f. curves versus time: 1, Na-glass in 6 N NaOH; 2, Na-glass in 2 N NaOH; 3, Na–K-glass in 2 N NaoH; 4, pumice in 2 N (Na, K)OH.
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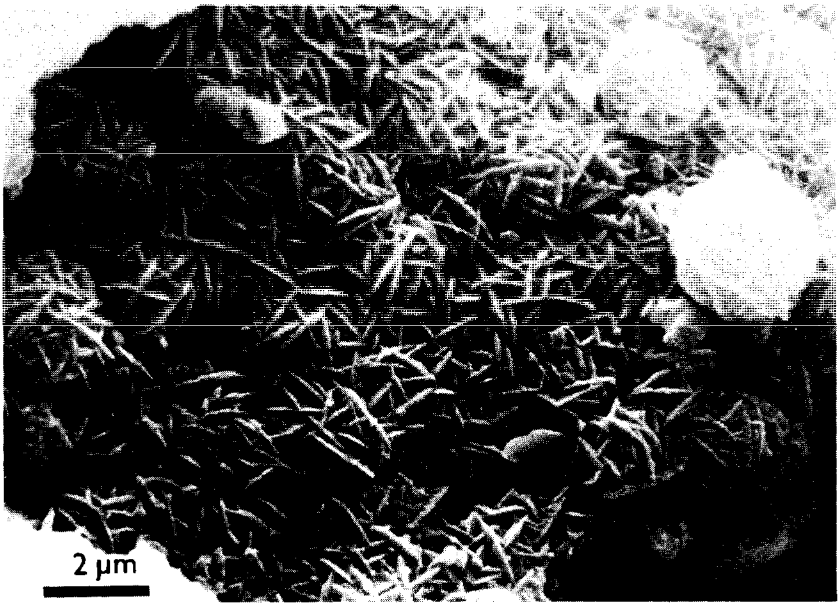

Fig. 3. SEM photograph of hydroxylsodalite aggregates (experiment 1).

Zeolite Na-P was observed by SEM as characteristic spherulites (Fig. 4, a and b). The phillipsite produced from the synthetic glasses is built up of spherulites with coarsely crystalline surfaces (Fig. 5), while that produced from pumice is characterized by specific cruciform twins (Fig. 6).

3.2. Development of the zeolitization process

Observations of natural materials and experimental data on zeolite formation have revealed that the zeolitization process in glassy ashes involves the following consecutive superimposing processes: glass hydration [9, 10], glass dissolution, and crystallization always being preceded by dissolution of the initial phase [11].

As seen in Fig. 2, the e.m.f. curves are quite complicated and they differ considerably from each other. The nature of the processes taking place was determined by stopping the experiments with Na glass and 2 N solution at different points on the curve.

Three peaks are clearly resolved in the experiments with 2 N solutions. The first peak occurs in the first minutes after immersion of the sample in the solution and is mainly due to wetting of the glass. In another experiment with pure water, a heat of -2.4 J g^{-1} was measured, which amounts about 1% of the total emitted heat. Under these conditions, one cannot expect other exothermic processes apart from the wetting of the glasses. In the experiments with 2 N solutions, the second peak is considerably broader than the first and maximizes at about 1–2 h after the start of the experiment. This peak derives from heats of hydration glass dissolution, because X-ray diffraction and

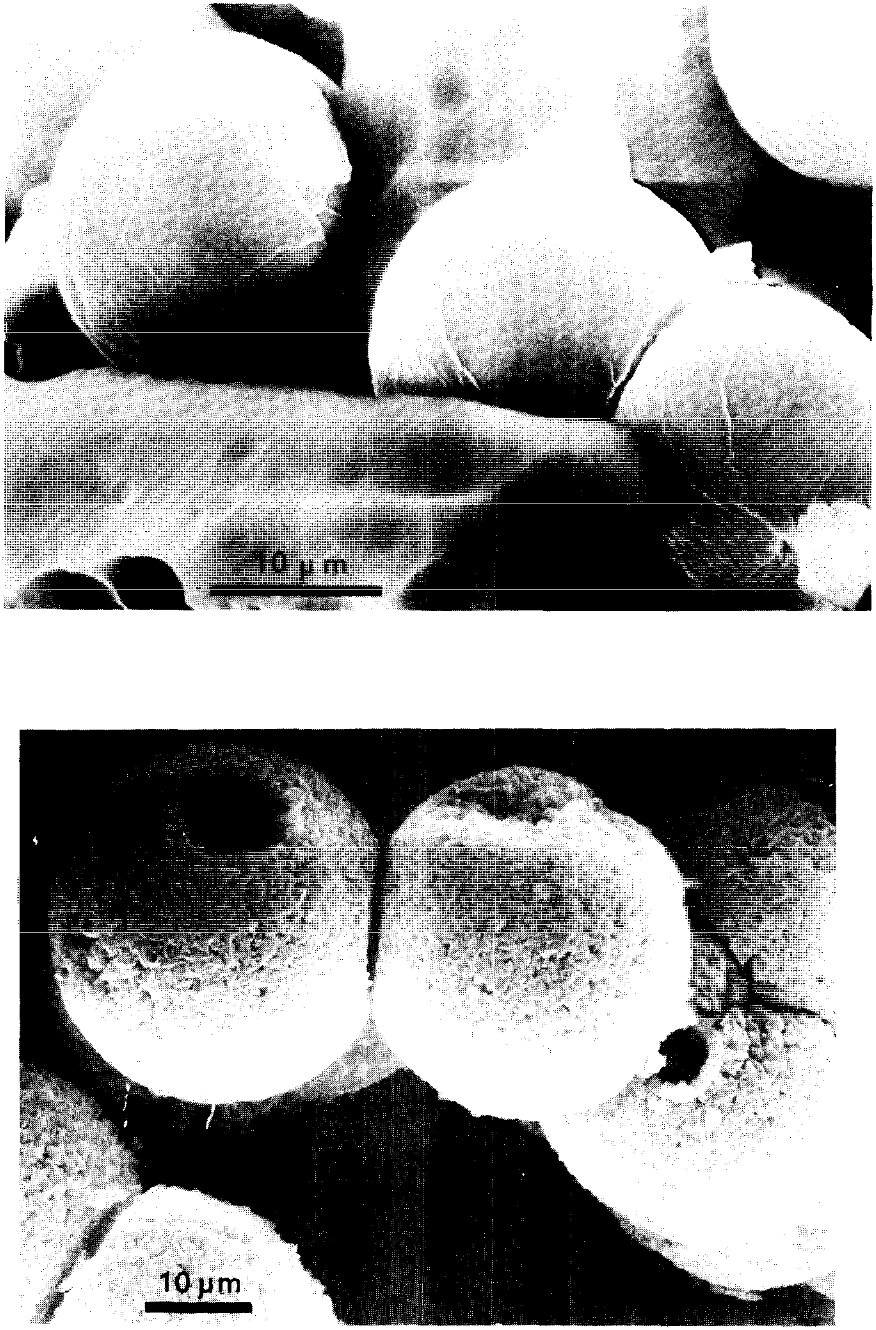

Fig. 4. SEM photographs of samples formed in experiment 2. a. 23rd hour, glass particles and zeolite Na-P spherulites. b. 45th hour, zeolite Na-P spherulites.

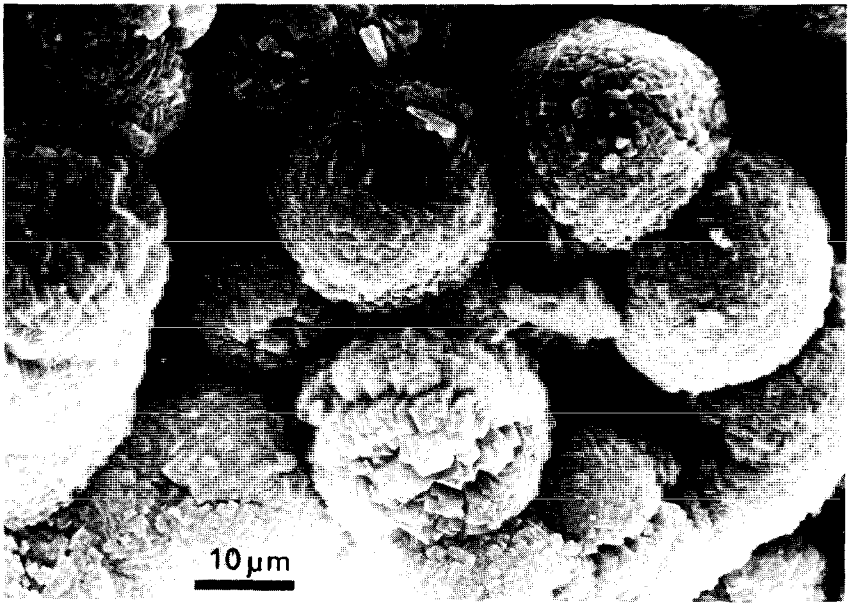

Fig. 5. SEM photograph of phillipsite aggregates in experiment 3.

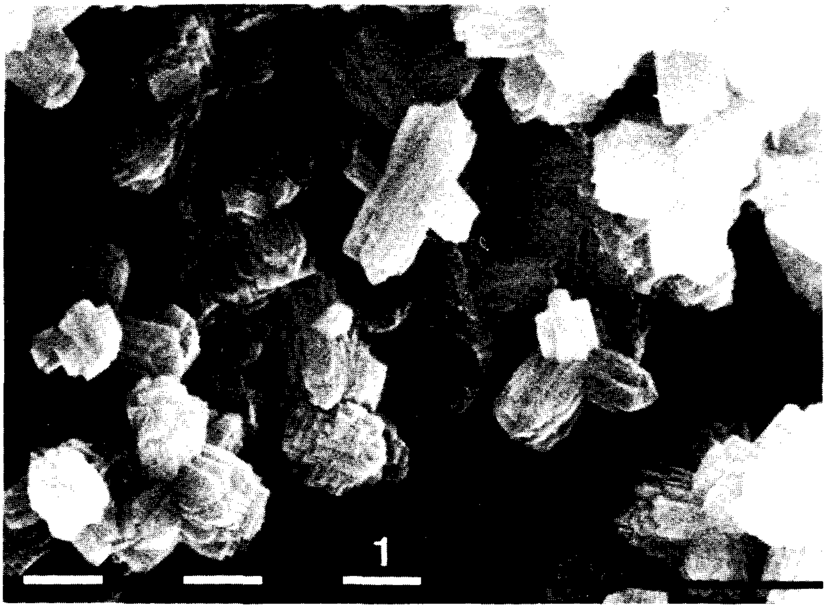

Fig. 6. SEM photograph of phillipsite aggregates in experiment 4.

electron microscopy analyses of the samples from the experiment with Na-glass and 2 N NaOH solution did not reveal the formation of any new phases at the 8th hour (Fig. 7, curve a). The first zeolite nuclei were observed at the end of this peak, at the 23rd hour (Figs. 7, curve b and 4a), while during the third peak the amount of crystallized zeolites gradually increased (Figs. 7 curve c and 4b). Consequently, the third peak is formed mainly by the crystallization heat of the zeolites and by the heat of dissolution of the remaining glass.

As seen in Fig. 4a, the spherulites of zeolite Na-P were formed in the coves of the remaining glass. They are smooth, without any cavities at the poles, and reach a size of 15–20 μm. During the next stage of crystallization,a crust of relatively large crystals was grown on the spherulites and cavities were formed at the poles (Fig. 4b). As stated in Ref. [12], this is the first time that ∞/m symmetry has been observed in crystalline objects.

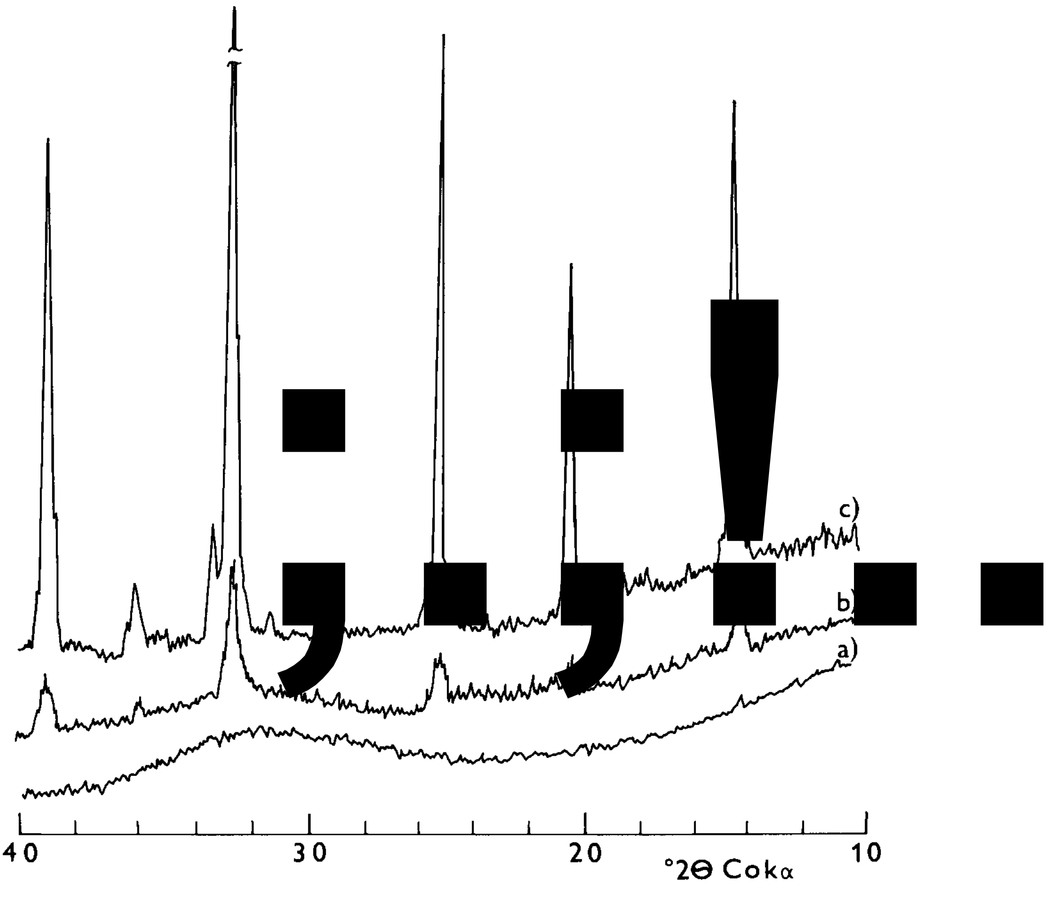

Fig. 7. X-ray powder diffraction patterns of samples formed in experiment 2: a, 8th hour; b, 23rd hour; c, 45th hour.

In experiments with 6 N solutions, the processes take place much faster, and the second and third peaks overlap.

Thus, the duration of the crystallization processes depends on the experimental conditions, i.e. it decreases with increasing alkalinity. As regards the cation composition of the glasses, the crystallization proceeds faster in Na–K-systems than in Na-systems.

In dacite glasses, which are partially hydrated, the zeolitization is the fastest.

3.3. *Heat effects*

All processes included in the zeolitization of glasses, i.e. hydration and dissolution of the glasses, as well as crystallization of non-zeolite and zeolite minerals, are exothermic.

The amount of heat emitted for pure Na-systems is higher than that for the Na–K-systems. This is probably due to the difference in the hydration heats of Na and K, -419 and -331 kJ $(\text{equiv})^{-1}$, respectively, [13].

The total amount of heat of zeolitization emitted is comparable with the heat of crystallization of quartz, -349.5 J g^{-1} [14], and albite, -192.6 J g^{-1} [15], emitted from the corresponding glasses. The heat of zeolitization is comparable with the heat emitted during the cooling of an intrusion [16]. This heat is sufficient to produce an adiabatic temperature increase per cubic centimetre of rock containing 0.1 g of water of up to 250–300 K.

4. Conclusions

The calorimetric equipment described is very useful for low-temperature hydrothermal synthesis of zeolite minerals under isothermal conditions and makes it possible to control the crystallization process.

The processes involved in the zeolitization of glasses (hydration and dissolution of glasses and crystallization of zeolite minerals) are exothermic, this determines the high heat of zeolitization which is comparable with the heat of a cooling intrusion and plays an important role in the formation and existence of natural hydrothermal systems.

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