EXPERIMENTAL TRANSFORMATION OF VOLCANIC GLASS FROM STREDA NAD BODROGOM (SE SLOVAKIA)

A. DERKOWSKI

Institute of Geological Sciences, Jagiellonian University, Oleandry 2a, Kraków, Poland

Abstract: The volcanic glass from Streda nad Bodrogom was used for experimental transformation into zeolites. Samples of obsidian were treated with the NaOH solutions of various concentrations and kept in autoclave in 75-175ºC for 72 hours. Four zeolite phases were obtained: analcime-O (ANA), NaP1 (GIS), sodalite-OH (SOD) and hydroxycancrinite-type phase (CAN). Analcime has shown the highest crystallinity and has been found in the highest amount among products of syntheses.

Key words: obsidian, zeolitization, hydrothermal synthesis, Streda nad Bogrodom

Introduction

Zeolites are materials of unique framework structure. As they include channels from angstroms to nanometers of size inside, they have useful properties: high cation exchange capacity and molecular sieving. Zeolites are widely used, eg. in the building and chemical industries. The huge deposits of zeolites form as a result of zeolitization of the volcanic glass. This process is studied by geochemical modelling and hydrothermal experiments (Alberti and Brigatti 1985, Petrova and Kirov 1995). Laboratory simulations are needed to better understanding of zeolitization processes of natural glass and formation of great zeolite deposits. These studies have been already carried out in order to explain the possibilities of transformations in natural geological environment (Wirsching 1981, Gottardi 1989, Hall 1998)

This paper concentrates on experiments on hydrothermal zeolitization of the Sarmatian volcanic glass from Streda nad Bodrogom (SE Slovakia)

Materials and methods

The sample of volcanic glass was collected in the quarry near Streda nad Bogrodom. Chemical composition of the obsidian was determined as an average composition from many point analyses with energy dispersive spectrometry (EDS), during scanning electron microscope (SEM) observations.

Chemical composition (wt. %): SiO_2 – 74.30; Al_2O_3 – 16.29; Fe_2O_3 – 1.12; MgO – 0.08; CaO – 1.35; Na_2O – 3.27; K_2O – 3.59;

This composition corresponds with the data from chemical analysis of bulk sample (dr Broska and dr Ba o; personal information).

Hydrothermal treatment. Samples of obsidian (500 mg) were grounded in the agate mortar and treated with 15 ml of NaOH solution of the following concentrations: 0.1M, 0.2M, 0.5M, 1M, 2M and 5 M. Reactions were carried out in Teflon (PTFE) autoclave for 72 hours, in temperatures: 75ºC, 100ºC, 125ºC, 150ºC and 175ºC. The samples after reactions were separated from supernatant liquid, then they were washed in distilled water and dried.

The products were identified by X-ray diffractometry (XRD) and the patterns were compared with PDF-2 JCPDS database (names and classification of zeolite phases after Baerloche et al. 2001 and Treacy, Higgins 2001). Some of the samples were studied using SEM, with EDS system.

Results and discussion.

Four zeolite phases were identified as the products of the reactions: Analcime-O (ANA), NaP1 (GIS), hydroxycancrinite-like structure (CAN), sodalite-OH (SOD). Trace amounts of unidentified PHI phases were detected in some samples. The changes of the amount (from XRD intensities of characteristic peaks) of zeolite phases during reactions in relation to temperature or NaOH concentration have been studied in details (Fig. 1, 2, 3, 4, 5).

In lower temperatures (75-100 ºC) the NaP1 phase occurs as the main product and is replaced by sodalite in reactions at highly concentrated NaOH solutions. NaP1 is present in the products of high temperature syntheses only at low concentrations of NaOH solutions (0.1-0.5M), while analcime is the predominant phase. Hydroxycancrinite was found among products of syntheses in the highest temperature and at the highest concentration of NaOH.

The amount of each zeolite phase was determined semi-quantitatively in relation to the reactions parameters (temperature and concentration of NaOH solution), in order to define fields of their crystallization conditions (Fig. 6). The highest crystallinity (among zeolites obtained during syntheses) has been reached for XRD monomineral samples of analcime. Other zeolite phases show minor crystallinity.

Conclusions

Analcime can be formed within the broad range of synthesis conditions and reach the higher crystallinity. This suggests that the transformation of volcanic glass (of composition similar to one from Streda nad Bodrogom) to analcime is very probable however, the natural hydrothermal conditions are ussually more complex than applied in experiments.

References:

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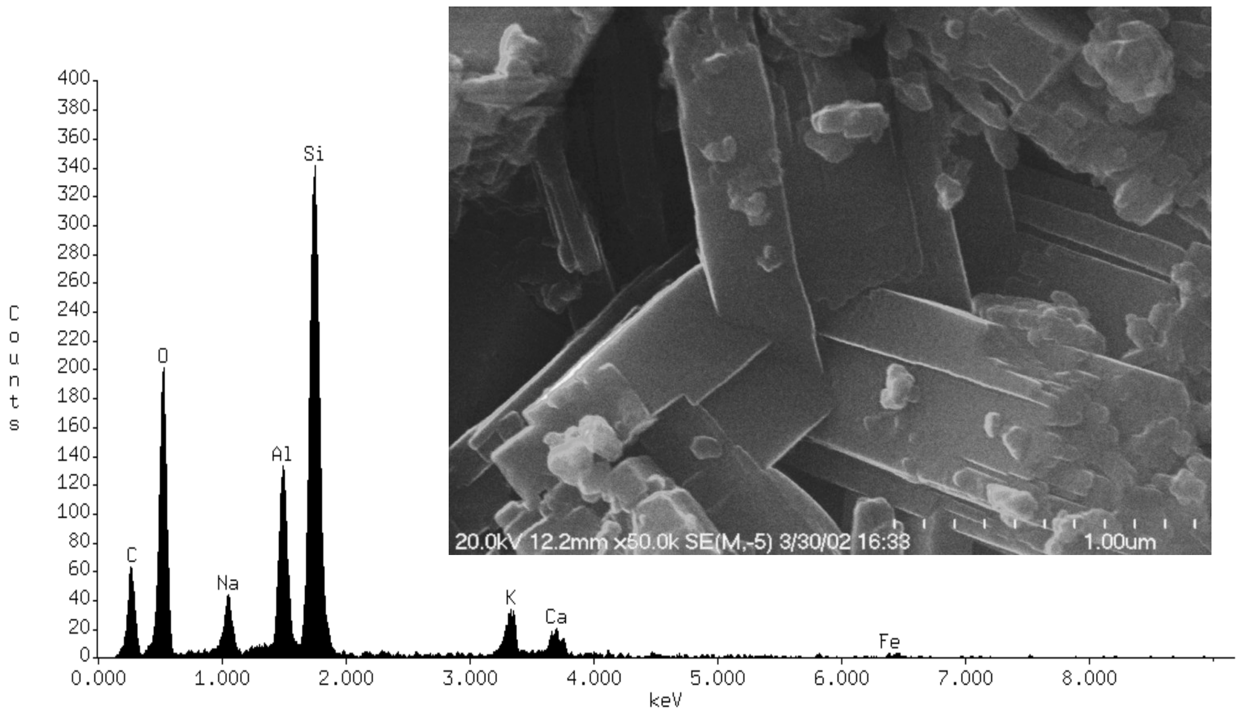


Fig. 1. SEM image and EDS spectrum of NaP1 (GIS) phase synthesised in 125 ºC and at 0.1M NaOH solution.

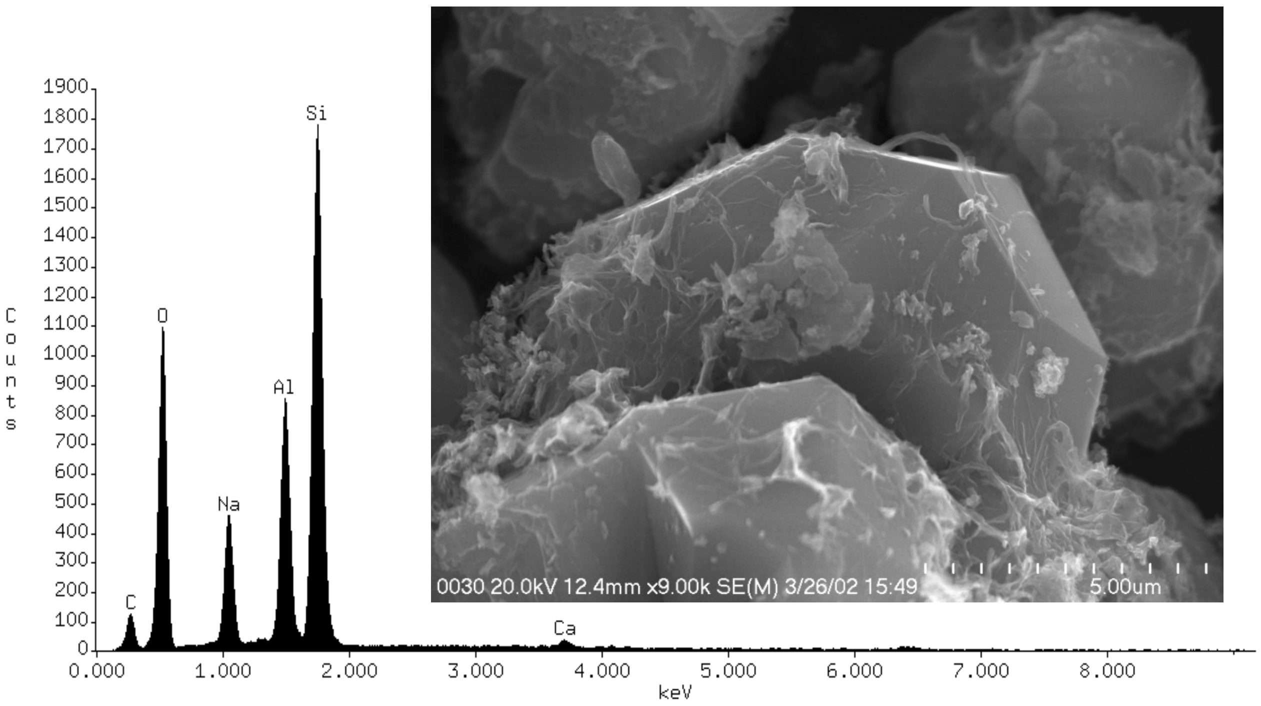


Fig. 2. Crystal of analcime (SEM image) and its chemical composition (EDS spectrum). Sample after reaction in 125 ºC, with 1M NaOH solution.

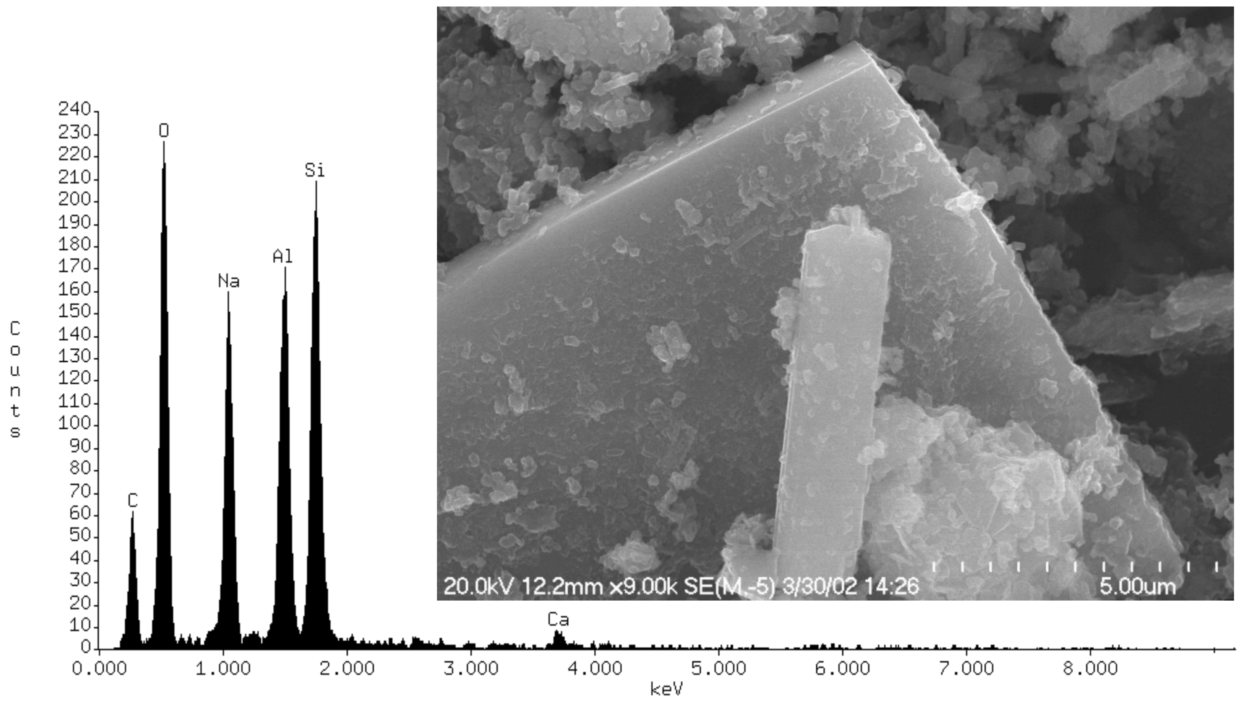
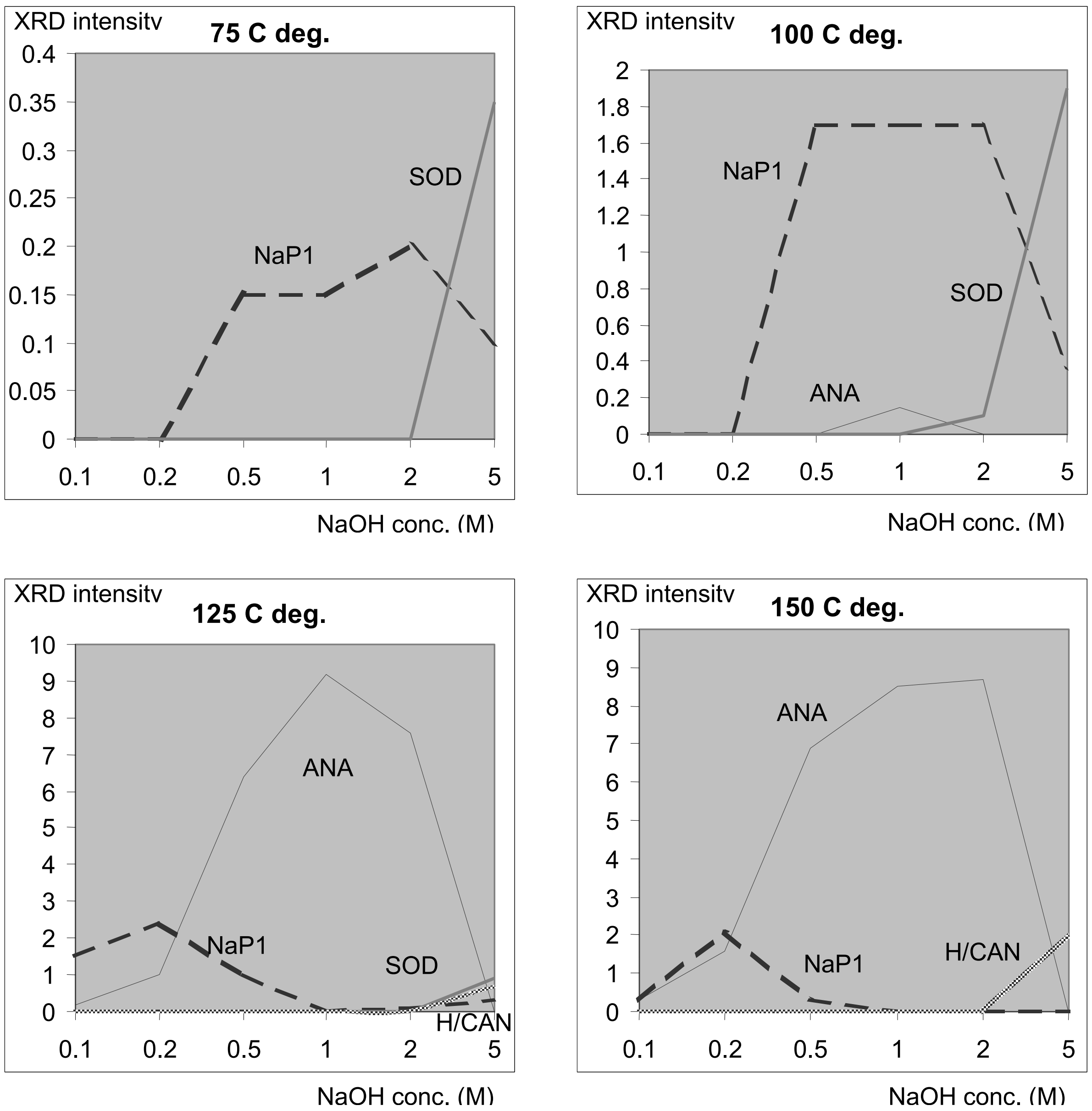


Fig. 3. Crystals of hydroxycancrinite-type phase (CAN) obtained during reaction with 5M NaOH solution, in 175 ºC (SEM image and EDS spectrum)



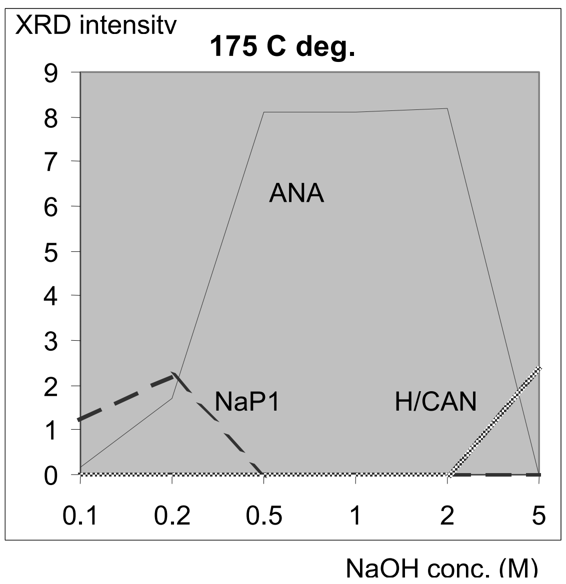


Fig. 4. Changes of XRD peaks intensity of zeolite phases in relation to the concentration of NaOH solution used in reaction, for various temperatures. ANA - analcime-C (ANA-group), NaP1 - NaP1 phase (GIS-group), SOD - sodalite-OH (SOD-group), H/CAN - hydroxycancrinite-type phase (CAN-group)

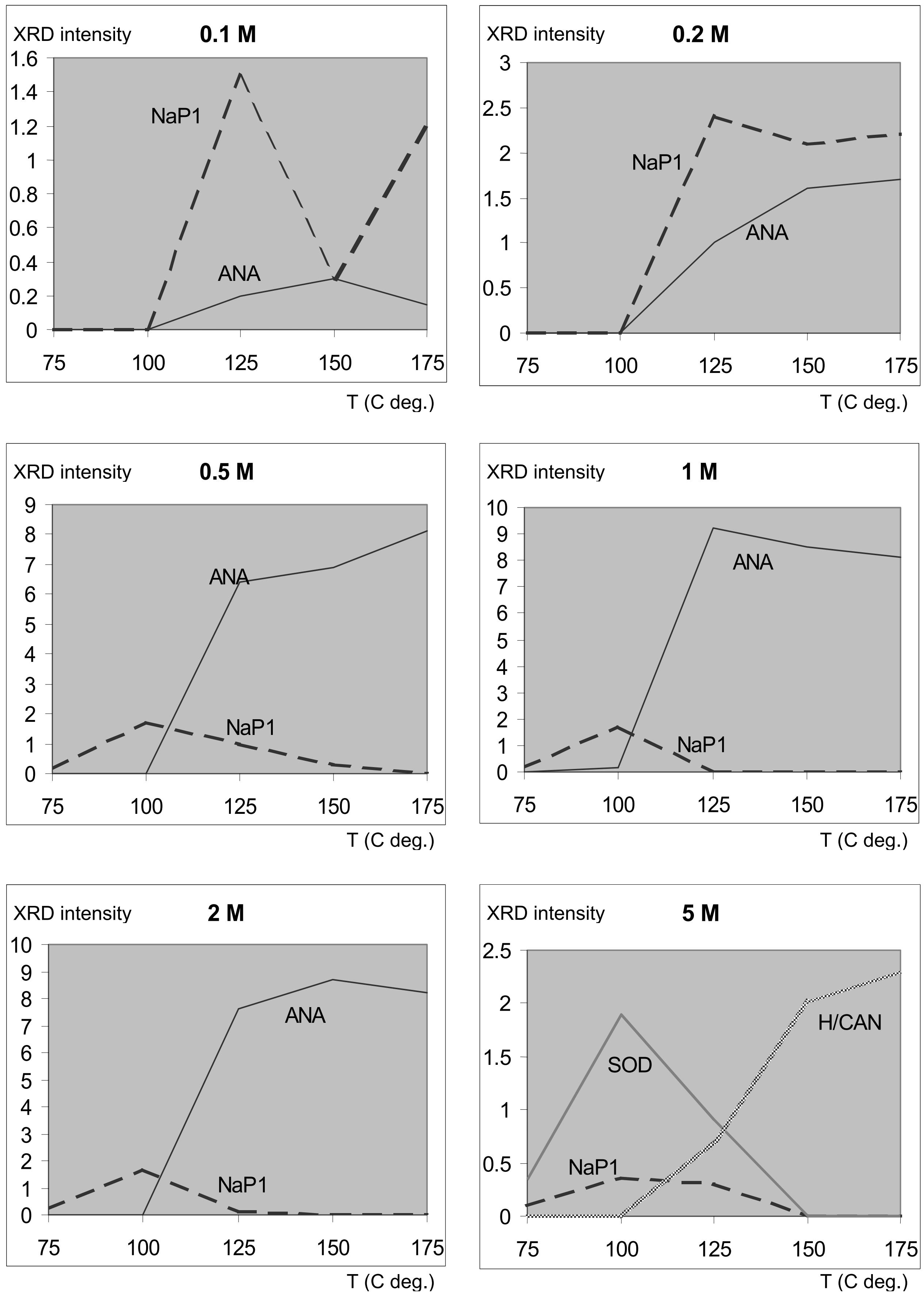


Fig. 5. Changes of XRD peaks intensity of zeolite phases in relation to the temperature of reaction, for various concentrations of NaOH solution.

ANA - analcime-C (ANA-group), NaP1 - NaP1 phase (GIS-group), SOD - sodalite-OH (SOD-group), H/CAN - hydroxycancrinite-type phase (CAN-group)