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INVERTED PHASE RELATION IN THE FORMATION OF NEPHELINE AND CARNEGIEITE FROM THE SYSTEM KAOLINITE—SODIUM CARBONATE

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INTRODUCTION

In the system with the composition $NaAlSiO_4$, such phases as low- and high-nepheline with the structure related to that of tridymite and low- and high-carnegieite with the structure related to that of cristobalite

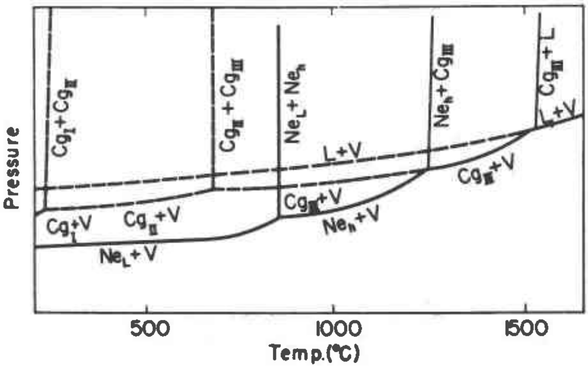

FIG. 1. System $NaAlSiO_4$; p–T; schematic. L = liquid, V = vapor, Cg = carnegieite, Ne = nepheline.

are present, and they have high-low inversion points at 850° C. and 690° C. respectively. Low-carnegieite is formed as metastable phase. The stability relations among these phases are shown in Fig. 1 (Tuttle and Smith, 1958). When the excess amounts of Na_2O are present, alkali-rich carnegieite $NaAlSiO_4$ x Na_2O is formed.

In the present experiments, crystalline kaolinite was used instead of a glass with nepheline composition mainly used as starting material in the previous studies. In this case the process never followed the above-mentioned sequence, but an inverted phenomenon was observed that the decomposition of the starting mixture, at around 600° C. was followed by a formation of a phase with a high-carnegieite structure at lower temperatures, around 700° C., with its subsequent transformation to a low-nepheline at elevated temperatures.

EXPERIMENTAL

Zettlitz kaolinite with the composition as shown in Table 1 and Na_2CO_3, E.P. grade chemicals, were mixed thoroughly by an alcohol wet ballmill for 24 hr. Several mixtures with compositions $Al_2O_32SiO_2$ $2H_2O$-a Na_2CO_3 (a = 1.00, 1.25, 1.50 and 1.75) were thus made. Grinding by an alcohol wet ballmill scarcely showed any effect upon the *x*-ray diffraction pattern of the original kaolinite. The reaction process was

TABLE I. CHEMICAL COMPOSITION OF ZETTLITZ KAOLIN USED AS RAW MATERIAL (%)

Ig-loss	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Total
14.05	45.13	36.93	0.55	0.24	0.83	0.49	98.22

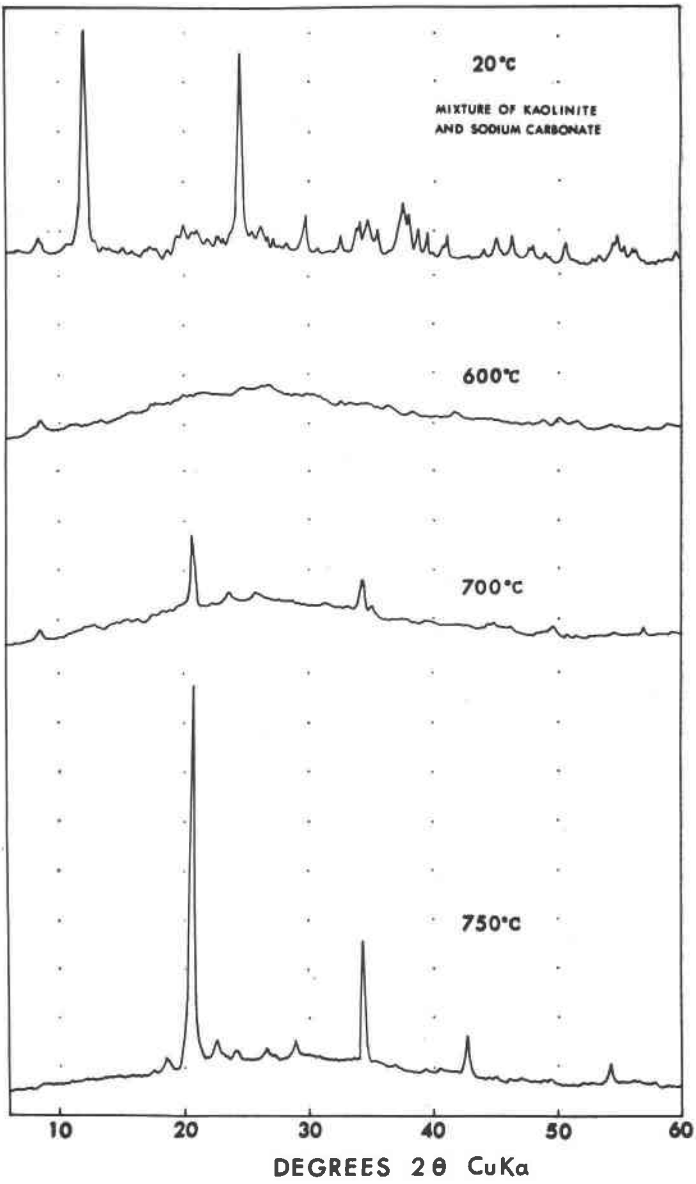

FIG. 2 (1). High temperature x-ray diffraction patterns of an equimolar mixture of kaolinite and sodium carbonate, with Cu-Kα radiation at scanning speed 2°/min.

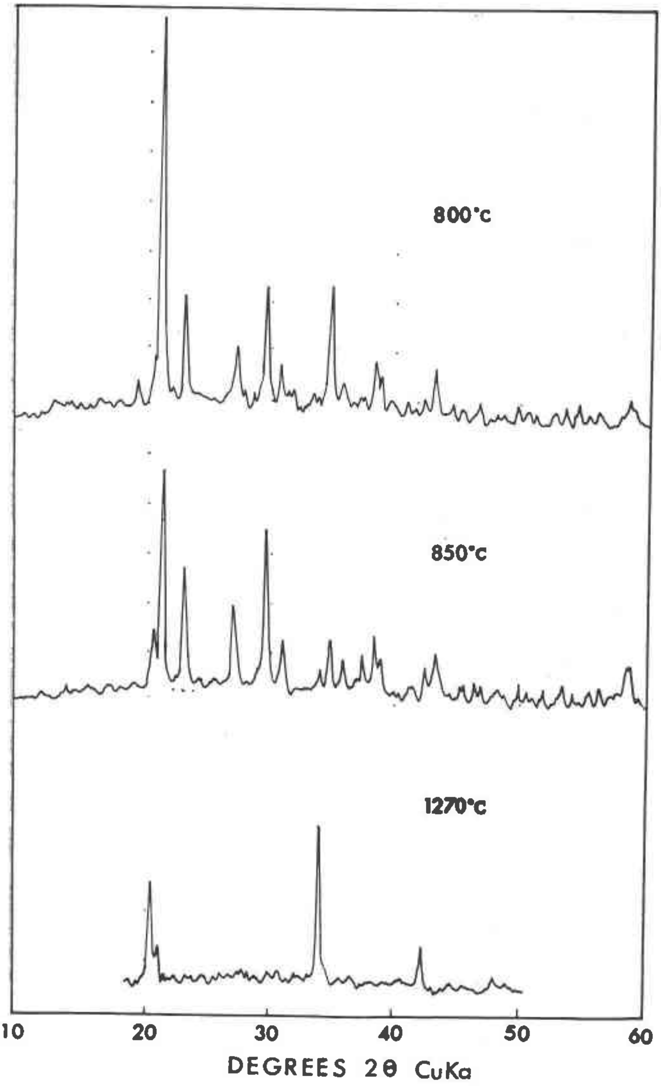

FIG. 2 (2). Continued.

examined by a high temperature *x*-ray diffraction method as well as thermal analyses.

RESULTS

Figure 2 shows the results of high temperature *x*-ray diffraction of an equimolar mixture of kaolinite and sodium carbonate. It is seen that the mixture was decomposed almost completely at about 600° C. forming an amorphous phase, from which the peaks of high-carnegieite, (111) and (220) at 2θ of 21.0° and 34.7° (Cu-Kα) respectively, appeared at about 700° C. which grew stronger up to 750° C., then diminished gradually followed by the appearance of low-nepheline peaks between 800° and 850° C. At 1270° C. a transformation into high-carnegieite took place again which was quenchable into the stability field of nepheline. This high-carnegieite underwent an inversion into low-carnegieite at a temperature near 700° C. The intensity distribution of this high-carnegieite at 1270° C. is somewhat different from that of normal high-carnegieite owing to a change in the preferred orientation caused by sintering shrinkage (Tuttle and Smith, 1957). When the specimen was quenched and pulverized again, the intensity distribution gave almost the same pattern as that of high-carnegieite structure formed at lower temperatures. With increased amounts of sodium carbonate, the temperatures of decomposition, high-carnegieite structure formation, inversion into nepheline, and inversion into high-carnegieite were lowered; for example, by 100° C. for a mixture, 1.5 Na_2CO_3-kaolinite. The relative diffraction intensities of these phases, including high-carnegieite structure formed at lower temperatures, were affected by the amount of excess alkali.

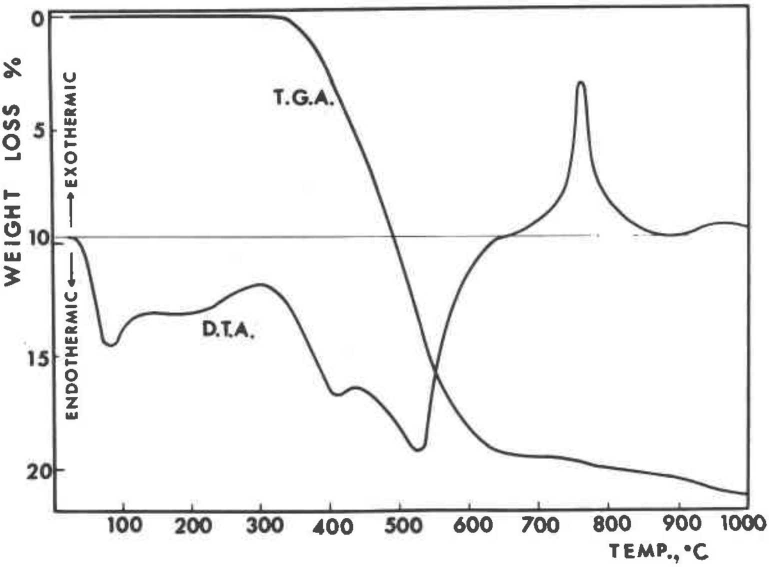

FIG. 3. Thermal analyses of an equimolar mixture of kaolinite and sodium carbonate. Specimen weight: 164.7 mg; heating rate: 2.5°C/min; atmosphere: In air.

By a differential thermal analysis as shown in Fig. 3, it was found that there was an exothermic effect at a temperature near 760° C. which seemed to indicate a transformation of high-carnegieite structure into low-nepheline. At the same time, thermal gravitational analysis curve showed that this transformation was accompanied with a loss of a little amount of water, about 1%.

There may be three possible interpretations for this phenomenon; the one that the structure of decomposed kaolinite is inherited readily by high-carnegieite rather than nepheline, another that the water present in kaolinite has some effects on the phase relation and the other that impurities in kaolinite such as Fe_2O_3 and CaO, the total of which reaches about 2%, play some roles on the reaction process. With respect to impurities the following points were revealed by careful *x*-ray diffraction. In the original kaolinite some mica was detected which remained undestroyed up to 700° C. in the mixture with Na_2CO_3. In the specimen quenched from 700° C. additional peaks of low-carnegieite and other unidentified phases were recognized which, however, were quite slight as compared with the main peaks of the phase with the high-carnegieite structure. Details will be reported in a separate paper.

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SCANDIUM BORATE, $ScBO_3$

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Single-crystals of scandium borate have been grown from a barium borate flux. The sample was cooled slowly—30° C. per day—from 1160° to 850° C. Another run was cooled from 1170° to 740° C. at a rate of 20° C. per day.

The crystals are equant, up to one half millimeter in size. A study on the optical goniometer revealed trigonal symmetry; the most prominent

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