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Changes in the crystal morphology of synthetic reedmergnerite ($NaBSi_3O_8$) during ordering experiments

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SUMMARY. The morphologies of hydrothermally grown reedmergnerite crystals change systematically with time and rate of change of B, Si order. Three stages in this process are recognized: (1) Growth of well-faceted crystals. (2) Development of etching leading to the formation of irregular grains. (3) Modification of irregular grains to form rounded or ellipsoidal crystals. A solution-reprecipitation process is responsible for the morphological changes and the increase in degree of order of B and Si with time at constant temperature and pressure.

THERE have been few studies of the morphologies of synthetic feldspars and Smith (1974) has summarized the work in this field. This paper is concerned with the changes which take place in synthetic reedmergnerite as a function of time at constant temperature and pressure. These changes in morphology provide evidence of the mechanism by which aqueous solutions interact with reedmergnerite and promote changes in the degree of B, Si order on tetrahedral sites.

Experimental techniques. Details of the hydrothermal synthesis technique and the methods used to estimate the degree of order are given by Mason (1980).

Selected samples were mounted on aluminium specimen stubs. To prevent charging, a coating of gold was applied using an ISI PS2 coating unit. Observations and photographs were made with an ISI Super II Scanning Electron Microscope operating at 25 kV.

Results. The morphologies of the reedmergnerite crystals are dependent on temperature, pressure, and duration of the experiment. This work is concerned chiefly with the variation in morphology as a function of time but some comments on the temperature and pressure variation are appropriate here. These descriptions apply mainly to the products of short experiments; in experiments longer than about 100 hours the initial morphology is lost, as described below. The use of the SEM allows the morphological details of very small crystals to be observed but has the disadvantage that Miller indices cannot be given to the faces. The descriptions of crystal morphology are therefore limited to qualitative terms such as 'prismatic' or 'lamellar'. Pictorial representations of these terms as used in this work are given by Bloss (1971, p. 340).

At temperatures of 300 and 350 °C at a pressure of 1 kbar and at 400 °C at a pressure of 100 bars the crystals are predominantly lamellar in form. There is no morphological evidence of twinning. At 400 and 500 °C at a pressure of 1 kbar the crystals are prismatic in habit (fig. 2*a*).

The morphologies of reedmergnerite crystals have been studied as a function of time at 400 and 500 °C at a pressure of 1 kbar. The illustrations of figs. 1 and 2 have been selected from about 100 photographs. The crystal morphologies shown may be related to time and degree of order by referring to fig. 3. The degree of B, Si order on tetrahedral sites is measured by the quantity $2\theta 131-2\theta 1\bar{3}1$ which is called the '131 indicator' (Smith, 1974). Fig. 3 shows the 131 indicator as function of time at 400 and 500 °C at 1 kbar. In reedmergnerite the value of 131 indicator increases as the degree of order increases. Fig. 3 is drawn with the 131 indicator increasing downwards so that the curves describing the 131 indicator as a function of time have a negative slope. When drawn in this way the diagram resembles those representing the time dependence of the 131 indicator in albite (MacKenzie, 1957; Eberhard, 1967; Mason, 1979). Numbered points on fig. 3 refer to Table 1 of Mason (1980).

The morphological variation at 400 and 500 °C may be divided into three stages:

(1) Growth of well-faceted crystals with sharp edges and corners (fig. 2*a*).

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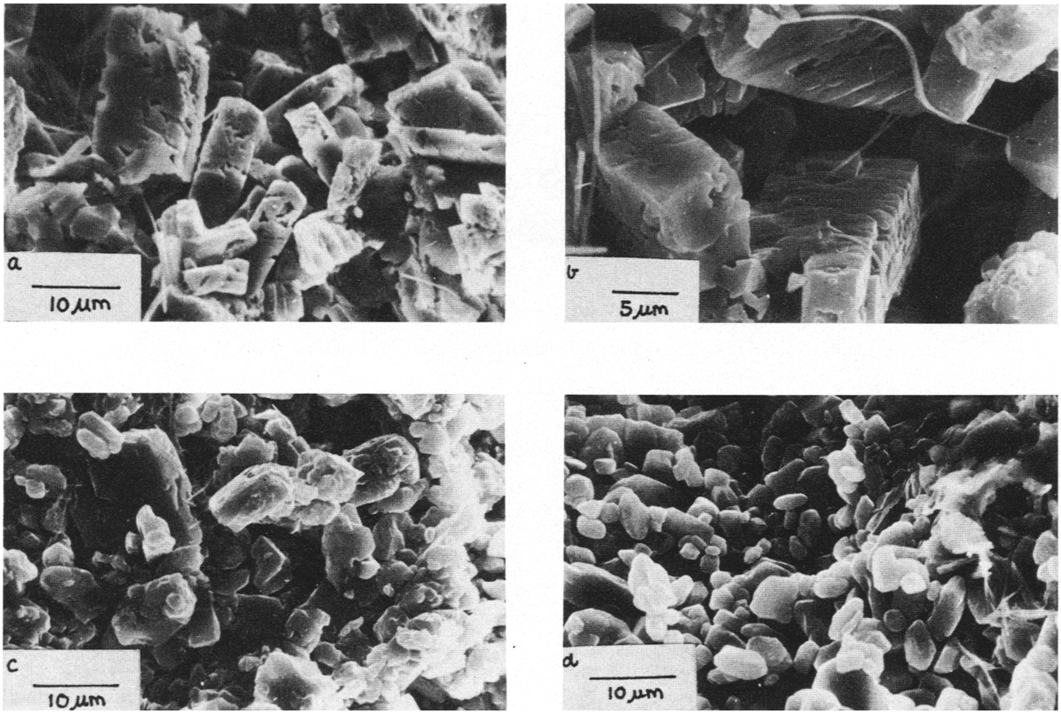

FIG. 1. Scanning electron micrographs of reedmergnerites synthesized at 400 °C, 1 kbar. (*a*) No. 47, H_2O, 21 hours. Magnification: × 1157. (*b*) No. 60, 1m NaOH, 23 hours. Magnification: × 1736. (*c*) No. 50, 1m NaOH, 167 hours. Magnification: × 1157. (*d*) No. 21, H_2O, 638 hours. Magnification: × 1157.

(2) Development of etching (plates 1*a* and 2*b*). The final products of this stage are irregular, heavily indented crystals lacking faces (figs. 1*c* and 2*c*).
(3) Progressive loss of indentations to produce a rounded or ellipsoid form (figs. 1*d* and 2*d*).

The stages identified above have a well-defined relationship to the rate of change of the 131 indicator (fig. 3). The crystals grown in short experiments are well faceted at both 400 and 500 °C (fig. 2*a* shows an example grown at 500 °C). Etching develops in the time interval during which ordering is at its most rapid. In the region where the rate of ordering is slowing down on approaching a steady value the crystals are invariably heavily indented and almost completely lack faces and edges. In the longest experiments, where the degree of order has ceased to change, the crystals have rounded outlines, sometimes becoming ellipsoidal. By observing the morphology it is possible to predict whether or not a particular sample is the product of a long or short experiment and whether or not the degree of order has reached the final value appropriate to the temperature of the experiment. The morphologies seen in duplicate experiments are always the same (compare figs. 1*a* and 1*b*).

In the shortest experiments the crystals are generally free of etching. The time taken to develop visible etch features is variable but usually about 10 hours at both 400 and 500 °C. This uncertainty is indicated on fig. 3 by the dashed lines separating the regions labelled 'stage (1)' and 'stage (2)'. Stage 2 takes about 200–50 hours to complete at 400 °C and about 150–200 hours at 500 °C. The development of rounded outlines takes place after about 500 hours at both temperatures. The synthesis experiments were performed in the presence of 10 wt % of pure water or of 1 m NaOH solution (Mason, 1980). Both the pattern and time dependence of the morphological changes described above are independent of the composition of the fluid in which the crystals have grown. Similarly the ordering behaviour is independent of fluid composition (Mason, 1980).

Discussion. The growth of feldspars in a disordered state occurs when changes in degree of order are slow relative to the speed of crystal growth (Goldsmith and Laves, 1954). If the growth rate is slow enough the crystals may grow in an

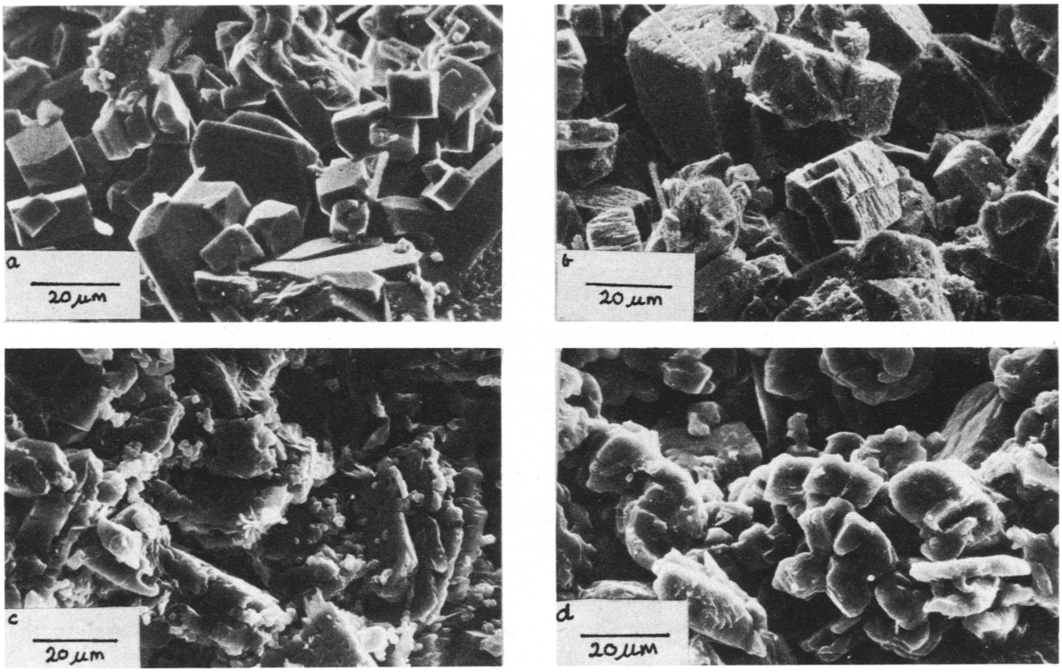

FIG. 2. Scanning electron micrographs of reedmergnerites synthesized at 500 °C, 1 kbar. (*a*) No. 131, H_2O, 5 hours. (*b*) No. 77, H_2O, 70 hours. (*c*) No. 81, H_2O, 101 hours. (*d*) No. 138, 1m NaOH, 1580 hours. All at magnification ×583.

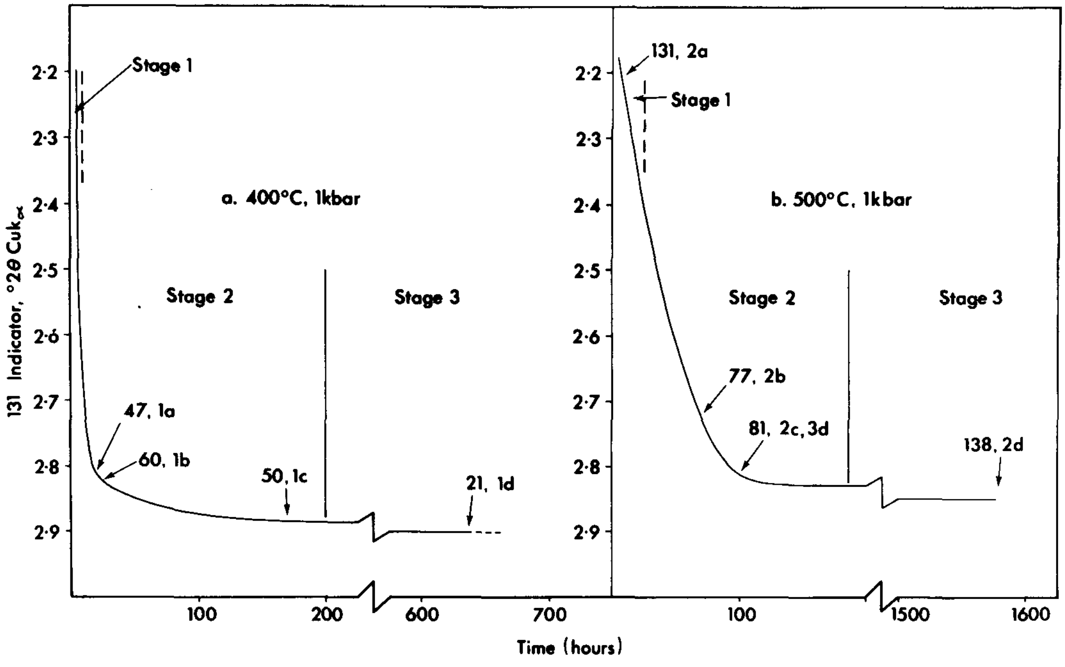

FIG. 3. The variation of the 131 indicator as a function of time (*a*) 400 °C, 1 kbar, (*b*) 500 °C, 1 kbar. Numbered points refer to Table 1 of Mason (1980); numbers 1*a*, 1*b*, etc., refer to the plates in this work.

ordered state. Indeed Akizuki and Sunagawa (1978) have interpreted the sector structure of adularia in terms of differences in the relative rates of growth and Al, Si ordering in the different sectors. Flehmig (1977) has synthesized ordered alkali feldspars under conditions of slow crystal growth at 80 °C and claims that they grew directly in an ordered state without involving transformation from a disordered state.

In the case of reedmergnerite, however, it seems that crystal growth is rapid relative to the rate of B, Si ordering; reedmergnerites synthesized in experiments of short duration are disordered (Mason, 1980). Disordered material is unstable relative to ordered material and will tend to go into solution preferentially. The etching described as 'stage 2' above is the evidence for this process. If equilibrium is maintained between fluid and solid there will be a continuous process of solution and precipitation. Some material will be precipitated in the disordered configuration and some in the ordered configuration. The latter material will be less prone to solution than disordered material so that a gradual increase in the average degree of order will occur.

Ordering of B and Si is initially rapid but slows after about 200–250 hours at 400 °C and 150–200 hours at 500 °C. The crystals observed at this stage are typically heavily indented and irregular in shape (end of stage (2)). Such grains will have higher surface energy than faceted crystals and should change towards that morphology. The crystals seen in the longest experiments are, however, rounded or ellipsoid. This is interpreted as being an intermediate stage in the development of crystal faces. The development of such shapes allows a reduction in total surface energy by reducing the surface area whereas the development of crystal faces would reduce surface energy per unit area. If the products of longer experiments were available they would probably show the gradual development of faces.

The identical behaviour observed for 1 m NaOH solution and pure water suggests that the solution-reprecipitation process operates at the same rate in both fluids. This correlates well with the observation that ordering rates are the same in both types of fluid (Mason, 1980).

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