

Nobuo Morimoto (in press) independently has found the same mineral in a number of localities. He and the writer have agreed to both use the name, djurleite.

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VACUUM-FIRING AND HIGH-TEMPERATURE REPLICATION OF KAOLINITE

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INTRODUCTION

Electronoscopic observations of kaolinite at elevated temperatures have been limited to replicas of the material after heat treatment and cooling. This gives no assurance that the structure observed is truly representative of the surface at elevated temperatures. In order to eliminate this difficulty, experiments were conducted with a technique for replication of hot surfaces. This technique introduced an additional variable that was not considered when the experiment was originally conceived, namely, the effect of firing in a high vacuum. The purpose of this note is to describe the technique and to present representative electron micrographs of kaolinite fired in air and in vacuum, and replicated while hot and after cooling.

EXPERIMENTS

One gram of kaolinite was suspended in 50 ml of distilled water and shaken thoroughly. Ten drops (*ca.* 0.5 ml) of the suspension was placed on a molybdenum boat (Fig. 1) and allowed to dry at room temperature. The specimen was next dried at 60° C. for 12 to 24 hours in a laboratory oven. After drying, the boat was attached to one pair of electrodes of a high-vacuum evaporator. A small piece of gold (m.p. 1063° C.) or a small flake of manganese (m.p. 1260° C.) was placed on the dried clay surface to serve for temperature calibration. A tungsten basket with platinum (*ca.* 3 mg) was positioned on another set of electrodes to provide shadowing at a 30° angle to the plane of the surface. The bell jar

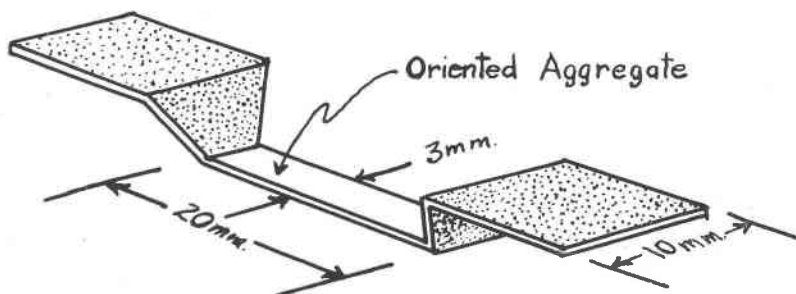


FIG. 1. Sketch of molybdenum boat used as a heating element for vacuum-firing.

was evacuated to less than one micron pressure. The boat was heated by a power supply consisting of a Variac and a step-down transformer. The temperature was increased gradually by manual adjustment of the Variac until the gold or manganese melted. The temperature was maintained at that level for 20 hours. After this time, the platinum was evaporated onto the hot clay surface. After cooling, carbon was evaporated onto the surface at normal incidence to provide a backing for the replica. Attempts to deposit carbon onto the hot surface were unsuccessful.

The platinum-carbon replicas were removed from an area adjacent to the calibrating metal by treatment with hydrofluoric acid for several hours. The replicas were washed with distilled water and picked up on collodion or Formvar coated grids. Replicas prepared in this manner are referred to as high-temperature replicas. Platinum-carbon replicas of cold surfaces of air-fired and vacuum-fired kaolinites were prepared in the same manner and are referred to as conventional replicas.

At least three replicas were taken from each specimen and examined with an EMU-2 microscope. From five to fifteen photographs were made of each replica. The single photographs judged to be most nearly representative of each specimen are shown in Fig. 2.

RESULTS AND DISCUSSION

The use of calibrating metals as temperature indicators was not entirely satisfactory. It is believed that the indicated temperatures are slightly lower than those actually achieved. Evaporation of molybdenum from the boats also contributed to a slight rise in temperature during the 20-hour heat treatments. Use of a thermocouple for temperature determination and use of platinum for heating elements would minimize these difficulties.

Replicas of the kaolinite fired in air are quite similar to those published

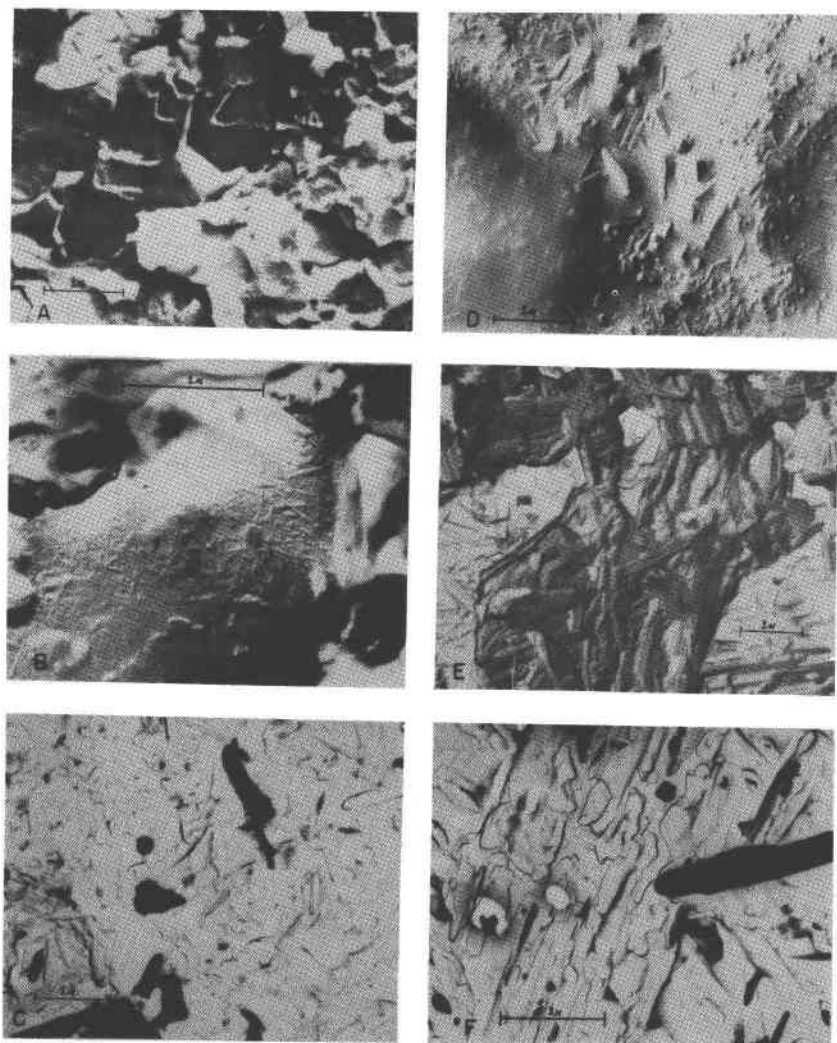


FIG. 2. Kaolinites fired for 20 hours at: (A) 1063° C. in air, conventional replica; (B) 1063° C. in air, conventional replica showing enlarged view of mullite needles; (C) 1063° C. in vacuum, high-temperature replica; (D) 1260° C. in air, conventional replica; (E) 1260° C. in vacuum, conventional replica; (F) 1260° C. in vacuum, high-temperature replica.

by Comer (1959) and by other authors. At 1063° C. the material as a whole retains the "metakaolinite" structure with some hexagonal outlines still visible (Fig. 2A). However, close examination reveals some development of mullite needles (Fig. 2B). Mullite needles are very well developed after firing in air at 1260° C. for 20 hours (Fig. 2D).

There is a striking difference in the appearance of the kaolinite fired in vacuum from that fired in air. The kaolinite heated in vacuum at 1063° C. and replicated hot (Fig. 2C) is completely transformed to irregularly shaped mullite needles. The edges are rounded rather than sharply defined straight lines. There are no structures that can be identified as partially degraded kaolinite plates as was the case with kaolinite heated in air at 1063° C.

The structure of the kaolinite heated in vacuum at 1260° C. for 20 hours (Figs. 2E and 2F) is very complex. The material is completely transformed into an agglomerate of well-formed crystals with lath-like outlines, distinct striations, and step-like structures. The conventional replica (Fig. 2E) and the high-temperature replica (Fig. 2F) are very similar. There is evidence, however, that platinum did not adhere to the hot surface as well as to the cold surface.

The high-temperature replication technique appears to be a relatively easy method for investigation of materials at elevated temperatures. If a pronounced change occurred on cooling, the replica would probably be somewhat disrupted. Careful study of the replica, however, should enable one to interpret the magnitude and nature of the change.

The observed differences in air-fired and vacuum-fired kaolinites lead to some interesting questions regarding the effects of atmosphere, pressure, relative volatilities of major constituents and impurities, and firing times on phase development in kaolinite. Further investigations of this type, coupled with x-ray diffraction studies, may provide considerable information as to the mechanisms and factors involved in thermal transformations.

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VALIDITY OF TINTICITE

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Hugo Strunz in his *Mineralogische Tabellen*, Akademische Verlagsgesellschaft, 3 Auflage, Leipzig 1957, on page 246 says, "Eleonorit ist mit Beraunit identisch, vielleicht auch Tinticit (Stringham 1946)," thus casting doubt on the validity of tinticite. In the original paper, the close compositional relationship of tinticite to beraunite was recognized, but x-rays by the Bureau of Mines, Salt Lake City and J. M. Axelrod of the U. S. Geological Survey showed them to be different.