

## MINERALOGICAL NOTES

DJURLEITE,  $\text{Cu}_{1.96}\text{S}$ , A NEW MINERAL<sup>1</sup>

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Until recently the only known sulfides of copper were covellite ( $\text{CuS}$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), and digenite (about  $\text{Cu}_{1.8}\text{S}$ ). Then Djurle (1958) described three polymorphs of a new synthetic compound,  $\text{Cu}_{1.96}\text{S}$ . The writer has found the low-temperature polymorph of this compound, Djurle's  $\text{Cu}_{1.96}\text{S}$  III, in nature and proposes the name djurleite.

The identification of djurleite is based primarily on the close correspondence between  $x$ -ray powder diffraction data and those of Djurle's  $\text{Cu}_{1.96}\text{S}$  III, as shown in Table 1.

The main problem in the identification of djurleite is to distinguish it from chalcocite. The two minerals possess superficially similar  $x$ -ray patterns, differ chemically by only about 0.3 weight per cent S, and resemble each other under the metallographic microscope.

The three strongest  $x$ -ray powder diffraction lines of djurleite, which are shown in Fig. 1, are very close to the three strongest lines of chalcocite, suggesting a structural similarity. Many of the weaker lines of the two minerals have similar  $d$ -values, but the relative intensities are very different. About one-third of the djurleite lines have no chalcocite equivalents and these include the fifth strongest djurleite line [ $d = 3.386$  Å,  $2\theta$  ( $\text{CuK}\alpha$ ) =  $26.32^\circ$ ]. Nine different specimens of djurleite from seven localities yielded virtually identical  $x$ -ray diffractometer patterns, three of which are shown in Fig. 1. No patterns transitional between djurleite and chalcocite were observed. The existence of a limited chalcocite solid solution between about  $\text{Cu}_{1.99}\text{S}$  and  $\text{Cu}_2\text{S}$  was demonstrated by Kullerud (1960) in the system Cu-S. The writer has obtained similar results and found all synthetic chalcocites to have nearly identical  $x$ -ray diffractometer patterns at room temperature.

All specimens of djurleite examined in polished section contained sufficient finely disseminated digenite, bornite or pyrite to render a chemical analysis meaningless in view of the small difference in composition between djurleite and chalcocite. However, H. J. Rose, Jr., of the U. S. Geological Survey, examined U. S. National Museum specimen No. 92349 by means of  $x$ -ray fluorescence analysis, using synthetic copper sulfides as standards. The analysis indicated a composition between chalcocite and digenite. About 0.8 per cent of Fe was present (probably as pyrite). No As or Sb was detected. Djurle's (1958) study places the composition of his phase,  $\text{Cu}_{1.96}\text{S}$  III, between  $\text{Cu}_{1.95}\text{S}$  and  $\text{Cu}_{1.97}\text{S}$ . His

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TABLE 1. X-RAY DIFFRACTION d-VALUES IN Å AND RELATIVE INTENSITIES OF DJURLEITE FROM BUTTE, MONTANA, AND SYNTHETIC  $\text{Cu}_{1.96}\text{S}$  III AFTER DJURLE (1) ( $\text{CuK}\alpha$  RAD.). DJURLE'S d-VALUES ARE CONVERTED FROM  $\sin^2 \theta$

Djurleite		$\text{Cu}_{1.96}\text{S}$ III		Djurleite		$\text{Cu}_{1.96}\text{S}$ III		Djurleite		$\text{Cu}_{1.96}\text{S}$ III	
I	d	I	d	I	d	I	d	I	d	I	d
1	4.28	w	4.291	2	2.89	w	2.885	$\frac{1}{2}$	2.289	w	2.292
1	3.89	w	3.893	2	2.87	w	2.867	$\frac{1}{2}$	2.142	w	2.144
2	3.752	m	3.751		2.82	w	2.833	$\frac{1}{2}$	2.107	w	2.109
2	3.586	w	3.593	1	2.78	w	2.816	1	2.069	w	2.071
5	3.386	m	3.381	$\frac{1}{2}$	2.78	w	2.788	$\frac{1}{2}$	2.047	w	2.048
1	3.35	—	—	1	2.69	w	2.691	9	1.964	m	1.965
3	3.282	w	3.278	1	2.654	w	2.655	9	1.957	m	1.958
3	3.192	w	3.191	$\frac{1}{2}$	2.595	w	2.601	10	1.871	s	1.871
2	3.100	w	3.102	1	2.557	w	2.561	—	—	w	1.832
3	3.04	w	3.038	$\frac{1}{2}$	2.514	w	2.519	2	1.693	m	1.691
3	3.01	w	3.014	1	2.477	w	2.477	1	1.683	w	1.681
—	—	w	2.965	$\frac{1}{2}$	2.41	w	2.417	—	—	w	1.514
—	—	w	2.940	9	2.387	s	2.391	—	—	m	1.274
—	—	w	2.892	—	—	w	2.318	—	—	w	1.121

$\text{Cu}_{1.95}\text{S}$  samples always contained traces of digenite and the  $\text{Cu}_{1.97}\text{S}$  samples, traces of chalcocite.

In polished section, djurleite is similar to chalcocite in color, hardness and anisotropism. A polished section of chalcocite and two of djurleite gave identical results when etched with solutions of  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{KCN}$ ,  $\text{FeCl}_3$ ,  $\text{KOH}$ , and  $\text{HgCl}_2$  in the concentrations described by Short (1940, p. 99). The results of etching were essentially those described by Short (p. 113) for chalcocite except that all these specimens tarnished a faint yellow brown with  $\text{HgCl}_2$ . The failure of these tests to distinguish between chalcocite and djurleite is not surprising in view of the small compositional difference and the probable similarity in structure. Djurleite behaves differently from chalcocite during polishing, a feature which was pointed out to the writer by J. W. Greig of Pennsylvania State University. During polishing, individual grains of djurleite show many different shades of blue and gray, suggesting that four or five phases are intermixed. However, continued polishing ultimately results in a uniform gray color.

The identity of djurleite and  $\text{Cu}_{1.96}\text{S}$  III was further confirmed by converting a sample of the mineral to another polymorph, Djurle's  $\text{Cu}_{1.96}\text{S}$  II, which has tetragonal symmetry and an x-ray pattern (Fig. 1) completely unlike that of chalcocite or any other phases in the system  $\text{Cu-S}$ . This was done by heating the sample in an evacuated sealed

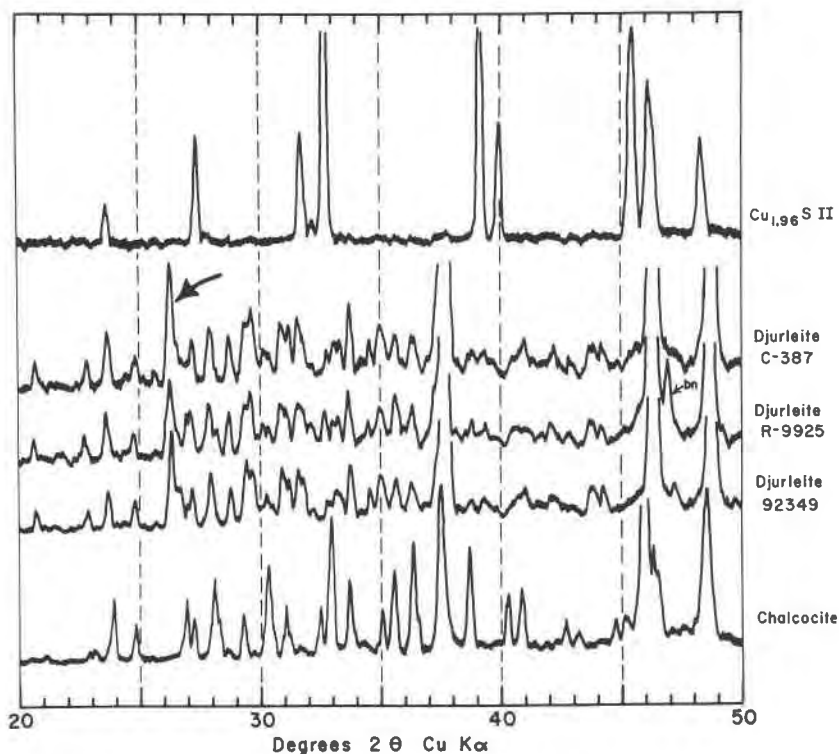


FIG. 1. X-ray powder diffractometer patterns of chalcocite, djurleite and synthetic  $\text{Cu}_{1.96}\text{S II}$ . The chalcocite is from Bristol, Connecticut. The djurleites are from the U. S. National Museum: No. 92349, Barrana de Cobre, Chihuahua, Mexico; No. R9925, Leonard Mine, Butte, Montana; No. C387, Tsumeb, Southwest Africa. The additional peak at  $47^\circ$  in R9925 corresponds to the strongest peak of bornite, which was observed in a polished section of this specimen. The heavy arrow at about  $26.3^\circ$  indicates the most diagnostic peak of djurleite.

silica tube at  $465^\circ\text{C}$ . for 15 hours, and quenching. By contrast, none of the higher-temperature chalcocite polymorphs can be quenched.

Djurleite should prove to be a common mineral. It was found in the following specimens from the U. S. National Museum: No. R7563, Salvador Mine, Milpillas, Chihuahua, Mexico; No. R9925, Leonard Mine, Butte, Montana; No. C387, Tsumeb, Southwest Africa; No. 112818, Bagacay, Samar Islands, Philippine Islands; No. 92349, Barrana de Cobre, Chihuahua, Mexico. In addition, the writer identified djurleite in specimens from Morococha, Peru, and from Butte, Montana, kindly loaned by Ulrich Petersen, Cerro de Pasco Corp., and H. W. Smedes of the U. S. Geological Survey.

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.

## REFERENCES

- DJURLE, S. (1958), An  $x$ -ray study on the system Cu-S. *Acta Chemica Scand.* **12**, 1415-1426.
- KULLERUD, G. (1960), The Cu-S system. *Carnegie Inst. Wash. Yearbook*, **59**, 110-111.
- MORIMOTO, N. Djurleite, a new copper sulfide mineral. *Mineral. Jour.* (in press).
- SHORT, M. N. (1940), Microscopic determination of the ore minerals. *U. S. Geol. Survey, Bull.* **914**.

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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