

faujasite to hydroxy-sodalite. At 100°C faujasite formed more rapidly than at 90°C, but the apparent zeolite content did not increase so much because type *P* zeolite formed together with faujasite at the higher temperature.

The samples treated with sodium hydroxide change into faujasite or type *P* zeolite after passing through an amorphous state, and faujasite finally changes into hydroxy-sodalite while type *P* zeolite is stable under normal

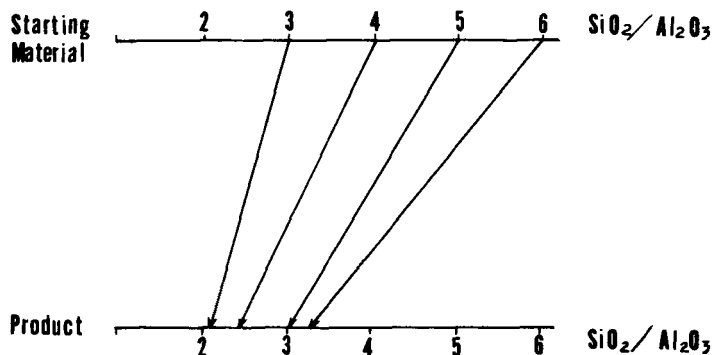
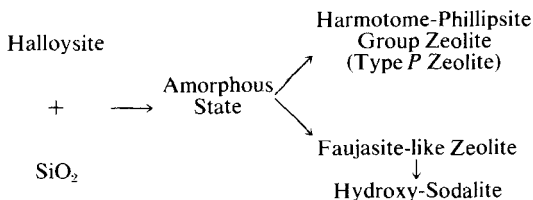


Fig. 3. Relations between the silica-alumina mole ratio of the starting materials and the products.

It is known that the silica-alumina mole ratio of faujasite-like zeolite ranges from 2.4 to 6.0, and the unit cell dimensions decrease with increasing silica-alumina mole ratio. The relations between the silica-alumina mole ratio of the products determined by precise measurement of unit cell dimensions and that of the starting material are shown in Fig. 3. As shown in this figure, faujasite-like zeolite at different silica-alumina mole ratios can be obtained from starting materials of differing silica-alumina ratios.

From these experiments, it appears that the structural change of halloysite mixed with water glass might have resulted from the sequence shown below:



pressure. The formation of either faujasite or type *P* zeolite from halloysite depends upon the treatment temperature, the amount of  $\text{Na}_2\text{O}$ , and the concentration of sodium hydroxide solution. For the formation of faujasite, the concentration of sodium hydroxide must be low when the sample is treated with a large amount of  $\text{Na}_2\text{O}$ , or the concentration of sodium hydroxide must be high when the sample is treated with a smaller amount of  $\text{Na}_2\text{O}$ .

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## Clay Alteration Associated With Mineralization in the Michigan Copper District

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### INTRODUCTION

Chlorite and vermiculite occur in close association with native copper ore in the Keweenaw County, Michigan, copper district. The main clay phases include (1) chlorite in "skull" replacements of conglomerate pebbles, (2) chlorite-montmorillonite in red clay fault gouge, and (3) mica and chlorite in red brown fault gouge.

### GEOLOGIC SETTING

The Keweenaw, Michigan, Copper District, (see location map, Fig. 1) is unique in North America in that native copper is the dominant ore mineral. Some native silver and copper sulfides and arsenides are present, but these are of minor importance.

Mineralization is found chiefly in a number of amygdala-

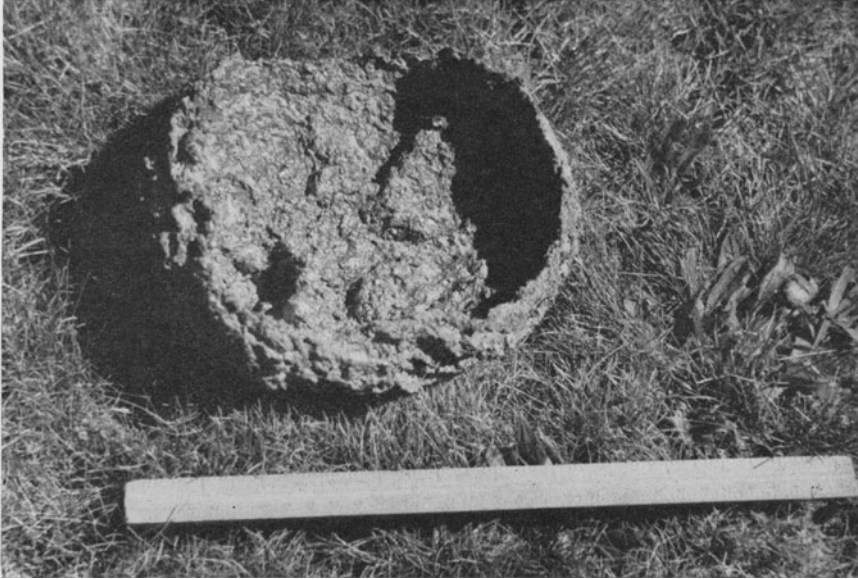


Fig. 2. A typical "copper skull", shown with 12 in. engineer's scale.

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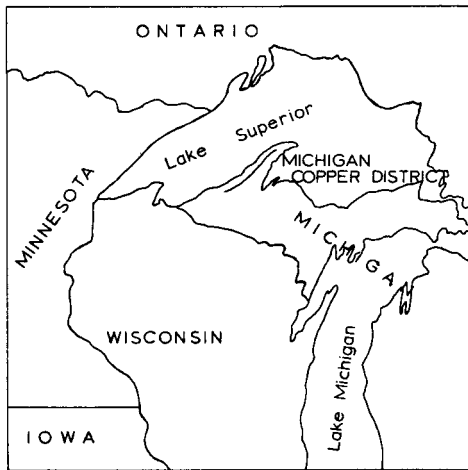


Fig. 1 Location map.

loidal basalts of the Portage Lake Lava Series (Late Precambrian) and in some interstratified conglomerates. In the early history of the district, dating back nearly one and a quarter centuries, some significant production was obtained from fissure veins. The reader is referred to Butler and Burbank (1929) for details of the geology of the district.

Native copper is closely associated with calcite, epidote, quartz, feldspars, chlorite, hematite, and zeolites—most commonly laumontite—and to a lesser extent pumpellyite and prehnite. The deposits are generally thought to represent low- to intermediate-temperature hydrothermal types, in the sense that they represent deposition from hot water solutions. However, there is no general agreement on the source of either the copper or the hot water solutions. Butler and Burbank (1929), Lindgren (1933), Broderick (1935), Broderick and Hohl (1935), Cornwall (1951), and Stoiber and Davidson (1959) have discussed hypotheses on origin of copper and of ore-forming fluids.

#### ROCK ALTERATION

Rock alteration has taken place during and after formation of the lava flows. The early stage represents reaction of basalt flows to the atmosphere and is evidenced by alteration of olivine to serpentine, of magnetite to hematite, and to a reddening of flow tops, ascribed by Butler and Burbank (1929) to iron oxidation by escaping gases.

The early ore-forming period was characterized by formation of feldspar, chlorite, and epidote. The intermediate period, during which copper was deposited, was characterized by chlorite, epidote, quartz, calcite, pumpellyite, and prehnite. The late ore-forming period was characterized by laumontite, saponite, and analcite.

Chlorite is the most extensive alteration product. Well-crystallized chlorite is commonly found as vesicle fillings as well as massive alteration products of basaltic lava flows. Late stage saponite is present also in small amounts as vesicle fillings and as replacements or as crusts on

other minerals. Kaolinite occurs in small amounts on laumontite or as crusts on red feldspars, and probably formed in the late ore-forming period.

In terms of volume, three occurrences of clays are important. These are:

1. Copper "skulls" in the Centennial No. 3 mine, Calumet Division, Calumet and Hecla, Inc.
2. The hanging wall "slip" of the Kingston mine, Calumet Division, Calumet and Hecla, Inc.
3. Fault gouge in the Allouez Gap fault which transects the ore zone in the Kingston mine.

X-ray diffraction analyses of the three occurrences were kindly furnished by S. W. Bailey, University of Wisconsin. His results are summarized below.

#### COPPER SKULLS

Copper "skulls" consist of spherical or subspherical sheaths of native copper surrounding quartz, potash feldspar and bluish-gray clay material. A photograph of a skull, with matrix removed, is shown in Fig. 2. These features are found in conglomerates, and resemble conglomerate pebbles or cobbles in size and shape. Skulls are generally thought to have resulted from hydrothermal alteration of conglomerate pebbles or cobbles with very nearly simultaneous deposition of native copper around the pebble. In the matrix of the skull examined in this investigation, the pebble probably was a coarse-grained or porphyritic rock of felsitic composition because the matrix contains unaltered feldspar fragments up to 2 mm across and quartz fragments up to 1 mm across.

The clay fraction consists largely of hematite and a 14 Å clay which was identified as the common IIb structural type of chlorite.

#### HANGING WALL "SLIP"

The hanging wall slip is generally thought to represent a fault gouge in a fault that is very nearly concordant with regional dip and strike in the area. The material from the slip consists of red clay material, with some copper and small patches of green clay. Red and green clay materials differ only in the amount of hematite present. Potash feldspar is present in both red and green clays.

The green clay consists of the ordinary IIb chlorite, but with an (001) intensity stronger than it should be for chlorite. Red clay material solvated with glycerol shows a spread of spacings from 14 Å to 17 Å. Film patterns of red clay material heated to 510°C and 60°C show that a few layers shrink to 10 Å and 12 Å.

#### ALLOUEZ GAP FAULT GOUGE

The Allouez Gap fault gouge consists of red clay material with white to green clay pockets. The red and white to green materials differ largely in that hematite is abundant in the red material.

The bulk clay consists of a mixture of 10 Å mica and 14 Å clay. The white clay is predominantly a dioctahedral mica, probably of 1Md type. The darker green material consists largely of the 14 Å clay with a trace of mica. The green clay was subjected to glycerol solvation, and was heated to 350°C, 510°C, and 600°C. Bailey concludes that the green clay is a IIb chlorite similar to that in the hanging wall slip, and in which some interlayers are either incomplete or absent.

### CONCLUSIONS

Much of the rock alteration has involved felsite pebble conglomerates. The transformation of this rock type to highly magnesian chlorite suggests the addition of magnesium and the loss of  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$ . Analysis of the hanging wall slip clay indicates that  $\text{K}_2\text{O}$  has been added to and  $\text{CaO}$  has been subtracted from an originally basaltic rock.

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Special thanks are due S. W. Bailey for his identification of clay phases.

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