

CLAY-MINERAL ALTERATION IN THE UPPER MISSISSIPPI VALLEY ZINC-LEAD DISTRICT*

by

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ABSTRACT

Clay-mineral alteration in a carbonaceous shale bed seems to be related to hydrothermal zinc-lead depositions in the Upper Mississippi Valley district in southwestern Wisconsin, northwestern Illinois, and northeastern Iowa. A 3-in. thick, dark-brown, carbonaceous shale at the base of the Quimbys Mill Member of the Platteville Formation can be traced accurately in the Thompson-Temperly mine near New Diggings, Wis., through the ore bodies into alteration aureoles around the ore bodies and out into areas barren of mineralization or apparent alteration.

X-ray diffraction studies indicate a progressive alteration of the clay-mineral and, in part, nonclay-mineral components of the shale from unaltered rock into ore-zone rock. Illite of md polymorph in unaltered rock is altered to 1 m and 2 m illite in the altered rock, and 2 m illite polymorph increases markedly within the ore bodies. Accompanying this alteration, calcite decreases and dolomite and microcline increase in amount toward the ore zone; quartz remains unchanged. The conclusion that the alteration was effected by low-temperature and low-pressure environment over a geologically long period of ore deposition is supported by fluid-inclusion studies of the associated ore minerals, which indicate a maximum temperature of 120°C to 130°C, and the known stability of synthesized 1 m and 2 m mica polymorphs at 200°C and 15,000 psi water pressure.

INTRODUCTION

THE possibility of clay-mineral alteration related to the deposition of zinc-lead ore deposits in the Upper Mississippi Valley district was investigated by the authors in the field and laboratory during 1960-63. This is the first published clay-mineral alteration study made in a Mississippi Valley-type ore district, even though this kind of investigation has been fruitful in such western mining districts as Butte, Mont. (Sales and Meyer, 1948); Tintic, Utah (Lovering, 1949); Arizona porphyry copper deposits (Anderson, 1950; Kerr, 1951; and Schwartz, 1953); and Central City, Colo. (Tooker, 1963). A continuation of this study may produce

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data that would be of value in developing guides for finding ore either in the mine or by exploratory drilling.

The Quimby's Mill Member of the Platteville Formation, a thin limestone and shale unit of distinctive lithology, which can be traced for considerable distances, was studied in the Thompson-Temperly mine, where it passes from one ore body and its surrounding alteration aureole into a barren rock zone and then into a second ore body and its alteration aureole.

The Thompson-Temperly mine is at the southwest edge of New Diggings, Wis., a village about nine miles north-northeast of Galena, Ill. It is in the highly productive south-central part of the Upper Mississippi Valley zinc-lead district of southwest Wisconsin, northwest Illinois, and northeast Iowa (Fig. 1). The mine is opened by a truck incline that slopes toward the northeast into the small Temperly ore body. From this body the truck haulage crosscut extends for about 1000 ft into the larger Thompson ore body.

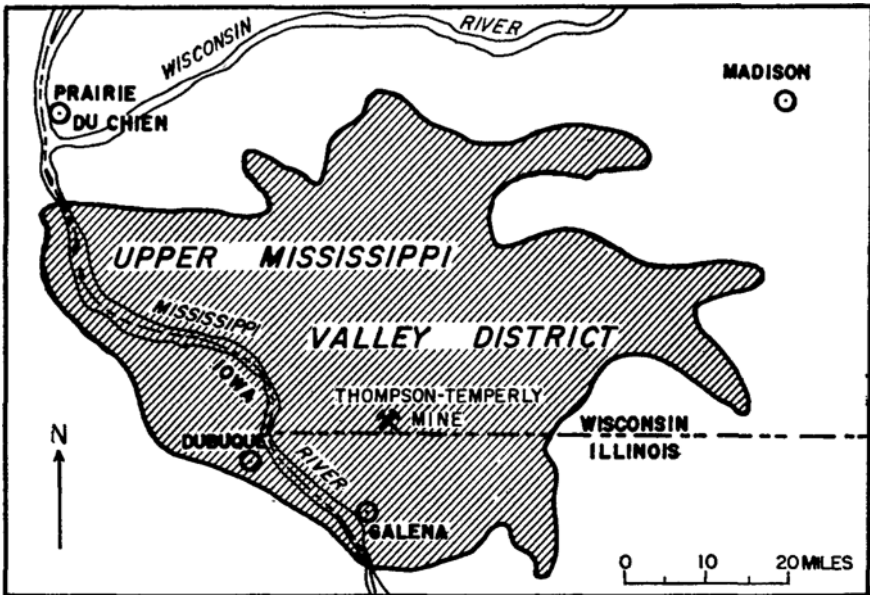


FIGURE 1.—Index map showing location of Thompson-Temperly mine.

Permission by John Lackey, Manager, Wisconsin Division of American Zinc Mining, Smelting and Refining Company, to enter the mine and collect samples is gratefully acknowledged. The following men, all of the U.S. Geological Survey, assisted either in the field or in the laboratory: W. E. Hall, Irving Friedman, J. W. Whitlow, R. M. Bromery, and R. G. Klein.

GEOLOGY

The zinc-lead deposits in the Thompson-Temperly mine, like others in the Upper Mississippi Valley district, occur chiefly in the Galena Dolomite, the Decorah Formation, and in the Quimbys Mill Member of the uppermost part of the Platteville Formation (Fig. 2), all of which are of Middle Ordo-

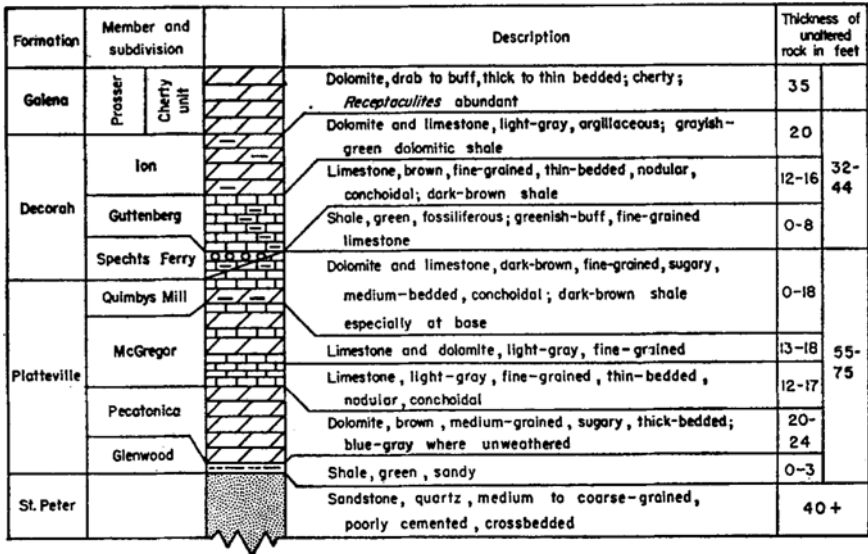


FIGURE 2.—Stratigraphic column of Platteville and Decorah Formations and lower part of Galena Dolomite in Upper Mississippi Valley zinc-lead district.

vician age. The Temperly ore body is a small irregular linear mass, and the Thompson ore body is an elliptical doughnut-shaped mass (Fig. 3). The ore is in the form of veins, replacements, and impregnations along small open reverse and bedding-plane faults related to gentle folds. The main primary minerals in the ore bodies are quartz (mostly cherty jasperoid), dolomite, pyrite, marcasite, sphalerite, galena, chalcopyrite, barite, and calcite.

The ore solutions have produced alteration aureoles (Fig. 3) in the host-rock limestones and, to a lesser extent, in the dolomites in and around the vicinity of the deposits. Alteration aureoles extend laterally as much as 200 ft out from the ore bodies. Alteration is more intense within ore bodies and visibly decreases in intensity outward from these bodies. The alteration aureoles result from five main processes (Heyl and others, 1959, pp. 101-

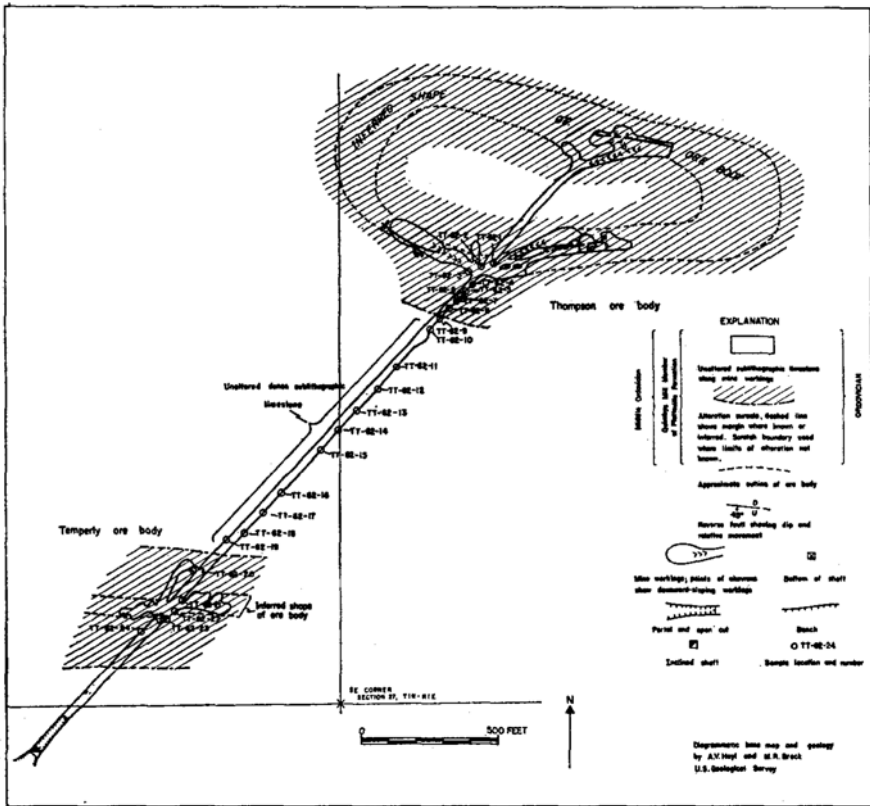


FIGURE 3.—Sketch of the Thompson-Temperly mine showing approximate location of samples.

108): solution, dolomitization, and silicification of the carbonate rocks, development of sanded dolomites, and clay-mineral alteration. Solution of the carbonate rocks has considerably thinned the limestones of the Quimbys Mill Member as well as other carbonate beds above and below it. The limestone part of the carbonaceous shale bed at the base of the Quimbys Mill has been largely replaced by dolomite, thus preventing much thinning. Fossils and some of the shale beds have been silicified. Within the ore bodies the previously dolomitized limestones have been sanded, forming a friable or noncoherent mass of dolomite crystals in which the cementing bond between the crystals has been weakened or removed by intergranular solution. Wavy beds of brown residue shales separate the sanded dolomite layers. The relative amount of shale to carbonate rocks visibly increases within the aureoles, and shale becomes the major component within the ore bodies.

The Quimby's Mill Member (Fig. 2), which was well suited for study because it is a thin unit of distinctive and unusually uniform lithology throughout the district, consists of dark-brown limestone with thin brown carbonaceous shale partings and a carbonaceous shale bed at the base. The limestone beds are fine grained, dense, sublithographic, and have a conchoidal fracture. The basal dark-brown shale unit is a very persistent, uniform marker bed approximately 3 in. thick. The shale unit was selected for the detailed sampling in the Thompson-Temperly mine because it can be traced accurately from areas barren of mineralization through alteration aureoles around the ore, and through the ore bodies.

ALTERATION STUDIES

Scattered altered and unaltered samples of both the limestone and basal shale of the Quimby's Mill Member were collected in 1960. The basal shale bed was found to be better than the limestone for clay-alteration studies, because clay is very sparse in the limestone, and because methods of acid treatment required to separate clay from the limestone may alter the clay. Accordingly, the basal shale bed was sampled in detail in 1962 (Fig. 3). Samples were taken as follows: TT-1 to TT-3 at intervals of about 30 ft within the Thompson ore body; TT-4 to TT-8 at intervals of about 30 ft in the alteration aureole on the southwest side of the Thompson ore body; TT-9 to TT-19 at intervals of 30 to 200 ft throughout the barren zone between the two ore bodies; TT-20 in the alteration aureole on the northeast side of the Temperly ore body; TT-21 and TT-22 within the Temperly ore body; and samples TT-23 and TT-24 in the alteration aureole on the southwest side of the Temperly ore body.

Untreated whole samples were studied by X-ray diffraction, using $\text{CuK}\alpha$ radiation to determine the whole-mineral content (varieties and relative amounts); in addition an untreated clay fraction ($< 2\mu$) separate from these samples was analyzed. The whole-mineral data are summarized by the representative traces shown in Fig. 4, which were obtained from samples near the Thompson ore body, and show representative mineralogical changes in carbonaceous shale from unaltered to altered conditions. Excessive carbonate was largely removed by adapting the method of Ostrom (1961, p.128).

The samples were ground to pass through a 100-mesh sieve, placed in 0.3 M acetic acid, and stirred periodically until reaction was nearly completed. The acid insoluble residue was carefully washed free of acid, mounted on a tile, and placed on the X-ray diffractometer. Care was taken not to remove all the calcite because the presence of undissolved calcite helps to prevent alteration of the clay by acid. Three clay-mineral analyses, prepared in this manner, that are representative of the ore zone, alteration aureole, and the barren zone, are presented in Fig. 5. The arrow symbol (\downarrow)

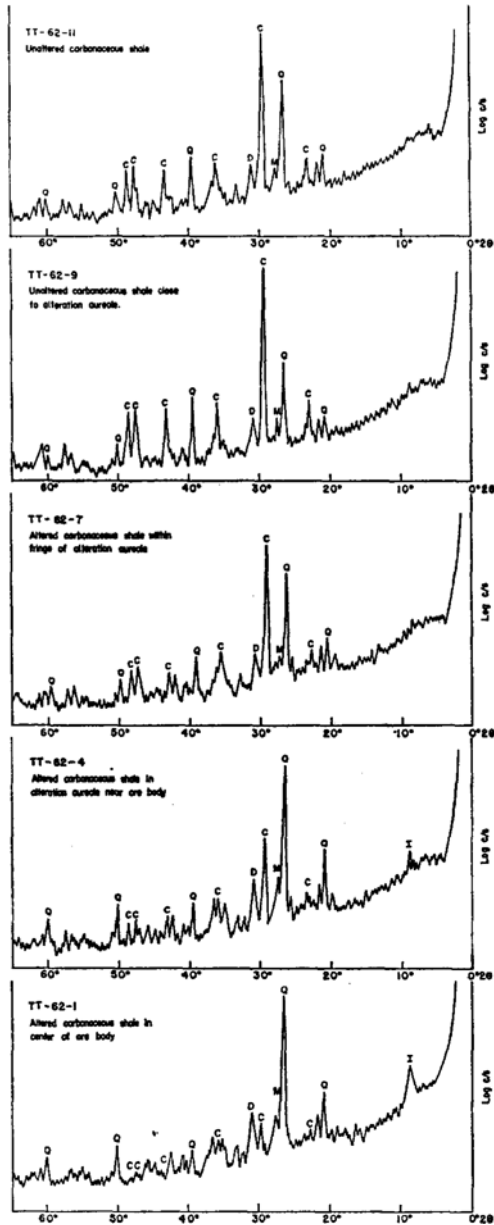


FIGURE 4.—X-ray diffraction traces (CuK α radiation) of five untreated carbonaceous shale samples of the clay fraction from the Thompson-Temperly mine. C, calcite; D, dolomite; Q, quartz; I, illite, M, K-feldspar (microcline ?).

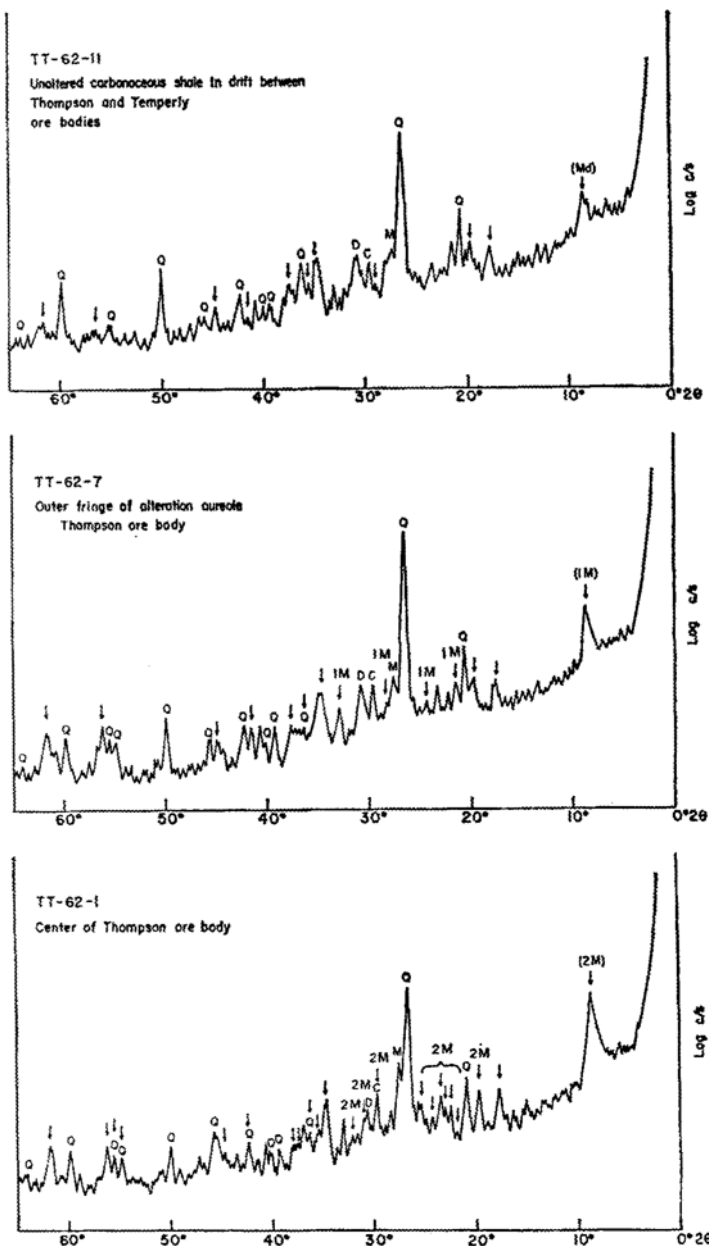


FIGURE 5.—X-ray diffraction traces (CuK α radiation) of the clay fraction from three acid-treated carbonaceous shale samples, Thompson-Temperly mine. C, calcite; D, dolomite; Q, quartz; ↓, illite; M, K-feldspar (microcline?).

for illite in each diagram is specifically for the dominant mica polymorph present. The mica polymorphs were distinguished by utilizing the criteria described by Yoder and Eugster (1955, pp.243 and 247), and summarized by Brown (1961, p.237).

X-ray analyses of untreated samples of unaltered basal carbonaceous shale of the Quimbys Mill Member showed quartz, calcite, a trace of dolomite, potassium feldspar, probably microcline, and a very small amount of unidentifiable clay-mineral (Fig. 4, samples TT-9 and TT-11). The acid insoluble residue of sample TT-11 contains considerable quartz, very little potassium feldspar, and sparse illite.

Untreated samples of shale within the alteration aureole contain quartz, calcite, an appreciable quantity of dolomite, traces of microcline and of a nonexpansible 10Å mineral, illite. Both dolomite and illite increase in quantity from sample TT-7, on the outer fringe of the aureole, to sample TT-4, on the inner side of the aureole adjacent to the ore body (Fig. 4). Furthermore, calcite decreases in amount from the outer fringe of the aureole toward the ore body. Thus, within the alteration aureole, the wall rock becomes more dolomitized, and the clay-mineral alteration becomes more intense near the ore body and reaches a maximum intensity within the ore body. Acid-insoluble residue of the alteration aureole sample shows that microcline is present in small quantities (Fig. 5, sample TT-7) and quartz remains unchanged.

An untreated sample of carbonaceous shale from the ore body contains quartz, illite, and appreciable quantities of dolomite, microcline, and calcite. Dolomitization and clay-mineral alteration in the ore body are intense enough that dolomite is more abundant than calcite, and an excellent 10Å peak for illite is produced (Fig. 4, sample TT-1).

Illite, a clay-size dioctahedral mica, is present in all samples, but it occurs in different polymorphs and quantities, and it is more accurately identified in the acid-treated samples (Fig. 5). In the barren carbonaceous shale (TT-11), the illite occurs in very small quantities as a $Md > 1 M$ mica (Figs. 4 and 5). Illite in the alteration halo occurs in moderate amounts as a $1 M$ mica, and in the ore body there is a large quantity of $2 M > 1 M$ or $2 M$ mica. The structural ordering of the illite has increased markedly. Potassium has probably been added and water content decreased in the mineral structure to form the better grade polymorph and the larger quantity of illite within the ore bodies. Furthermore, the potassium was not obtained from microcline, because it is more abundant in the ore body than in the barren rock.

Laboratory studies of geologic thermometry and mineral syntheses may give clues to the environment that produced the clay-mineral alterations. According to studies by Bailey and Cameron (1951, p.635) of sphalerite fluid-inclusion temperatures in the main ore deposits of the Upper Mississippi Valley zinc-lead district, the temperature of ore deposition reached a maximum of about 120°C to 130°C after the temperatures are corrected

for estimated pressure of about 1000 ft (about 1000 bars). Yoder and Eugster (1955, pp.245–246) have shown that by increasing either the temperature or the duration of the experimental run, the synthesis of mica results in a completely ordered 1 M mica structure that can be superseded by the 2 M structure at higher temperatures. Their data show that on long runs (5 to 7 months) the 1 M–2 M transition occurs between 200°C and 350°C at 15,000 psi water pressure. We suggest that under geologic conditions of time, the 2 M polymorph may occur at lower temperatures and pressures in the natural environment. The period of ore deposition which caused the clay alteration in the Upper Mississippi Valley was probably long, perhaps millions of years, thus providing sufficient time for the illite polymorphs to change from md < 1 M to 2 M and become stable at relatively low temperatures.

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