A HEATING MICRO-COIL FOR THE STUDY OF MINERAL FRAGMENTS AND HEAT-ETCHING OF POLISHED SECTIONS

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ABSTRACT

A small heating coil is described that can be used to heat selected minerals grains in a microscopic field of view to partially controlled temperatures as high as 400° C. Preliminary tests have been made on mineral fragments and minerals in polished section. Samples can be watched as they are heated. A wide variety of effects such as color changes, release of sublimates, dehydration, melting, and the cracking and explosion of grains have been observed in testing mineral fragments. Many of the more heat sensitive ore minerals studied in polished section showed unusual reactions to the heat of the coil. The copper sulfides and some silver minerals proved to be most reactive. Heat-etching of chalcocite produced the distinctive patterns previously described by Stephens (1935).

INTRODUCTION

In the study of mineral fragments or polished ore sections, valuable data might often be gained by the application of known heats to mineral grains. For this reason, the writers have designed and constructed a small heating coil which can be brought into a microscopic field of view and there be used to heat selected grains to partially controlled temperatures as high as 400° C. A mineral may be continuously observed as its temperature is raised, and any reaction such as a loss or change of color, dehydration, release of a sublimate, or melting may be seen and recorded.

The coil is very effective in producing heat-etch patterns in chalcocite. A variety of effects, some diagnostic, may be obtained with other heat-sensitive minerals in polished section.

The apparatus has neither the range nor the accuracy of differential thermal analytical equipment and is certainly not proposed as any substitute for that method. It merely provides some types of information that cannot be won from a differential thermal curve.

This paper is presented to describe the instrument and to discuss the results of its preliminary trials with some minerals.

EQUIPMENT

The micro-coil control circuit was assembled into a single unit designed to stand beside a microscope as shown in Fig. 1. The coil, mounted in a phone plug, is inserted into the side of the control box and extends over the microscope stage. The coil was wound from a short length of chromel A 30 gauge wire. A convenient method of winding the filament is

Fɪɢ. 1. The micro-coil in position for heat-etching of a polished section.

to wrap the chromel wire around a piece of bare 20 gauge wire. About $2\frac{1}{2}$ turns are sufficient to produce a satisfactory coil. The free ends of the chromel wire should be about 2 cm. long after the coil has been wound. A junction between these free ends and 20 gauge copper leads is formed by clamping the chromel wire into the ends of the copper leads. This junction must be smooth enough to permit it to be drawn into the tubular openings in the porcelain insulator and tight enough to prevent open circuits. It is important to have at least 1.5 cm. of chromel wire between the coil and the copper wire to prevent too rapid heat conduction along the leads. The lower chromel wire portion of the leads should be bent up sharply at the coil to prevent irregular heating below the coil.

The probe assembly consists of the micro-coil with its associated leads and insulator enclosed in an aluminum tube and attached to a Mallory, Type 75, Standard Phone Plug as shown in Fig. 2. This type of assembly has proved to be convenient to use and permits rapid replacement of the entire probe in case of burn out. Filament life varies with temperatures at which the coil is used and with the types of material studied. Sulfur fumes liberated by some minerals cause corrosion of the chromel wire and reduce the coil life. When used under varying conditions, a single coil can be expected to last about 20 hours.

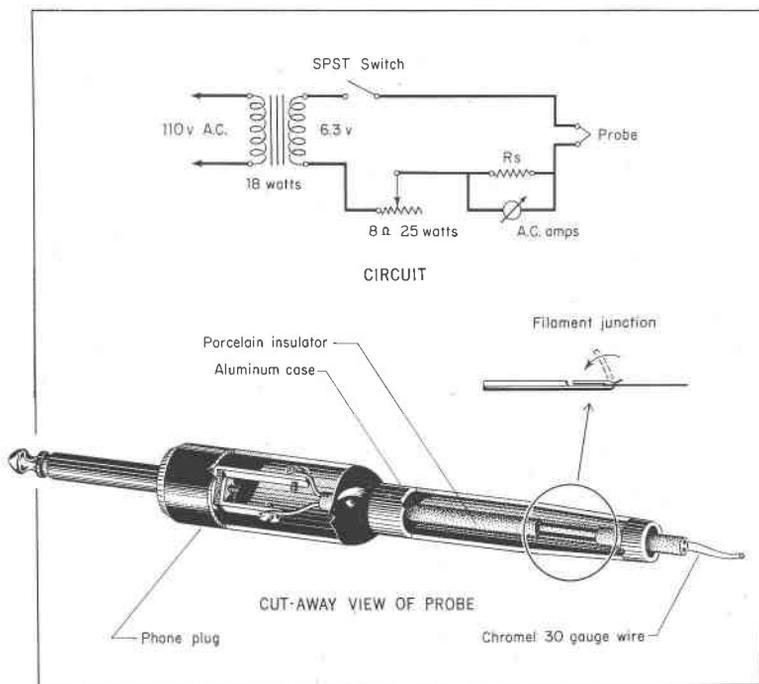A 0-1 ampere A.C. ammeter with a shunt resistor, Ri, was used to

Fig. 2. Cut-away view of the heating probe and circuit diagram for the micro-coil apparatus.

measure the current flowing through the coil. The shunt resistor was made from the same resistance wire as the micro-coil and attached directly to the terminals in back of the meter. Ranges of current measurement from 0-1 to 0-4 amperes can be easily obtained by varying R_s. For most purposes a standard 0-3 ampere A.C. meter should prove satisfactory. If such a meter is used the resistor, R_s would not be necessary.

One difficulty encountered in operation of the equipment results from the heat liberated by the control circuitry. The rheostat and shunt resistor become quite hot when large currents are used. Rubber insulation in contact with these elements melts producing short circuits. This danger can be reduced by using stiff wire that will stay in place and attaching it so that it will not tend to come in contact with circuit elements that may become hot. As an added precaution, wire that is covered with heat resistant insulation can be used.

In operation, the coil must be used with an objective of low magnification that focuses at a safe distance from the hot wire. A 32 mm. lens with a working distance of 27 mm. was used throughout the present work without any evident damage.

CALIBRATION

The micro-coil was calibrated by repeated measurements of the amounts of current required to melt fragments of "Tempil Pellets." These are commercially available temperature standards whose melting points are known within 1% limits.

The Tempil fragments were tested on glass slides placed on the stage of a mineralographic microscope which could be racked up toward the fixed height of the heating coil. A constant distance between the upper surface of the slide and the lower surface of the coil was maintained in all operations by use of a hard manila spacer.

The current required to melt any given Tempil material varied with the size of the fragment tested. This variation is illustrated in Fig. 3 (right). Higher currents are required for smaller grains because their upper surfaces lie at greater distances from the coil. Greater variance in current readings was also detected with smaller grains probably due to the facts that they respond more rapidly to small temperature fluctuations such as those caused by air currents and that any variation due to inhomogeneities of the Tempil Pellets is most apt to appear when these are finely subdivided. Fragments over 0.5 mm. gave consistent readings provided they were not so large as to touch the inside surface of the coil (inner diameter = 0.76 mm.).

The calibration curve for the heating coil is shown in Fig. 3 (left). Due to the changing slope of this curve, the temperature range indicated by
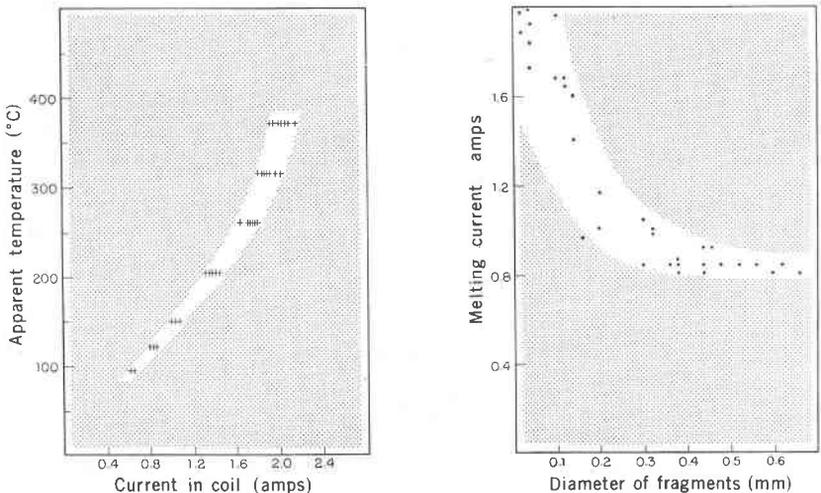

FIG. 3. (Left) Calibration curve of the micro-coil.
(Right) Effect of fragment size on the current required to melt a given standard material.

any setting on the instrument becomes larger as the temperature goes up. With elaborate equipment these temperature readings would undoubtedly be refined.

TESTING MINERAL FRAGMENTS

Table 1 presents a summary of the thermal tests made on different minerals by use of the heating coil. Published reaction temperatures are also listed for comparison, and, unless otherwise indicated, these data were taken from a recent review of geologic thermometry by Ingerson (1956).

Known mineral fragments were tested by selecting grains 0.5–0.6 mm. in diameter, bringing them to focus in the center of the field, and very gradually increasing the current flowing through the heating coil. Any change in the appearance of a fragment was noted and the corresponding ammeter reading was recorded. By simply watching a fragment heated in this manner different types of reactions can be distinguished and an approximate temperature range assigned by reference to the calibration curve (Fig. 3 left).

Minerals that melted within the range of the instrument usually showed marked color changes, development of droplets on the grain surfaces, or sudden conversions of a fragment to globular form. In some cases, melting was accompanied by the formation of condensates on that part of the glass slide surrounding the grain tested. Realgar, for example turned a deeper red and finally black on melting and a bright yellow condensate formed around the melted grain (Figure 5A).

Chalcanthite, gypsum, melanterite and goethite were analyzed as representative hydrated minerals. In the case of hydrates that decompose in several stages, the first and last dehydrations may usually be detected but the intervening reactions are masked by the opacity developed in the first stage. The final dehydrations of melanterite and chalcanthite were evidenced by contraction of the grains and changes in color.

The decomposition of goethite ($FeO \cdot OH \rightarrow \alpha Fe_2O_3$) proved sluggish and coil settings well above the equilibrium temperature were required before any visible signs of reaction appeared. A differential thermal analysis of the same material (heating rate, 12.5° C./min.) showed the first trace of an endothermic decomposition at 250° C. and the peak occurred at 320° C. When the heating coil was set at temperatures over 300° C. the goethite changed from yellow to red very rapidly, but there was no observable change in the mineral when the coil was left for five minutes at the equilibrium decomposition temperature. The heating rate of the micro-coil is manually controlled and so the instrument should prove of value in estimating reaction rates.

TABLE 1. THERMAL TESTS OF MINERAL FRAGMENTS

Mineral	Known Reaction		Observed Reactions		
	Reaction	Reported Temp. (° C.)	Observation	Current (Amps)	Appr. Temp. (° C.)
1) Sulfur, S	Melting	119°	Fragment melts, yellow condensate on glass slide	0.84	115°–130°
2) Realgar, AsS	Melting	320°	Fragment becomes a darker red, yellow condensate on slide	0.45	255°–320°
			Fragment turns black, melts	0.50	305°–400°
3) Orpiment, As$_2$S$_3$	Melting	310°	Fragment yellow→red, melts yellow condensate on slide	0.47	273°–350°
4) Bismuth, Bi	Melting	271°	Melting, silvery globules form white condensate on slide	0.45	255°–320°
5) Lead, Pb	Melting	327°	Fragment becomes iridescent	0.47	273°–350°
			Starts to melt, silvery globules form	0.50	305°–400°
			Entire fragment melts, white condensate on slide	0.54	345°+
6) Amber*	Softens	150°	Surface becomes soft, tacky	0.30	162°–187°
	Melting	250°–300°	Fragment→liquid globules	0.38	208°–245°
7) Copal	Melting	120°–166°	Rapid melting→globules	0.19	105°–120°
8) Niter, KNO$_3$	Melting	333°	Fuses rapidly to transparent droplets	0.51	315°–425°
9) Soda Niter, NaNO$_3$	Melting	310°	First signs of melting, some fragments move, edges melt	0.45	255°–310°
			Rapid melting, →globules	0.57	273°–350°
10) Chalcanthite, CuSO$_4$·5H$_2$O	a) Dehydration b) Dehydration c) Dehydration	95° 114° 250°	Lowest coil temp. blue transparent grains slowly→white opaque cannot distinguish 1st & 2nd dehydration	0.17	95°–110°
			Fragments contract, surface appears sintered, tan color	0.43	240°–295°
11) Gypsum, CaSO$_4$·2H$_2$O	a) Dehydration b) Dehydration	128° 163°	Transparent fragment→milky white, opaque sluggish at this setting (30 seconds)	0.23	122°–140°
			Same change very rapid, second dehydration not detected	0.25	133°–155°
12) Goethite, FeO·OH	Dehydration	135°	Yellow fragments→red (sluggish)	0.32	170°–200°
13) Melanterite FeSO$_4$·7H$_2$O	a) Dehydration b) Dehydration c) Dehydration	57° 100° 300°	Lowest coil setting, fragments →opaque, white; coil left at this setting for five minutes —then turned up—No sign of 2nd dehydration	0.17	95°–110°

* Data from Dana, E. S., Textbook of Mineralogy (1932).

TABLE 1 (*Continued*)

Mineral	Known Reaction		Observed Reactions		
	Reaction	Reported Temp. (° C.)	Observation	Current (Amps)	Appr. Temp. (° C.)
			Rapid change, white→dark brown	0.49	295°–385°
14) Malachite, $CuCO_3 \cdot Cu(OH)_2$	Decomposes	200°	Tan spots appear on green translucent fragments, sluggish	0.40	220°–262°
			Fragments move, turn brown	0.52	325°+
15) Azurite $2CuCo_3 \cdot Cu(OH)_2$	Decomposes	200°	Grains→deeper blue to blackish blue	0.43	240°–295°
			Grains fuse, sinter, turn black	0.60	415°+
16) Smithsonite, $ZnCO_3$	Decomposes	296°	Grains→yellow, crack	0.57	380°+
17) Siderite, $FeCO_3$	Decomposes	282°	Gradual color change, white →tan	0.48	285°–365°
			Grains move, turn reddish brown	0.51	315°–425°
18) Magnesite, $MgCO_3$	Decomposes	373°	Grains move, turn lt. yellow, sintered appearance	0.53	335°+
19) Rhodochrosite, $MnCO_3$	Decomposes	400°	Gradual cracking of surface, grains become opaque: sluggish	0.50	305°–400°
			Grains→brown to black iridescent	0.55	360°+

Malachite, azurite, smithsonite, siderite, magnesite, and rhodochrosite were studied as examples of minerals losing CO_2 on decomposition. As a group, these reactions proved sluggish and were usually visible only at temperatures above published equilibrium values. The decompositions were evidenced by cracking, movement, and in some cases explosion of grains that disappeared from the field of view. Some of the decompositions were accompanied by a color change as indicated in Table 1.

Several specimens of fluorite were heated in a darkened room with the micro-coil to determine whether thermoluminescence could be observed with this equipment. The instrument proved unsatisfactory for this purpose, because the thermoluminescent glow, if any, is obscured by the red glow of the hot coil. Loss of radiation colors can, however, be detected and approximate temperatures assigned to the color loss. A specimen of violet fluorspar, for example, showed no change in color as its temperature was gradually raised to 400° C., but at coil settings above this the grains became less transparent in the center and fading began at the edges.

In Fig. 4, a graphical correlation is made between published and experimental thermal data. For the majority of reactions, the measured temperatures agreed with published data within the experimental errors. Exceptions are the more sluggish reactions such as the decomposition of goethite and some of the carbonate minerals as previously discussed.

HEAT-ETCHING OF POLISHED SECTIONS

The photochemical properties of metallic minerals in polished section have been investigated by Guild (1917), Whitehead (1917), McKinstry (1927), Petrulian (1931), Schneiderhohn and Rahmdohr (1931), and Stephens (1931, 1935). In the majority of these studies, effects of intense light and heat were tested by bringing the beam of a carbon arc to focus on a mineral surface at high magnification. Among the many minerals studied by these researchers, the silver haloids and sulfo-salts, silver sulfide, some gold-silver tellurides, and some of the copper sulfides proved to be most reactive.

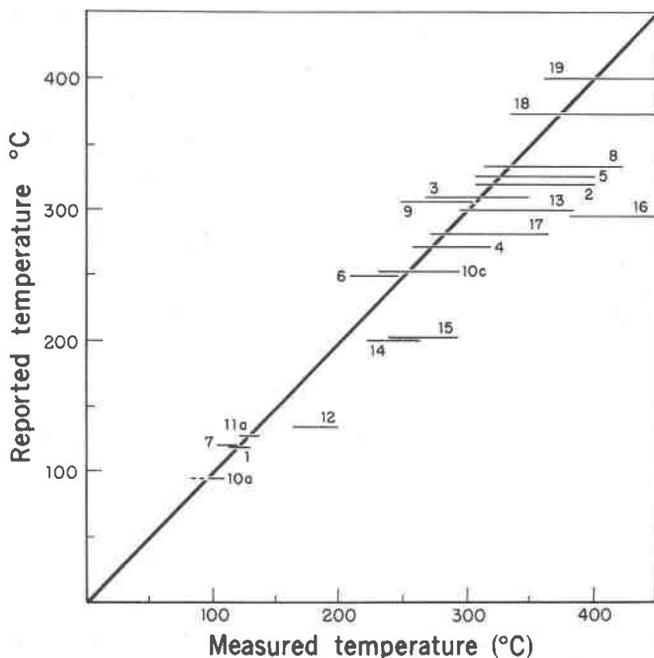The most recent and extensive studies in this field are those of Stephens

FIG. 4. Correlation of known reaction temperatures with temperatures determined with the heating coil. Numbers on the diagram refer to reactions listed in Table 1.
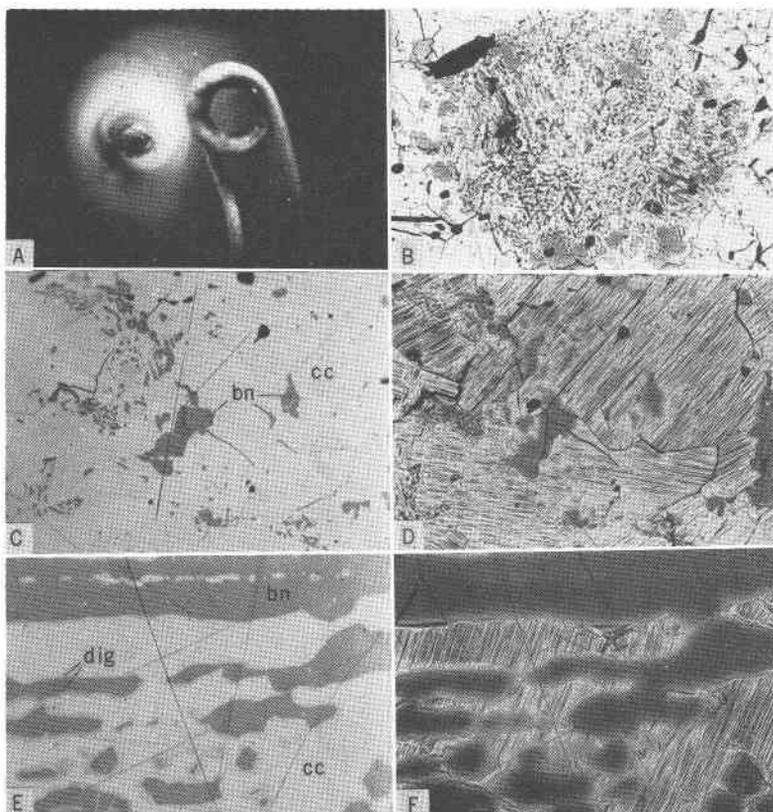
FIG. 5(A). The micro-coil moved aside for view of realgar fragment that has just been heated to 305°–400° C. The relict of realgar is red and is surrounded by a yellow condensate on the glass slide. (Magnification 8.9×.)

(B). Polished surface of chalcocite (white) and bornite (grey) heat etched for two minutes at 420° C.+. Etched chalcocite originally under the micro-coil is seen in the center of the photograph. (Magnification 20.8×.)

(C). Field of chalcocite with scattered remnants of unreplaced bornite before heat-etching. (Magnification 64.2×.)

(D). Same field as 5C after heat-etching at 135°–155° C. The bornite has become a light pinkish-violet and a distinct parallel etch cleavage has appeared in the chalcocite. Nitric acid etching produced a weaker two-directional cleavage in this same chalcocite. (Magnification 62.4×.)

(E). Field of chalcocite replacing bornite before heat-etching. A barely visible isotropic blue mineral (presumably digenite) rims the bornite remnants. (Magnification 64.2×.)

(F). Same field as 5D after prolonged heating at 250°–305° C. Bornite has become a deep purple and has begun to replace the chalcocite. The chalcocite remains grey but develops a deep etch pattern parallel over the field. The digenite fades and migrates as a diffuse band at the moving contacts of bornite and chalcocite. (Magnification 64.2×.)

who investigated the effects of light on polished surfaces of silver minerals (1931) and the use of a carbon arc in identification of different genetic types of chalcocite (1935). In etching the silver minerals, Stephens used Wratten filters to control the wave length of light impinging on the mineral surface and a cupric sulfate bath to eliminate the majority of heat from the arc light. Realizing that the reactions of the copper sulfides are due primarily to heat, Stephens used the full spectrum of the carbon arc in etching sections of chalcocite. He viewed the specimens being tested through a camera attachment to avoid the discomfort of an unusually bright image. When heated, chalcocite developed a variety of etch figures some of which are diagnostic of the origin of the mineral. Stephens concluded that these figures can be used to distinguish (1) hypogene from supergene chalcocite, (2) separate generations of chalcocite, and (3) chalcocite after bornite as opposed to chalcocite without any relation to a paragenetic predecessor.

As a strong and controllable source of heat, the micro-coil seemed a practical device for producing some of the reactions described by these earlier workers. Any effects obtained could be ascribed primarily to heat since only a normal tungsten light source was used to observe the specimens during tests. No special equipment is required to view the polished sections as they are heated. At the maximum setting of the coil 420° C.+), the image of the specimen is still clear and there is no discomfort to the eyes.

A drawback to use of the coil is that its effects cannot be removed without re-surfacing the polished section. The area damaged depends on the temperature of the coil, the time of exposure, and the sensitivity of the mineral examined. A field of chalcocite heat etched at the maximum coil temperature for two minutes is shown in Fig. 5B. Grains of chalcocite near the edge of this field show no effects of heat but a large, roughly circular area in the center has developed one of the etch patterns characteristic of this mineral. The etched area has a maximum diameter of 2.1 mm. Another part of this same section was heat-etched at 135°–155° C. and details of this etch pattern may be seen at higher magnification in Fig. 5D.

A summary of observations made in applying the micro-coil to different minerals in polished section is presented in Table 2. A temperature range is given for each reaction based on the Tempil pellet calibration curve in Fig. 4. With polished sections, this range is only a relative indication of the temperature at which a reaction takes place. The principal source of error in applying the calibration curve to polished sections is the variable conduction of heat away from the tested area by adjacent mineral grains. In tests of mineral fragments on glass slides, the surrounding medium

TABLE 2. THERMAL TESTS OF POLISHED SECTIONS

Mineral	Composition	Observed Reactions
Argentite	Ag_2S	Rapid change from grey to dense black, finely pitted surface at 265°–325° C. Transparent film of sulfur released from argentite and spreads rapidly over the surface outward from the heated area. Numerous spheres with a silvery to iridescent luster appear on the surface and are most numerous near fracture, or scratches. These spheres can be remelted at 265°–325° C. They give an argentite x-ray pattern.
Bornite	$5Cu_2S \cdot Fe_2S_3$	Specimens originally orange turn reddish purple at 250°–305° C. With prolonged (2 minute) etching at this temperature, the color becomes a deep reddish purple. On prolonged etching over 400° C. bornite turns blue. Bornite that is originally violet purple becomes a lighter pinkish-violet at 140°–220° C. and then becomes progressively deeper purple on continued heating at this temperature. In presence of coarse chalcocite that has replaced bornite (Figure 5E–5F), the bornite dissolves chalcocite at 250°–305° C. Grains of bornite grow at expense of chalcocite.
Chalcocite	Cu_2S	*Chalcocite Replacing Covellite:* No change could be produced in chalcocite replacing covellite even at highest coil settings. However, veinlets of later chalcocite cutting across the non-reactive variety became visible on etching at 110°–125° C. This chalcocite develops an irregular etch pattern with very fine detail. *Chalcocite Replacing Pyrite:* Isolated blue patches of digenite (?) appear in the chalcocite at 110°–125° C. Fine-grained texture of chalcocite brought out at 115°–130° C. Parallel etch cleavage on fine scale appears at same temperature. No signs of reaction between chalcocite and pyrite after two minutes at 415° C.+. *Chalcocite Replacing Bornite:* Parallel etch cleavage (Figure 5E–5F) begins to develop at 110°–125° C. and forms rapidly at 135°–155° C. At 250°–305° C., chalcocite dissolves in bornite as contacts become diffused and migrate.
Covellite	CuS	Original material-laths and shreds of covellite surrounded and replaced by chalcocite. At 370° C.+, covellite reacts from borders inward. Contact with chalcocite remains sharp and stationary but covellite changes from blue to chalcocite grey losing vivid orange interference color. The grey alteration product is moderately anisotropic. Its surface appears rough in contrast to the adjacent chalcocite and unreplaced covellite. On prolonged heating at 370° C.+, the entire field is converted to a uniform grey color but original areas of covellite are still defined by relief at contacts and rough texture of material that has replaced the covellite.

TABLE 2 (*Continued*)

Mineral	Composition	Observed Reactions
Digenite	$Cu_{2-x}S$	Greyish-blue digenite turns grey at 150°–170° C. On prolonged heating, the color becomes a violet-grey. After cooling, areas originally hottest become blue again.
Freieslebenite	$Ag_5Pb_3Sb_5S_{12}$	Freieslebenite swells and cleavage fragments heave upward at 265°–335° C. Fluid emitted at this temperature spreads across the surface imparting a permanent dull gun-metal grey color to the mineral.
Goethite	$FeO \cdot OH$	Decomposition of goethite, especially coarsely crystalline varieties, very sluggish in polished section. Some specimens showed no effects of heating even at maximum settings of the coil. One specimen heaved and cracked at 370° C.+ but no pronounced color changes were observed.
Hessite	Ag_2Te	Original specimen grey. Anomalous yellow-brown to bluish-grey interference colors. A permanent change of color to light brown takes place at 350° C.+. No changes in anisotropism on cooling.
Petzite	Ag_3AuTe_2	At 370° C.+, petzite heaves and cracks as vermiform black markings appear on light grey mineral surface. In oblique light, a delicate network of crystalline gold is seen to have replaced the original petzite grain. Adjacent tellurides, in this case altaite, are unaffected by heat.
Proustite	$3Ag_2S \cdot As_2S_3$	At 405° C.+, surface of proustite suddenly melts. The liquid solidifies to a silvery metallic substance which can be remelted at 405° C.+. This material still gives an x-ray pattern for proustite.
Realgar	AsS	Color changes from grey to tannish-grey at 255°–320° C. At 308°–400° C., realgar melts and a bluish iridescent ring forms around the heated area. In oblique light, this ring is red to yellow.
Tellurium	Te	Metal begins to change at 305°–400° C. as a yellow coating of oxide collects on surface. Mineral melts at 415° C.+ forming a small liquid filled depression under the coil.

was air in every case, but this control does not apply to polished sections.

Of the results obtained and described in Table 2, it is most significant that the etch patterns of chalcocite described by Stephens (1935) can be produced with a device as simple as the coil. With the exception of some chalcocite replacing covellite, all specimens of this mineral formed a pronounced etch pattern on heating (Figs. 5C–5F). Additional specimens

and study would be required to determine whether patterns obtained with the heating coil differ in any way from those described by Stephens.

Reactions noted in the heat-etching of argentite and proustite are also worthy of some comment. McKinstry (1927) observed the formation of blebs, presumably of native silver, on surfaces of argentite and pyrargyrite etched with a carbon arc. When argentite was heated with the coil at 265°–325° C. numerous globules of an iridescent to silvery luster appeared on the blackened surface. It was at first assumed that these were native silver, but these spheres could be re-melted at 265°–325° C., well below the melting point of silver. Similar effects were noted with proustite which melted quickly at 405° C.+ forming a liquid with a bright metallic luster. After cooling, this material could be re-melted again at 405° C. Fragments of each of these minerals were extracted, transferred to glass slides, and there heated until they liquefied. On cooling, the samples were scraped from the slides, crushed, and x-rayed. The resulting powder patterns were those of the original minerals, not native silver. Flecks of what appeared to be silver were seen admixed with the crushed heated products of proustite but the metal comprised only a small proportion of the original liquid globule.

Along with the minerals listed in Table 2, a number of others were tested that proved negative to the heat of the coil. These include bismuthinite, chalcopyrite, cinnabar, copper, domeykite, dyscrasite, enargite, galena, pyrite, silver, sphalerite, stannite, stibnite, sylvanite, teallite, tetrahedrite, and violarite.

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