

Spontaneous polarization associated with porphyry sulfide mineralization

Charles E. Corry*

ABSTRACT

In the years 1978 through 1981, many spontaneous polarization (SP) surveys of porphyry sulfide deposits and prospects were done in the western United States. Effective depth of exploration using SP was found to exceed 1 km for large porphyry sulfide orebodies. The relationship between depth of erosion since time of emplacement and the spontaneous polarization observed on the surface, together with the effects of weathering, are presented from field surveys over known deposits.

Successful use of the spontaneous polarization technique in porphyry sulfide exploration led to an investigation of the causative mechanism. The field data do not support the electrochemical model first proposed in Sato and Mooney (1960). The measured potential appears to be simply the oxidation potential ΔE between a reference electrode outside the mineralization and a roving electrode within the mineralization. The ΔE measured in the field is dominated by the difference in Eh (ΔEh) potential between the two electrodes, but it is not equivalent due to the unavoidable inclusion of other potentials in the field measurement. Without a wire connecting the electrodes, current between the sulfide mineralization and the surrounding country rock is sensibly zero, as evidenced by the persistence of the sulfides through geologic time.

INTRODUCTION

For more than one hundred and fifty years (Fox, 1829, 1830a, 1830b) it has been known that sulfide mineralization may have a naturally occurring negative electrical potential with respect to the surrounding country rock. Only magnetic prospecting for iron ores in Sweden has been used longer than the spontaneous polarization, or self-potential (SP) method in the exploration for minerals. A review of early surveys and a general history was given in Kelly (1924). A description of the notably successful SP survey at Noranda mines in Quebec during 1924 was given in Kelly (1957). Fedynsky et al. (1970) and Semenov (1974) reviewed the work in Russia. Parasnis (1970, 1975),

Malmquist and Parasnis (1972), and Logn and Bölviken (1974) presented some of the SP work done in Sweden. An extensive bibliography can be found in Hulse (1978).

In the years 1978 through 1981, AMAX ran in excess of 3 000 line-km of SP data over both known deposits and sulfide prospects in the western United States. Portions of the results of these surveys are reproduced here.

Despite its long history, many investigators have not used the SP method apparently because of problems with reliability and reproducibility in the field data. Recent improvements in field techniques (Corwin and Hoover, 1979) and instrumentation, notably stable, millivolt-range, hand-held digital voltmeters, have reduced these problems to insignificance in mineral surveys. An easily attainable standard of repeatability is illustrated in Figure 1. In general, the data can be seen to repeat within ± 20 mV within a range of 750 mV. The remaining errors in the data are due to slightly different station positions in areas of steep gradients, and aliasing due to a station interval of 100 m in areas where the spatial wavelengths are less than 200 m. While these errors are correctable, the increased cost of closer station spacing or better positioning is not usually justified for a porphyry sulfide SP survey.

Due to its relative abundance, pyrite is the sulfide most commonly located by an SP survey. Pyrrhotite is the next most common sulfide mineral correlatable with SP anomalies. Other sulfides which have been associated with SP anomalies are chalcopyrite, chalcocite, covellite, other copper and copper-nickel sulfides, cobalt ores, and molybdenite.

Other than sulfides, graphite was the most common mineral encountered which produced correlatable SP anomalies. High-grade anthracite coal is also reported to cause SP anomalies. However, in the one area surveyed with known high-grade anthracite, a correlatable SP anomaly was not found. SP anomalies have also been reported in association with siderite (Wilckens, 1955), manganese oxides, e.g., pyrolusite, alunite (Kruger and Lacy, 1949; Gay, 1967), and magnetite.

The exploration success of the SP method naturally led to an investigation of the causative mechanism. The Sato and Mooney (1960) model was investigated, but field data did not support their model. A series of experiments was then undertaken in an attempt to determine the mechanism. These experiments indicate that the potential measured in the field is the oxidation potential ΔE between a reference electrode outside the mineralization and an electrode within the sulfide system.

Manuscript received by the Editor July 26, 1984; revised manuscript received December 11, 1984.

*Department of Geology and Geophysics, University of Missouri—Rolla, Rolla, MO 65401.

© 1985 Society of Exploration Geophysicists. All rights reserved.

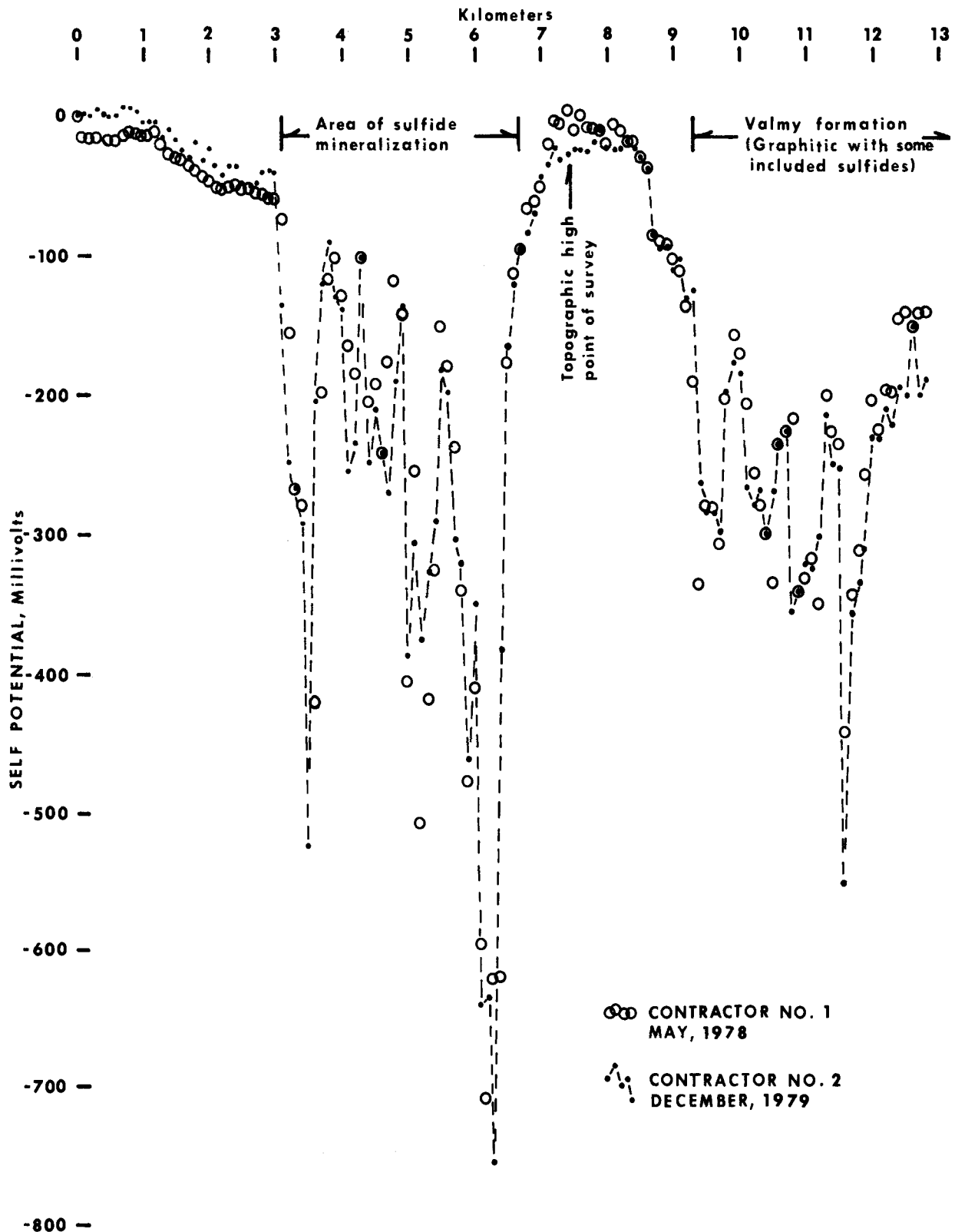


FIG. 1. Repeat of 13 km of SP line at Little Cottonwood Canyon, Battle Mountain, Nevada, showing easily attainable standards of reproducibility in SP data. Station spacing was 100 m. Cu-CuSO₄ electrodes were used. With the exception of the base station, no attempt was made by the second contractor to relocate old stations.

FIELD PROCEDURE

The basic equipment required is very simple: two non-polarizing electrodes, commonly the copper-copper sulfate type; several reels of wire, usually with 4 km of wire per reel; and a stable, high-impedance, millivolt-level digital voltmeter. A detailed equipment list can be found in Corry et al. (1983).

The field procedure is shown schematically in Figure 2 and presented in detail in Corry et al. (1983). If these techniques are closely followed by the field crews, loops ≥ 20 km in circumference will always tie within ± 25 mV. By careful observation of noise sources (principally tellurics and cultural noise), and by using as few base stations as possible, line tie errors may be reduced to $\leq \pm 5$ mV. However, the increased costs of such careful surveying are not usually justified in a mineral survey, where the amplitude of the anomalies commonly exceeds several hundred millivolts.

The technique of a fixed base station was used exclusively. The base-station reference electrode is placed in a shallow hole, and covered with a block of styrofoam. Dirt is scooped around both the electrode and the styrofoam cover to minimize temperature changes and variations in soil moisture. After establishing the base station, the wire is spooled out from a vehicle where possible, or from a walking reel when necessary. A measurement is made every 100 to 200 m by placing a roving electrode in a small hole 10 to 15 cm deep. The shallow holes serve to place the electrode contacts beneath the dry, resistive layer of soil at the surface. The self-potential is measured between the roving electrode and the reference electrode at each station. The high input impedance ($\geq 10^7 \Omega$) of the digital voltmeter negates any effects of the electrode contact resistance, typically < 50 k Ω . The holes for the electrodes are *never* wa-

tered. When the measurement is completed, the holes are refilled with dirt to minimize changes in soil moisture in the event the station must be reoccupied for any reason. Changes in soil moisture may cause variable local potentials to develop (Corwin and Hoover, 1979). While the ground may be wet or dry during measurement along a line, the soil moisture content should not change appreciably during the time it takes to run the line. The electrodes must also be protected from direct sunlight to avoid photovoltaic potentials.

In porphyry sulfide exploration, the common station spacing is 100 to 200 m, because any target with possibly economic reserves has been determined to have an SP anomaly > 1 km in diameter. Therefore, a station interval of 100 to 200 m is certain to sample the intended target adequately.

Experience showed that if a base station was located within areas of steep gradients, or within the boundaries of large SP anomalies, lines run from such a base station did not tie with lines run from base stations outside the anomaly. Considerable care was taken to ensure that the survey base, and subsequent base stations, were placed outside areas of known or suspected mineralization (discussed subsequently with the proposed mechanism). Additionally, it was found that base stations must not be placed where reducing conditions might be encountered near the surface, e.g., bogs, marshes, swamps, etc.

The location for the roving electrode requires only that electrical contact can be made with the ground or rock. We have been able to obtain stable and repeatable SP values with the roving electrode in contact with crystalline rock, on frozen ground, in marshes and swamps, and underground. Corwin (1980 pers. comm.) has run SP surveys over snow, and offshore (Corwin, 1973).

Reconnaissance lines were usually extended approximately

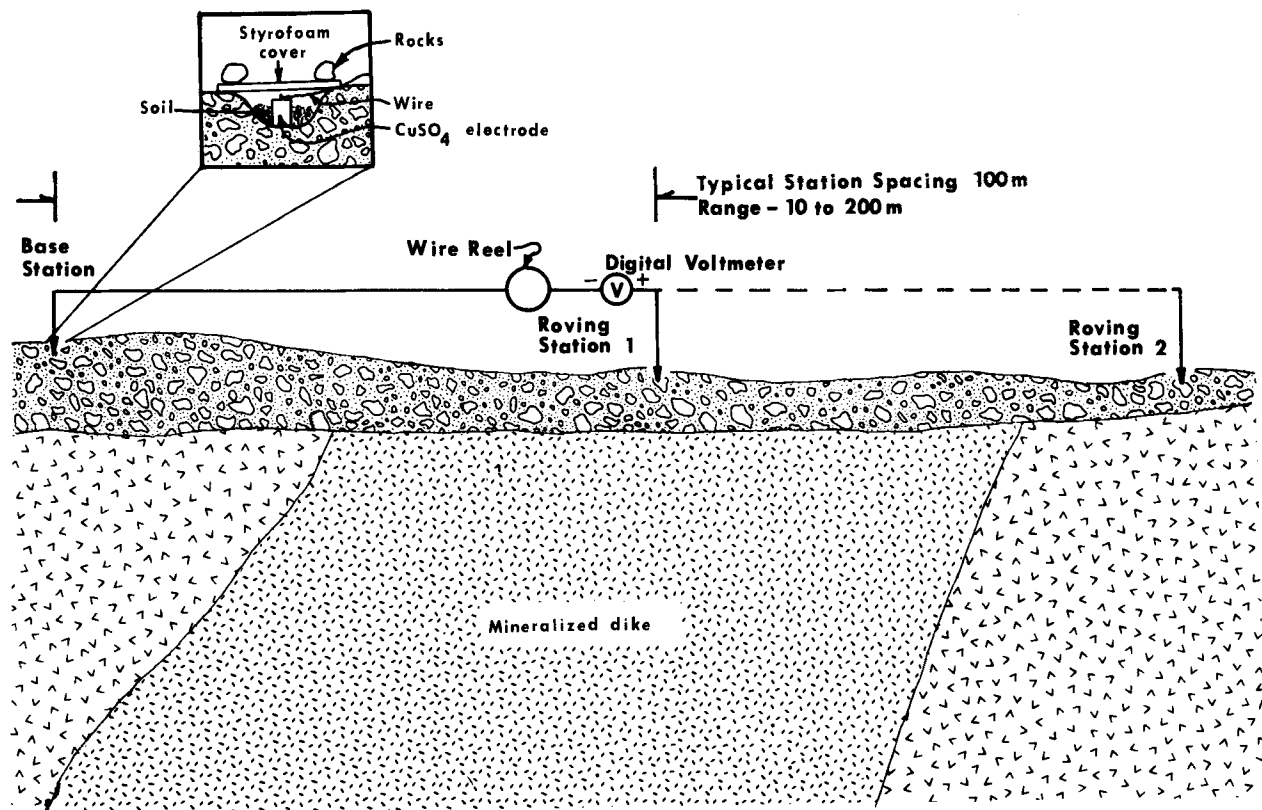


FIG. 2. Schematic of the procedure used to collect SP data.

10 km in at least four directions from the primary survey area to ensure that background data were available. Significant SP anomalies encountered during the reconnaissance phase (and there were many) were explored while the crew was in the field.

Large mining operations, power stations, and pipelines with cathodic protection present severe local noise problems, which at times preclude an SP survey in the vicinity of such installations. On a small scale, culverts, grounded fences and powerlines, drill-hole casings, and other metallic objects in the ground should be avoided. Natural interference is usually in the form of telluric currents, the effects of which are amplified as the length of the wire increases away from the base station.

When not in use, an electrode pair is kept in a saturated copper sulfate bath to return the pair to chemical, temperature, and hence, voltage equilibrium. Electrodes are cleaned with a nylon brush before returning them to the bath. Cleaning minimizes contamination of the solution in the bath and reduces spurious potentials due to different soil types sticking on the electrode. The potential difference between the reference and roving electrodes in the copper sulfate bath is read at the beginning and end of each line. These values are used to correct for any differences in potential between the electrodes.

The relative amplitudes of SP anomalies associated with sulfides are commonly so large that the transition potentials encountered when crossing different soil or rock types are normally insignificant. Also, potentials arising from changes in vegetation and the type or amount of ground cover are not significant during mineral surveys.

SPONTANEOUS POLARIZATION FIELD SURVEYS

The SP surveys on which this paper is based have been primarily in search of, or over and around known disseminated porphyry sulfide systems, although massive sulfides were occasionally encountered. No difference in the SP response was found between porphyry and massive sulfide deposits. An example of the large SP anomalies which may be associated with porphyry sulfide systems is shown in Figure 3. The observed anomalies were found to correlate best with pyrite and pyrrhotite in the quartz-sericite-pyrite (QSP) halo commonly associated with porphyry sulfide systems.

Self-potential anomalies were consistently found in association with large, unoxidized porphyry sulfide deposits by the field surveys. However, several factors may reduce, eliminate, or

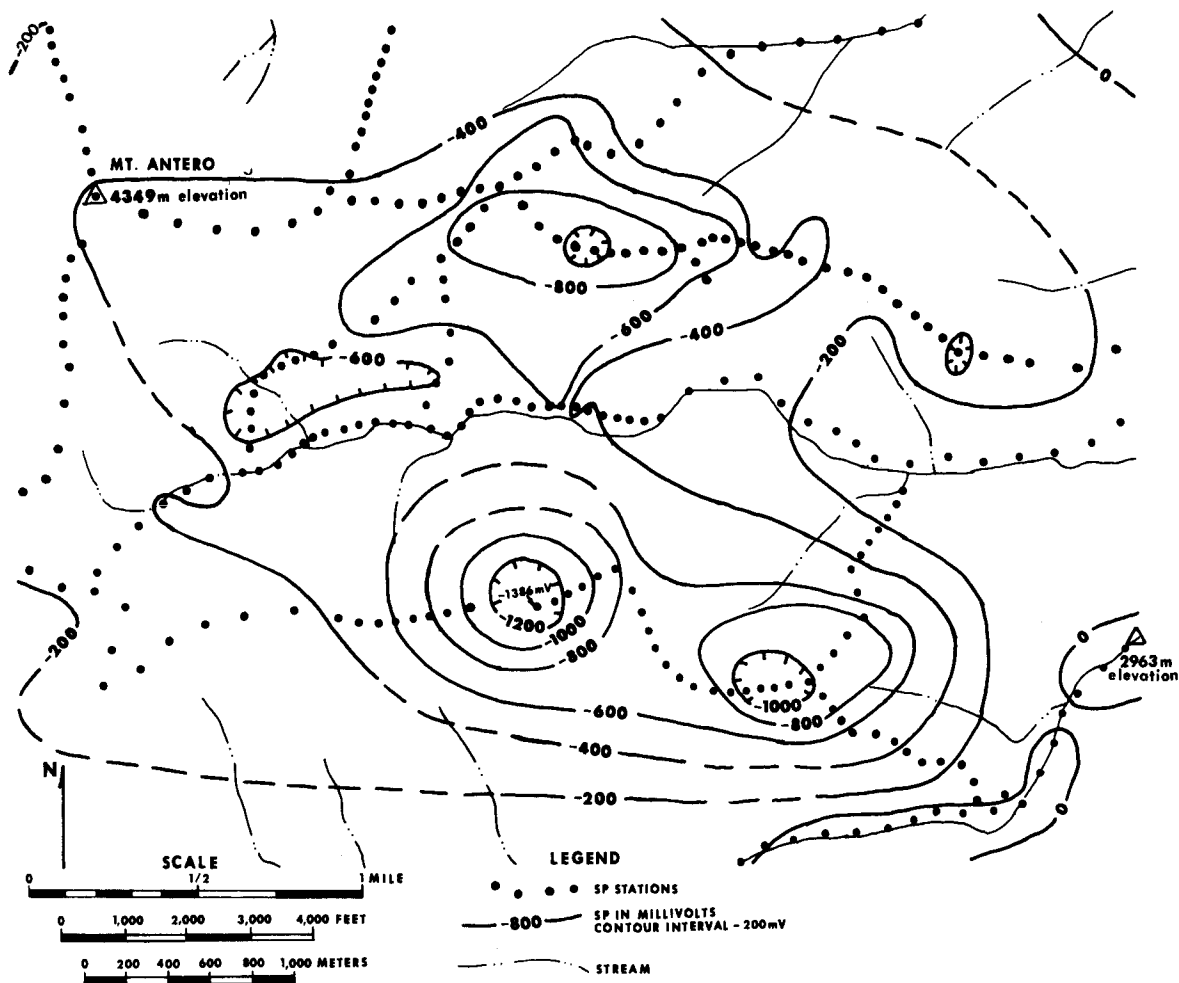


FIG. 3. SP anomalies associated with a sulfide system in the Sawatch Mountains, southwest of Buena Vista, CO. The base station for the survey is located approximately 10 km northwest of the area shown. The sulfide mineralization is outlined by the -200 mV contour. Large concentrations of sulfides have more negative values.

prevent detection of an SP anomaly. The most obvious factor is station spacing, and the 100 to 200 m interval used is more than adequate for anomalies with the areal extent of Figure 3. Another factor in detecting the sulfides is the depth of the deposit beneath the present erosion surface. In general, the SP anomalies associated with sulfide mineralization do not correlate directly with topography. However, there is a definite correlation between depth of erosion since emplacement of the mineralization and the amplitude of the associated SP anomaly. In addition to depth of erosion, depth of weathering beneath the erosion surface has also been found to affect the observed SP anomaly.

An attempt was made to determine what the effective depth of exploration for spontaneous polarization might be, within the limits of known, accessible porphyry sulfide orebodies. To determine the effective exploration depth, both the amount of erosion since the orebody was emplaced, and the depth of weathering must be considered. Erosion effectively moves the orebody nearer the surface and makes it an easier target. However, near-surface weathering may destroy the sulfides, and the associated SP, by oxidation.

Depth of erosion

There appear to be four significant levels of erosion, as shown in Figure 4, which determine the spontaneous polarization observed on the surface. The four orebodies over which these SP surveys were run are located at sufficiently high latitude and altitude that most sulfide minerals are stable at or

near the surface in the local environment. Thus, depth of weathering is not thought to be a factor in these surveys.

Figure 4 shows the approximate boundaries of ore grade mineralization for each of the four orebodies. Note that the deeper orebodies have smaller ore zones because a progressively higher grade of ore is required for an economic orebody as depth increases. If the deeper orebodies were at the surface, the ore zoning would be wider than for the shallow and elevated deposits used as examples.

The categories used in Figure 4 are not intended as an absolute standard, and not all of the surveys over similar orebodies showed exactly the same response. Further, the same orebody may exhibit responses characteristic of two different depths of erosion depending upon the direction in which the SP lines are run across the orebody. At lower elevations or latitudes such a variation in response could be due to differential weathering. However, in the present surveys the variation was usually due simply to differential erosion. Differential erosion may leave larger areas of the QSP halo intact in one area and remove it in another area. If erosion and weathering have removed most or all of the sulfides in a given area, then the SP anomaly will be weak or absent in those areas. These relations are illustrated as models in Figure 5.

Erosion levels

For porphyry sulfide systems the four significant levels of erosion appear to be as follows.

Deep deposit.—Erosion has not yet intercepted the QSP

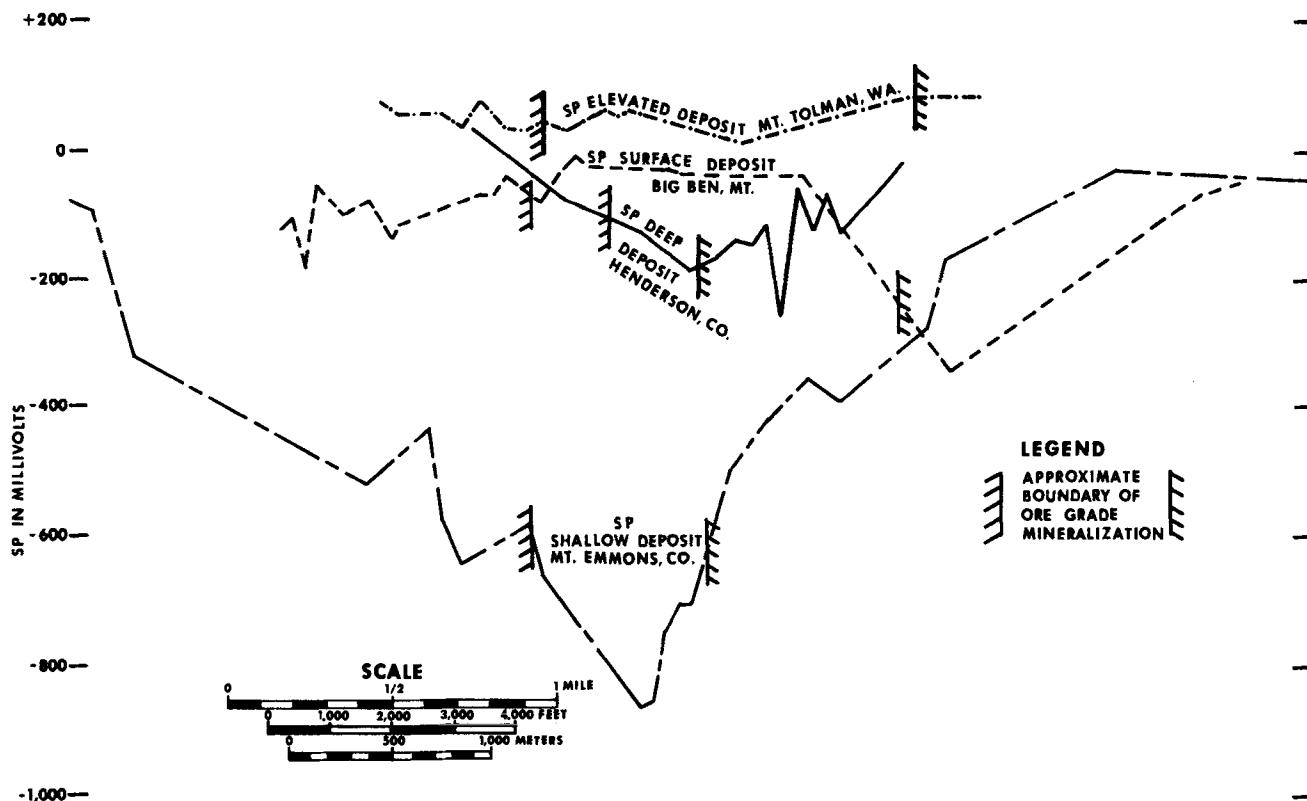


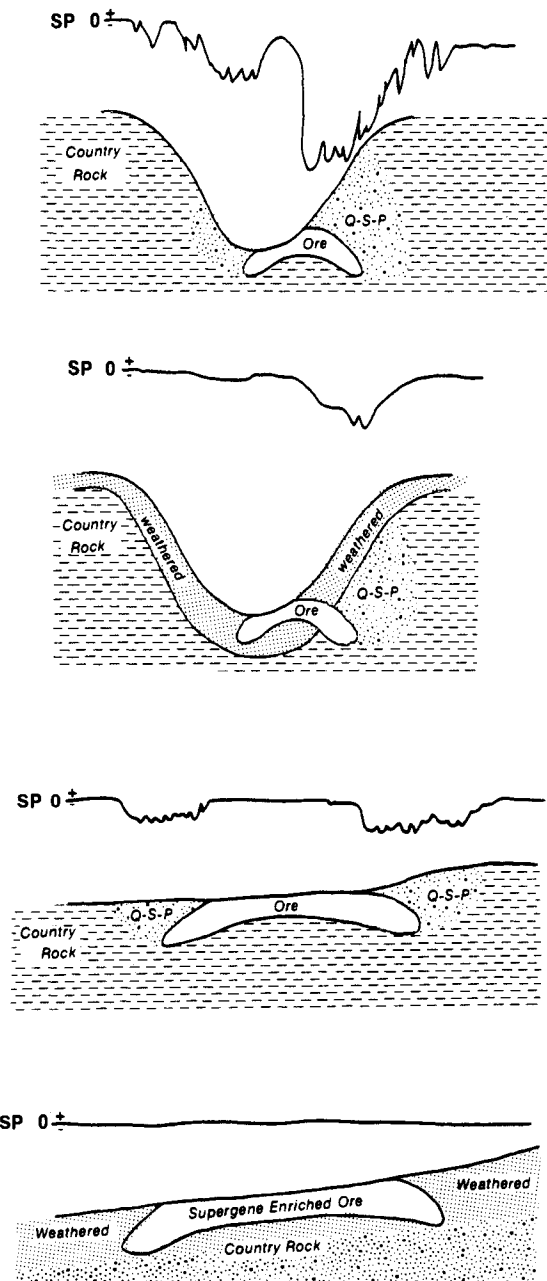
FIG. 4. SP anomalies observed above four known sulfide orebodies with various depths of erosion since emplacement. The anomalies correlate best with the QSP halo above or around the deposits.

alteration zone above the deposit. As shown in Figure 4, the response from a deep deposit is a broad, relatively low-amplitude (-100 to -300 mV) anomaly. The depth to the orebody for the deep deposit shown in Figure 4 is >1 km beneath the surface. Thus, under favorable conditions the effective depth of exploration for SP surveys exceeds 1 km. This is remarkable in that spontaneous polarization in the past has generally been regarded as a shallow exploration method.

Shallow deposit.—Erosion has exposed the QSP alteration zone, but not the orebody. As illustrated in Figure 4, the SP response at the surface is a broad, very high-amplitude anomaly (-400 to more than $-1\ 000$ mV as shown on Figure 3). The SP anomaly is generally centered over the orebody since that is

commonly the area of highest sulfide mineral concentration in the QSP halo. A map view of the spontaneous polarization above the shallow deposit shown in profile in Figure 4 is given in Figure 6. As seen in Figure 6, there are several negative centers which coincide with known concentrations of sulfides. Small, outlying negative anomalies may be veins. The central anomalies, with the highest amplitude and covering the largest area, are usually associated with mineralized intrusives in porphyry systems.

Surface deposit.—Erosion has intercepted the top of the orebody, and the deposit is partially exposed at the surface or shallowly buried beneath till or talus. In most cases only the outer portions of the QSP alteration zone remain, probably as



SP anomaly over an eroded, but essentially unweathered, porphyry sulfide deposit. Occurs at high latitudes and/or high elevations. Erosion may be due to water and/or glaciation. Weathering is retarded by climate.

SP anomaly over same body as above, but deeply weathered, as well as eroded. Occurs at low latitudes or low elevations. Erosion is usually due to water. Weathering is enhanced by high rainfall and high temperatures.

SP anomaly over deeply eroded, but essentially unweathered, porphyry sulfide deposit. Anomaly occurs as halo around exposed ore, and correlates with the remainder of QSP zone.

SP anomaly over deeply eroded and weathered porphyry sulfide deposit. Sulfides have been largely, or completely, oxidized.

FIG. 5. Models showing the relative effects of erosion and weathering on spontaneous polarization at the surface.

Downloaded 01/13/14 to 50.170.193.242. Redistribution subject to SEG license or copyright; see Terms of Use at http://library.seg.org/

a discontinuous halo around the orebody. Some mineralized veins may also remain with small associated SP anomalies. Figure 4 shows a broad halo for the surface deposit chosen as an example, but this halo is discontinuous around the orebody. The amplitude of the SP anomalies in the halo is usually from -200 to -300 mV, with an observed range of from -100 to -500 mV. The SP anomalies are commonly much weaker, or absent, in valley bottoms due to the deeper level of erosion, and usually deeper weathering. Where the QSP zone is intact and unweathered in hills and ridges surrounding the deposit, the amplitude of the SP anomaly in the halo will probably be higher. These relations are illustrated in Figure 5.

Elevated deposit.—The general level of erosion has proceeded to below the elevation of the orebody, with only a resistant core left as a topographic high. The QSP zone is almost entirely eroded away, and commonly much of the ore has also been removed. Spontaneous polarization, which may have existed prior to erosion, is now absent or at best is a very weak and discontinuous halo with very low amplitudes, seldom exceeding -100 mV. These isolated anomalies can be correlated with remnants of the QSP zone, or unweathered vein mineralization in the halo, but for elevated deposits the SP method is seldom as effective as geochemical sampling and geologic mapping.

Depth of weathering

The relationship between weathering and SP associated with

sulfide mineralization was first documented by Poldini (1938). In the Vardar district in Yugoslavia, old and secondary metaliferous formations have been denuded and oxidized before being partially covered by peat of Pliocene age. These deposits gave no SP response. Further upland from the Vardar valley Poldini found gossans outcropping in the hills bordering the plain, and these gossans did not give an SP response. Continuing up into the mountains, he found fresh sulfides with associated SP anomalies. Even higher up were areas where recent erosion had destroyed old gossans and exposed fresh sulfides with associated spontaneous polarization. Thus, he concluded (Poldini, 1938, p. 282)

... that SP phenomena begin only at a certain altitude and, roughly speaking, grow in intensity as one progresses further into the mountains, where finally the alpine type of reactions is found.

The same climatic effect can be achieved by moving to higher latitudes, where the cold inhibits oxidation and most sulfide minerals are stable in the near-surface.

Because of the cold climate, most sulfide minerals will be stable at or very near the surface at or above the timberline elevation, regardless of latitude. In areas which have been glaciated in the recent geologic past or are currently areas of permafrost, it can usually be safely assumed that sulfide mineralization, if present, is stable in the near-surface environment. SP surveys done at high latitudes and high altitudes have had a high success ratio.

Low latitudes and elevations are commonly associated with

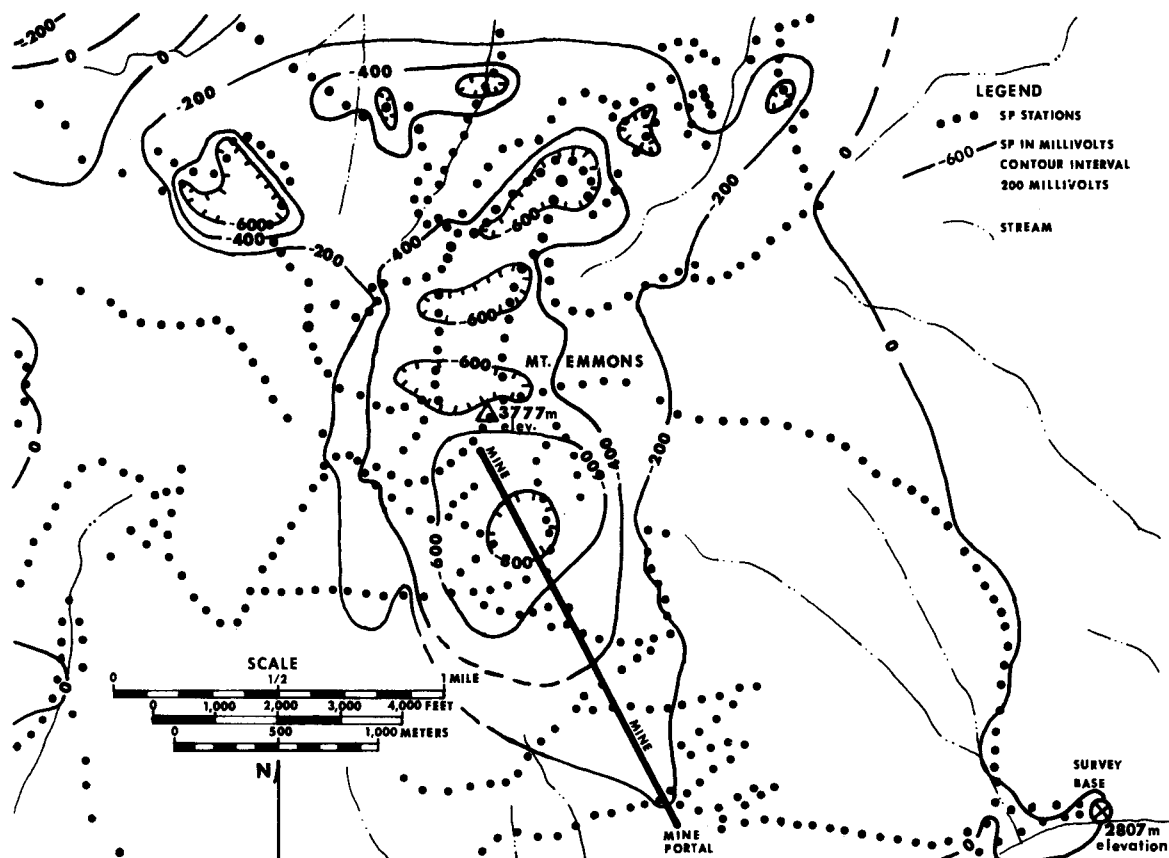


FIG. 6. Surface SP map of the Mt. Emmons porphyry sulfide deposit near Crested Butte, CO in the center of the Colorado Mineral Belt. The sulfide mineralization is outlined by the -200 mV contour. Large concentrations of sulfides have more negative values.

deep weathering. Deep weathering may also occur where fracture porosity extends to depth, or for a number of other reasons which may prevail in the local geology. In deeply weathered areas the SP observed at the surface may be greatly diminished, or absent, due to the destruction of the sulfides by oxidation.

A number of SP surveys were run over weathered sulfide systems. In all cases where the weathered zone was known to extend to the bottom of the mineralization, or where the depth of weathering was on the order of the width of the sulfide system, the spontaneous polarization measured on the surface was absent or very weak. Based on these surveys evolved, as shown in Figure 5, an empirical relationship between depth of erosion, depth of weathering, and the spontaneous polarization measured at the surface.

The mineralization at the Buckingham deposit, Battle Mountain, Nevada was outlined by an SP halo on the west, while the eastern half exhibited no SP anomalies with an amplitude more than -100 mV below background (0 ± 50 mV). Subsequent geologic investigation revealed weak supergene enrichment, with antecedent oxidation of the sulfide mineralization in the eastern portion of the deposit. Similar results are evident in an SP survey published by Robinson and Cook (1966), shown in Figure 7, over the Safford deposit in Arizona. Then known, oxide-enriched orebody at an approximate depth of 240 m has no directly associated SP anomaly (Figure 7). The prominent SP anomaly, with an amplitude of -600 mV and centered approximately 1.5 km southwest of the original deposit, was found by later drilling (circa 1972) to overlie the "deep deposit" which occurs at an approximate depth of 550 m.

Parasnis (1975, p. 89-91) presented similar results for an SP survey over the Kimheden massive sulfide orebody in Sweden. Distinctive SP anomalies are associated with two of three ore lenses. The western orebody, where drilling indicates weathering, has no SP anomaly, whereas the rock in the rest of the area appears fresh (Parasnis, 1975, p. 90).

SPONTANEOUS POLARIZATION MECHANISM

Stability of the SP phenomenon

With minor exceptions, spontaneous polarization associated with sulfide mineralization appears to be a stable phenomenon with respect to time and seasonal climatic variations. Poldini (1938, p. 348) found no variation in the self-potential over a ten year period, and no seasonal variations were noted. Parasnis (1970, Figure 10) in a test area in the Akulla region of Sweden found that even anomalies of small amplitude were stable over an eight-year period. Figure 1 shows no significant variation with time or season in Nevada over a nineteen month interval. SP lines in the area shown on Figure 6 were repeated over several years with no significant variation.

Spontaneous polarization can also be measured underground. The presence of negative anomalies at depth and in a reducing environment is shown in Figure 8 and in Figure 9 (redrawn from Parasnis, 1970). Malmquist and Parasnis (1972) and Logn and Bolviken (1974) also showed negative anomalies associated with sulfides at depth in drill holes. Thus, the ob-

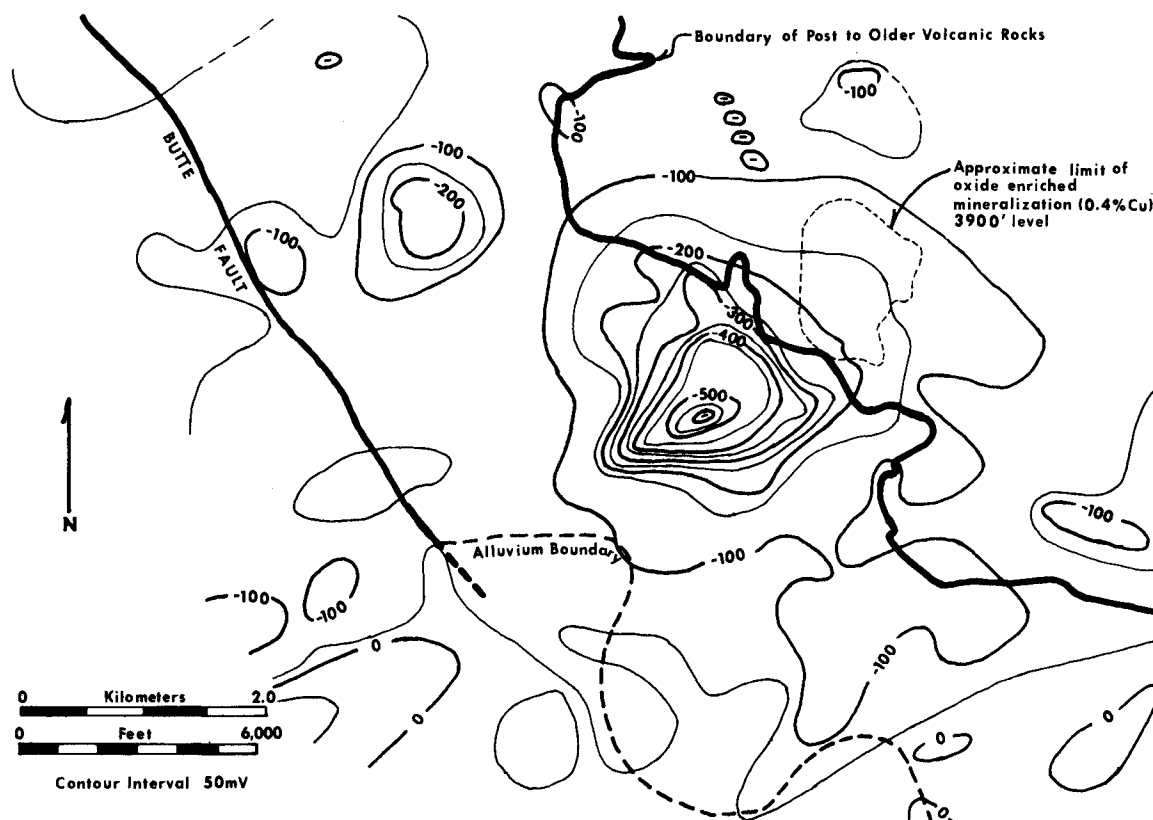


FIG. 7. Map of the spontaneous polarization observed on the surface above the Safford deposit, AZ. The "deep deposit" underlies the prominent SP anomaly. Redrawn from Robinson and Cook (1966).

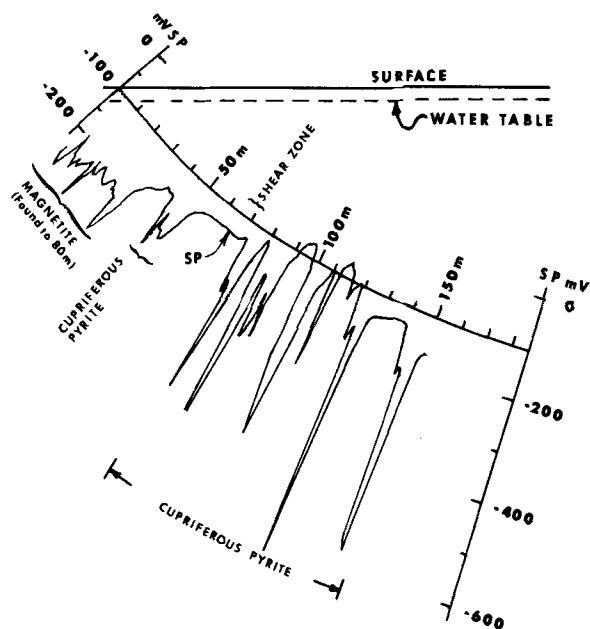


FIG. 9. Downhole SP in hole 65 intersecting the Kimheden orebody, Sweden. Redrawn from Parasnis (1970).

served spontaneous polarization remains negative below the water table and below any observable weathering and oxidation. I have found negative spontaneous polarization associated with sulfides in the subsurface to depths >1.5 km in downhole logs and to 550 m in an underground mine (Figure 8). There is no indication that the spontaneous potential reverses polarity or dies out with depth if sulfide mineralization is present.

The available evidence indicates the spontaneous polarization is created upon emplacement of the sulfide minerals and persists until exposed by erosion. The assumption that the spontaneous polarization associated with the sulfide minerals exists from the time of emplacement does not mean that the potential observed at the surface remains unchanged. Figure 4 can be viewed as a time-lapse photograph of the potential measured at the surface above sulfide mineralization through geologic time. Initially the surface potential is small due to the depth of the mineralization, which places the spontaneous polarization at a great distance from the observer. Over geologic time, erosion removes the overburden, bringing the sulfides closer to the surface, and the amplitude of the surface potential grows. Eventually, erosion exposes the sulfides, and they are oxidized, destroying the spontaneous polarization.

Poldini (1938, p. 348) found that radical changes in the

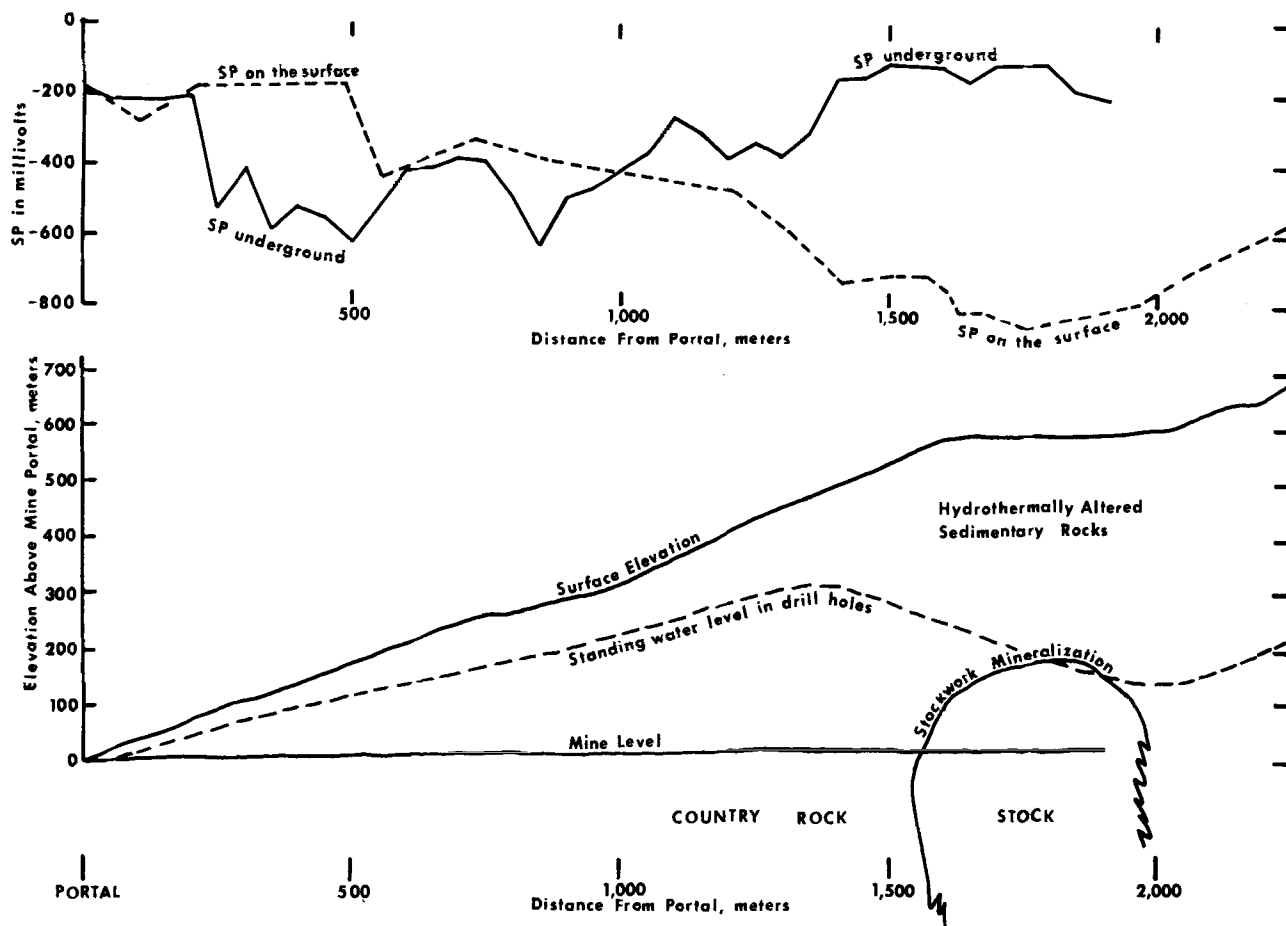


FIG. 8. The spontaneous polarization above and below the Mt. Emmons porphyry sulfide deposit. The location of the mine portal and the direction of the drift are shown in Figure 6. Both surveys are referenced to the survey base in Figure 6.

surface resistivity could slightly alter the distribution of the potential observed on the surface on a very short time scale. While working in desert regions, he noticed that heavy rainfall spread the SP anomaly a few meters by considerably lowering the resistivity of the surface layer. From Poldini's (1938) observation, it is inferred that a conductive surface layer may act to spread the diameter of an SP anomaly to some extent.

There is limited evidence that the spontaneous polarization at the surface may be greatly modified in a relatively short time by drilling, well casings, and pipelines. Pirson (1971) showed such behavior for spontaneous polarization observed over oil fields, where presumably the SP is the result of biodegradation of hydrocarbons producing sulfide mineralization as one end product (Sassen, 1980).

Based on my studies, I believe the effect of cultural noise (rails, electrical cables, etc.) on the measured potential in a mine (Figure 8) was to lower the amplitude of the spontaneous polarization relative to the amplitude measured downhole in nearby drill holes. Thus, the undisturbed potential in the mine would probably be more negative.

Geochemical work shows that the environment in the mine is reducing below the water table and away from the mine face. It is reasonable to assume that sulfides in the near-surface are more readily oxidized by introduction of galvanic currents associated with drill casing and pipelines, and that sulfides in a reducing environment at depth would not be so readily affected. Thus, rapid decay of the surface potential upon introduction of cultural artifacts, if it occurs, appears to be a near-surface phenomenon, and the spontaneous polarization at depth appears to be relatively unaffected.

Previous theories

Spontaneous polarization, or self-potentials, may arise from a variety of mechanisms, but only a few of these have been found to have geologic significance. One familiar mechanism is the galvanic cell of electrochemistry. If a wire is connected between two materials in electrolytic contact and the oxidation-reduction potential between the materials is such that they *spontaneously* react, a measurable electric potential will result. The physical arrangement is a galvanic cell, the electric potential is called the oxidation potential, and the reaction is termed electrolysis. Many early theories, e.g., Poldini (1938), used the mechanism of a galvanic cell, in which the conductive orebody replaced the wire connecting the two materials, to account for the observed spontaneous polarization as the negative end of an active galvanic cell. An oxidation reaction between the top of the orebody and a reducing reaction at depth was assumed to cause current flow through the country rock. However, such systems tend to self-discharge quite rapidly.

Another type of potential, the liquid junction potential, originates at the interface between two nonidentical solutions because charged ions diffuse across the interface at different rates. Humic acid from decaying vegetation, dissolved salts, etc., will result in varying electrolytic concentrations from place to place, with potentials set up between them. These potentials are generally small in comparison with the potentials associated with sulfide mineralization, and they do not appear to be significant in mineral SP surveys.

In geothermal exploration, potentials are known to result from thermoelectric coupling or streaming potentials, i.e., electrokinetic coupling, of electrolytes moving through rock pores

(Sill, 1983). Streaming potentials may produce very large anomalies on the surface. Zablocki (1976) reported a +1 600 mV anomaly on Kilauea volcano in Hawaii, which he accounts for as a streaming potential. Corwin and Hoover (1979) reported a -2 693 mV anomaly on Agadak Volcano, Adak Island, Alaska, also attributed to a streaming potential. Areas with large-amplitude streaming potentials are characterized by high rainfall and steep topography. Volcanoes in such environments are also subject to rapid weathering and adsorbed charged ions are common in the groundwater (electrolyte). Areas of lesser rainfall, more subdued terrain, or less rapid weathering will have much lower amplitude streaming potentials.

Streaming potentials are thought to exist in conjunction with the migration of hydrothermal fluids but in existing orebodies hydrothermal activity has usually ceased. It is probable that if large quantities of oxygenated groundwater were moving through the sulfide mineralization, the sulfides would oxidize and any associated spontaneous polarization would be destroyed. Where deep weathering has been observed at high altitudes or high latitudes, it is usually found associated with fracture porosity and groundwater migration. Thus, it is highly unlikely that streaming potentials are directly related to the observed spontaneous polarization associated with existing sulfide mineralization.

The most widely referenced theory for the spontaneous polarization associated with sulfide mineralization has been the electrochemical mechanism originally proposed by Sato and Mooney (1960); they proposed that the observed potential was the result of

... two electrochemical half cell reactions, occurring simultaneously at two different locations on the ore-rock interface. Normally one location is above the water table, the other below, with the ore forming a continuous structure between.

The ore in the Sato and Mooney model acts as an inert electrode for electron conduction from the orebody at depth to the near-surface, or at least above the water table. Electric current outside the orebody is assumed to be a net movement of positive ions toward the top of the orebody. Their model also implies (Sato and Mooney, 1960, Figure 7) that at or about the water table the potential should be neutral or zero relative to an electrode at infinity.

Sivenas and Beales (1982a) updated the work of Sato and Mooney (1960). They supported the concept that the "regional" potential field results from a redox cell, as proposed by Sato and Mooney (1960), with some modifications. They also proposed the addition of a sulfide galvanic cell where active electrolysis is occurring. However, the objections to the Sato and Mooney model (tabulated below) also apply to the models of Sivenas and Beales (1982a) and Kilty (1984) and similar models proposed by other investigators.

The problems are as follows.

Amplitude.—On the basis of the known *Eh* potentials for common sulfide minerals, Sato and Mooney (1960) found a maximum oxidation potential of approximately 0.8 V for minerals such as graphite and pyrite. Since in their model all current lines must begin and end on the orebody, the maximum anomaly expected in an SP survey on the surface would be one-half the maximum potential, relative to a point at infinity, or a maximum anomaly on the order of 400 mV. (Sato and Mooney, 1960, p. 246)

... were unable to account for reported anomalies of a volt or more, except by assuming unusual chemical con-

ditions or superposition of other potentials unrelated to the orebody.

However, negative potentials with amplitudes in excess of 800 mV (more than twice their predicted maximum) are commonly measured relative to a remote electrode. Figures 3 and 6 show two, of many, areas where large-amplitude negative anomalies associated with sulfide mineralization were found. Other investigators have also reported large-amplitude negative anomalies. Gay (1967) reported a $-1\,800$ mV SP anomaly from Peru, while Burr (1980) reported a $4\,000$ mV anomaly at the Sherman Iron Mine, Temagami, Ontario, Canada. Numerous other authors (see reference list in Hulse, 1978) have found anomalies on the order of 1 V or more. Several reviewers have suggested that such amplitudes are possible if several electrochemical cells are connected in series. The oxidation concentration and sulfide galvanic cells of Sivenas and Beales (1982a, p. 134, Figure 3) work in parallel, and I have not been able to propose a realistic model of how such electrochemical cells might be configured in series. Even if such a model is possible, it would seem unlikely that it would be such a common configuration. Thus, I am also unable to account for the observed potential amplitudes with the Sato and Mooney (1960) model.

Arid regions.—Because they related the SP mechanism with the water table, Sato and Mooney (1960, p. 247) predicted self-potentials in arid country will be small. In contrast, Figure 7 shows an SP anomaly with an amplitude of -600 mV in Arizona. Poldini (1938) used the SP method successfully in desert regions. A number of surveys were run in arid portions of Nevada as part of the present study, and in my experience, SP surveys have been notably successful in arid environments unless the depth of weathering is such that the sulfide minerals have been destroyed by oxidation.

Arctic regions.—Sato and Mooney (1960, p. 247) stated the following.

An arctic region is not favorable for self-potentials. The low ground temperature retards the rates of chemical reactions. Permafrost and other frozen layers impede the ionic conduction greatly. Tundra vegetation and high water table tend to maintain a reduced condition even in the vicinity of the surface.

However, field experience does not support this prediction. For example, Figure 3 shows an SP survey run at about 39°N , at an average elevation of nearly 4 km. The minimum value of $-1\,386$ mV was found at an elevation of 4 200 m, with timberline at 3 500 m. The climate at that elevation is arctic. Semenov (1974) reported SP surveys in northern regions of the USSR, with favorable results. Surveys in Canada and Sweden have produced good results with self-potential surveys in arctic and subarctic regions. It would appear that just the opposite of the prediction by Sato and Mooney (1960) is true. The retardation of the chemical reactions by low temperatures actually enhances the measured spontaneous polarization by impeding the oxidation of the sulfide minerals responsible for the observed potentials.

Reducing conditions in the near-surface caused by tundra vegetation and high water table were encountered in an area about 15 km north of the area shown in Figure 6. In this area self-potentials in excess of $-1\,000$ mV were measured in a willow bog in tundra. The only problem I have encountered with near-surface reducing conditions occurs when the base electrode is located in such an area.

Gradients.—It is reasonable to assume the potential field

lines in the Sato and Mooney (1960) model would vary relatively smoothly around the orebody, and gradients would be small. However, Poldini (1938) found gradients at the surface on the order of 10 mV/m, measured in the field as 1 000 mV per 100 m due to the handling of the survey. The maximum gradients observed on the surface in our surveys were > 5 mV/m, or > 500 mV per 100 m (Figure 1).

If potential measurements are made downhole, then the gradients become even larger. Parasnis (1970) made downhole surveys in the Kimheden orebody, Sweden. The gradients in hole 65 at Kimheden approach 500 mV per meter, as shown in Figure 9. In our downhole logging operations, as the tool passed from the country rock into massive sulfides, the gradient was greater than the dynamic response of the instrumentation, and certainly exceeded 500 mV per m. In fact, where the contacts of the sulfide vein were sharp, the gradient was infinite for all practical purposes. I cannot account for the observed potential gradients using a model involving ohmic potential drops in any geologically realistic rock mass.

No positive pole.—With gradients of the magnitudes measured in the field, it is unlikely that a positive pole of the same amplitude as the measured negative potential can be far away. A positive pole with a larger amplitude and tied to several negative poles could be farther away, but the probability of finding a larger positive pole should be greater.

Current can flow as proposed in Sato and Mooney (1960) and Sivenas and Beales (1982a) only if both a negative and a positive pole exist. To investigate their half-cell mechanism, I proposed locating the positive pole(s) and then attempting to map either the potential field lines or the current lines around the postulated electrochemical cells. Beginning in the summer of 1978 and continuing through the summer of 1981, I searched for positive potentials above, below, and around sulfide deposits. As mentioned previously, a number of downhole SP logs were run, but none showed any positive SP anomalies. Since nearly fifty holes were logged, it seems likely that if a positive pole existed it would have been detected in at least one hole.

Becker and Telford (1965), Parasnis (1970), as shown in Figure 9, Malmquist and Parasnis (1972), and Logn and Bölviken (1974) all conducted extensive downhole logging programs without finding any positive anomalies associated with sulfide mineralization. Occasionally, their downhole logs did give an apparent positive reading as a result of referencing the downhole electrode to a surface electrode placed near the drill collar (Becker and Telford, 1965, p. 180), or an electrode placed in the mud pit or clamped to the drill collar, a standard practice with logging trucks. Since the area in the vicinity of the collar of a drill hole above sulfide mineralization will almost certainly be negative, if the hole continues below the mineralization the downhole log will move in a positive direction as mineralization is left. However, for a downhole log to detect a positive anomaly, the algebraic sum of the positive excursion and the *independently* measured potential at the reference electrode on the surface must be greater than zero.

Becker and Telford (1965, p. 182, Figure 7) is the most widely referenced evidence for a positive potential at depth. The downhole log in *their* Figure 7 shows a positive excursion of slightly more than 200 mV. However, a traverse on the surface in the area of the drill collar (the location of the reference electrode) indicates a negative potential of -600 mV. Thus, it is probable that the downhole log was still measuring a *negative* potential of as much as -400 mV, since the positive excursion is only

~200 mV. Semenov (1974) also showed some downhole logs with positive excursions, but again the surface electrode was at or near the drill collar, and the results are thus ambiguous at best. Malmquist and Parasnis (1972) and Logn and Bölviken (1974) avoided this ambiguity in their downhole SP curves by referencing their downhole SP logs to a survey base outside the sulfide system, and they have found only negative anomalies associated with sulfides.

I also looked laterally around a sulfide system for indications of a positive pole. A few holes drilled for engineering studies were available around an orebody. These holes were logged with a standard SP tool using conventional slim-hole techniques. No positive anomalies were found; the logs either remained negative or went to zero as the tool went out of sulfide mineralization.

A mine extending into the stock underlying a sulfide deposit was accessible. An SP survey was run in the main drift of this mine. The results are shown in Figure 8 together with the potentials measured on the surface above the drift. Figure 6 shows the surface SP map of the deposit. Both surveys are referenced to the survey base shown on Figure 6. As seen in Figure 8, the underground potential has a maximum negative amplitude 300 to 900 m from the portal. The maximum negative potential occurs well below the water table. From 200 to 600 m in from the portal, the potential underground is considerably more negative than on the surface. However, from lows of about -620 mV, which occur at distances of 500 and 850 m from the portal, the potential slowly decreases to about -110 mV at a distance of 1 700 to 1 800 m. At that point the survey is approximately 550 m below the surface and 130 m below the stockwork sulfides capping the stock. On the surface, the potential has reached its maximum amplitude of -870 mV. At the minimum potential, the underground survey is approximately 150 to 250 m from the boundary of the stock, encountered at about 1 550 m from the portal. As the far boundary of the stock is approached, the potential again goes negative, indicating that the minimum potential for this level has been reached without ever becoming positive.

The field data presented above provide no evidence that a positive pole exists in conjunction with the observed spontaneous polarization. In the absence of a positive pole, the measured potentials cannot be the result of current flow through the rock.

Water table.—Sato and Mooney (1960, p. 247)

... believe that most significant self-potential anomalies will prove to be associated with the water table. ... Self-potential exploration in underground mines appears to lack promise, since oxidation potential would vary slowly from place to place in the immediate vicinity of the cut surface.

Sivenas and Beales (1982b) recently reported on underground SP surveys done in the Viburnum Trend lead-zinc deposits in southeast Missouri. Figure 8 shows our results underground in the Colorado Mineral Belt. Downhole SP logs to depths > 1.5 km showed high-amplitude negative anomalies which correlated with sulfide mineral zones in the drill core. In fact, no relation with the water table has been observed. If the orebody does exist above the water table, as pictured by Sato and Mooney (1960, Figure 7), or Sivenas and Beales (1982a, Figure 1), it would appear that the SP amplitude is actually diminished as shown in Figure 4.

None of the field tests of the Sato and Mooney (1960) model, or the models of Sivenas and Beales (1982a) and Kilty (1984), has demonstrated that the measured potentials are the result of active electrochemical cells. In fact, several tests produced results the opposite of their predictions. Thus, the concept of active electrochemical cells producing the observed potentials does not appear to be tenable.

Constraints on mechanisms of spontaneous polarization

Before proposing any mechanism for the observed spontaneous polarization, constraints on the system imposed by the field observations must be considered. These constraints are as follows.

Amplitude.—The mechanism must be capable of producing *negative* anomalies with amplitudes up to at least 2 V, and possibly as much as 4 V.

Gradients.—The mechanism must account for the large gradients observed on the surface, and even larger gradients observed in the subsurface beneath the water table.

Presence of sulfides.—The observation that the measured spontaneous polarization correlates directly with the presence of sulfide mineralization imposes the requirement that sulfides be chemically stable in an environment within the electrical regime of the measurement.

Stability.—The available evidence indicates the spontaneous polarization is stable in time unless perturbed by erosion, weathering, or cultural artifacts such as drill casing, mining, etc.

Water table.—No simple relation between the water table or the presence or absence of liquid water and the observed potentials has been found.

Proposed mechanism

The lack of evidence for a positive pole in the underground measurements, together with the demonstrable stability of the sulfides through geologic time, implies that current flow between the sulfide mineralization and surrounding country rock must be sensibly zero unless disturbed. Therefore, the measured potential must be the result of perturbing an otherwise stable field by making an electrical connection between the country rock and the sulfides through the electrodes and the connecting wire used to make the measurement. The simplest mechanism for perturbing the stable field is by establishing a galvanic cell. The measured potential is then the oxidation potential ΔE between the two electrodes. In the field, ΔE will be the sum of all potentials acting on the circuit, but in a galvanic cell driven by sulfide oxidation the oxidation potential will dominate. For an oxidation potential to be generated, the separate environments of the reference and roving electrodes must be such that an electrical connection between them results in the *spontaneous* occurrence of electrode reactions which produce electrical energy that can be converted into useful work. If, however, both electrodes are in an environment where the reaction between them is not spontaneous, then no mechanism for generating electrical current exists, and no E_h is measurable unless energy is added to the system.

The highest oxidation potentials are observed if the reference electrode is located outside the mineralized system, in an environment similar to point A on Figure 10. Point A is the

approximate median Eh - pH level found at the surface in most areas (Sato, 1960; Hansuld, 1966), and the surface is generally characterized by intense weathering and oxidation. Eh in the weathering zone given in Sato (1960) will be a positive value with a magnitude of several hundred millivolts (Figure 10). In a well-aerated soil, the Eh could be as high as 1 V, and in a bog or other reducing environment the Eh could be near zero. While exact values for Eh in soils are difficult to obtain (see Garrels and Christ, 1965, for a discussion of Eh measurements), the work of Sato (1960) and Hansuld (1966) would suggest that Eh in most soils will fall in the range +400 to +500 mV at the surface.

If the roving electrode is placed in an area where pyrite is stable in the near-surface environment (for example in an environment similar to point B on Figure 10), the Eh will usually be a negative value with a magnitude of several hundred millivolts. If pyrrhotite is also present in the near-surface, then the Eh must be even more negative. If magnetite is also stable, Eh must be even more negative than with the presence of pyrrhotite. These relations are shown in Figure 10.

As an example of what might be measured in the field, point A on Figure 10 has an Eh relative to a standard hydrogen cell of approximately +410 mV. The Eh of point B relative to the same standard hydrogen cell is approximately -290 mV. Under ideal conditions, the ΔE measured in the field would

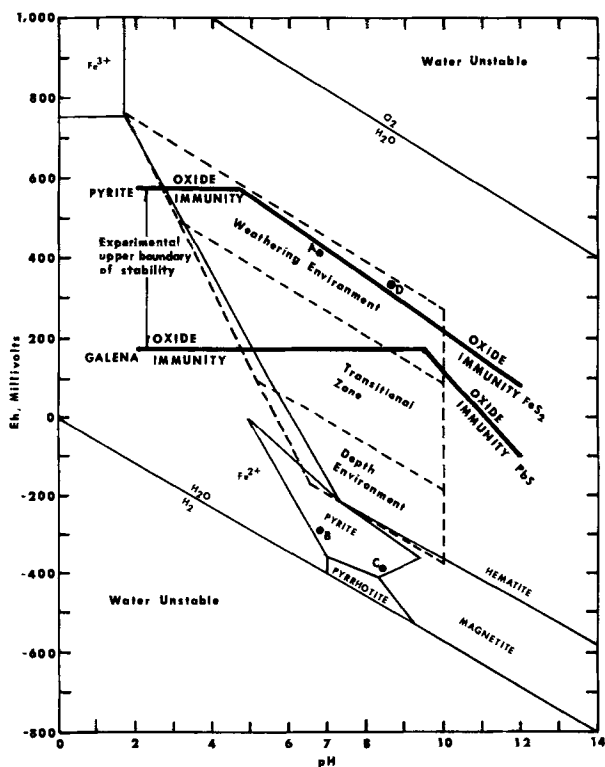


FIG. 10. Eh - pH diagram showing the weathering and depth environments of Sato (1960). Stability ranges for pyrite, pyrrhotite, and magnetite are from Garrels and Christ (1965, p. 223) with $\Sigma S = 10^{-6}$ and dissolved iron activity of 10^{-6} . If the values for dissolved sulfur and iron are not locally valid, then the stability fields will differ from those shown. The upper experimental stability boundaries for pyrite and galena are from Sato and Mooney (1960). Pyrite and galena represent the extreme stability range for common sulfide mineralization. Points A, B, C, and D are hypothetical Eh - pH conditions for base stations during an SP survey.

equal ΔEh measured between points A and B with a magnitude of 700 mV. Thus, if the reference electrode is placed in well-aerated, somewhat acidic soil outside the mineralization and is electrically connected to a roving electrode inside a mineralized zone with pyrite in the near-surface, the ΔE could easily approach 1 V. If pyrrhotite is also present, then the magnitude of ΔE will be even larger. From Figure 10, it is evident that within the stability range of water, a ΔE of 1 800 mV might be obtained. If the soil has no appreciable liquid water or is well-aerated, e.g., in a desert environment, it would seem reasonable to assume that the ΔE might reach even higher levels.

Eh is known to vary radically over short distances, and the observed gradients appear to reflect these variations in Eh .

In a region where sulfides are stable in the near-surface, the Eh is always negative relative to a point outside the mineralization. Thus, ΔE will always be negative. Regardless of the sign convention used, the electrodes must be located in areas where the ΔE between them results in a *spontaneous* reaction, or no potential will be generated.

The field observation that potentials from base stations located within mineralized areas did not tie with potentials obtained from base stations located outside the mineralized areas can be explained by the concept of immunity domains (Pourbaix, 1974), as shown for copper in Figure 11. Minerals in Eh - pH conditions where they are immune to oxidation are within their immunity domain. Thus, for potential measurements between two points, say B and C as shown in Figure 11, the ΔEh would be zero because copper does not oxidize under these conditions, and no *spontaneous* reaction can occur.

Assume a field survey is run on the surface so that base

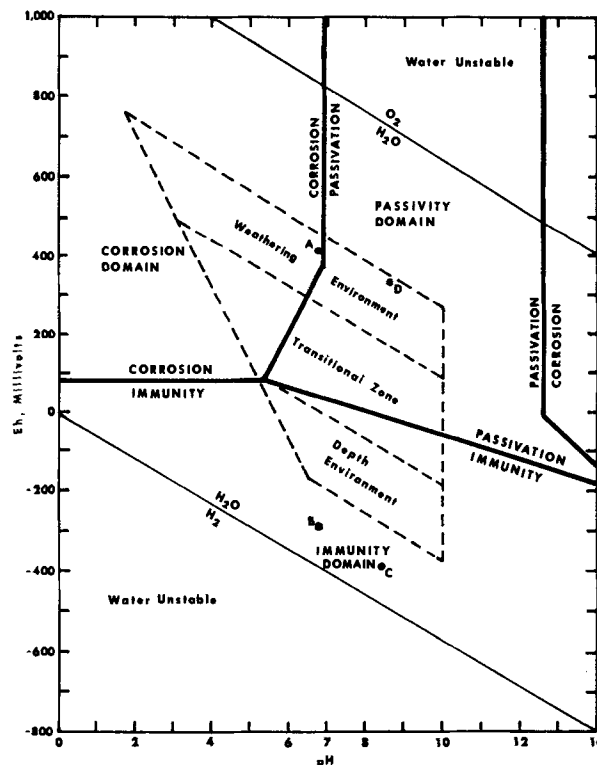


FIG. 11. Pourbaix diagram for copper, as given by Verink and Parrish (1970), superimposed over the weathering and depth Eh - pH conditions deduced by Sato (1960). Points A, B, C, and D are hypothetical Eh - pH conditions for base stations during an SP survey.

stations are established at points A, B, C, and D, as shown in Figure 12. Base stations B and C are within an area where sulfides are present in the near-surface. To be stable in the near-surface environment, the sulfides must be in an Eh - pH condition where they do not oxidize, i.e., they are within their immunity domain. The ΔEh between stations B and C will then be zero, because no spontaneous reaction can occur. Thus, the sum of the potentials between base stations $A \rightarrow B \rightarrow C \rightarrow D$ will not be equal to the potential measured between $A \rightarrow D$. The potentials referenced to base station A shown in Figure 12, i.e., $A \rightarrow B$, $A \rightarrow C$, $A \rightarrow D$, will all be valid because station A is located outside the immunity domain, as illustrated on Figures 10 and 11. Hence, a spontaneous galvanic cell, with potential ΔEh , exists for stations referenced to point A.

Under field conditions, the actual ΔE potential measured between stations B and C would probably never be exactly zero due to various mechanisms, including liquid junction potentials, streaming potentials, and differences in the soil electrolyte composition at the two sites. However, potentials measured relative to base stations within the mineralized area were commonly found to be much less than if measured relative to a base station outside the mineralization. In a similar manner, if the base station is located in a bog or other near-surface reducing environment, the ΔEh will be zero if the base station is within the immunity domain for the sulfides. With gradient array surveys, both electrodes may be located within the mineralized zone, or immunity domain, for the part of the survey that is of interest. The resultant signal loss makes gradient arrays particularly unsuited for mineral surveys.

In laboratory tests of the oxidation potential using galvanic cells, it is commonly observed that the oxidation potential decreases if the cell produces any significant amount of current. If the potential ΔE observed in the field is a measure of the ΔEh , it should therefore be possible to observe a decrease in the observed potential by drawing current from the system. However, if the observed potential lies on a field line from an active redox cell, as envisioned in Sato and Mooney (1960) or Sivenas and Beales (1982a), then no decrease in the potential should occur with time, because in their models the current is not produced by local electrolysis. On this basis an experiment was designed to observe possible time-dependence of the self-potential. An electrode located in the center of the -800 mV anomaly shown in Figure 6 and an electrode located approximately 4 km to the south of the anomaly were shorted together for 12 hours. The observed potential decreased from an initial value of -805 mV to -766 mV. After removing the short, the

voltage slowly recovered to -780 mV after 30 minutes. The results of this experiment are comparable to previously described effects of introducing drill casing, pipelines, or other similar cultural artifacts into an area where self-potentials exist. Because the experiment could not be continued due to weather, the results must be considered preliminary. Further experiments on other sulfide systems are recommended. However, the results to date support the contention that the observed potential ΔE is dominantly the ΔEh between points inside and outside the sulfide system. Therefore, in the absence of the wire connecting the electrodes, the current flow is sensibly zero between the sulfide mineralization and the surrounding country rock, which satisfies the condition imposed by the lack of an observable positive pole.

CONCLUSIONS

The spontaneous polarization technique is a fast, economical reconnaissance method of exploring for sulfide mineralization. The method has been underutilized in the United States, apparently due to problems with repeatability and reproducibility. Improved field techniques have virtually eliminated these problems, and the extensive surveys reported here have demonstrated again the effectiveness of the technique.

The amplitude and areal extent of an SP anomaly associated with sulfide mineralization are functions of the size and depth of the sulfide system, the volume, and the percent total sulfides. However, in practice it was found that the variables which primarily control the observed SP response are the amount of erosion since emplacement and the depth of weathering.

Field results (Figure 4) indicate that large porphyry sulfide deposits can be detected at depths > 1 km. However, the amplitude is reduced relative to a shallower deposit, and no direct method of distinguishing the SP anomaly over a deep deposit from the SP anomaly over a deposit at the surface with a thin cover of till or talus has been found.

In the present study, the anomalies of largest amplitude were found where erosion has exposed the QSP halo in areas where the climate or rock type is such that sulfide minerals are stable at or very near the surface. Continued erosion, or deep weathering, oxidizes the sulfides and causes the SP to die out. SP surveys over known deposits exposed at the surface showed haloes of weak to moderate SP anomalies (Figure 4) associated with remnants of the QSP zone. If erosion and/or weathering has proceeded to the point where only a resistant core of the orebody remains, essentially no measurable SP still exists. If erosion and weathering above the orebody have caused extensive supergene enrichment of the ore, then no SP anomaly is likely to be found (Figure 5). Self-potential surveys are still useful for reconnaissance around known surface deposits which do not themselves have an SP anomaly. Deeper, blind deposits may be unoxidized and have an SP anomaly associated with them. Figure 7 shows an example of an area where a deeper deposit gave a good SP anomaly, while the nearer surface, supergene-enriched deposit did not.

The mechanism responsible for the observed spontaneous polarization appears to be independent of time if undisturbed and to be stable over geologic time periods. No relation between the observed potential and the water table could be found. Stability through geologic time, together with the lack of a positive pole in, above, around, or below the sulfide mineral-

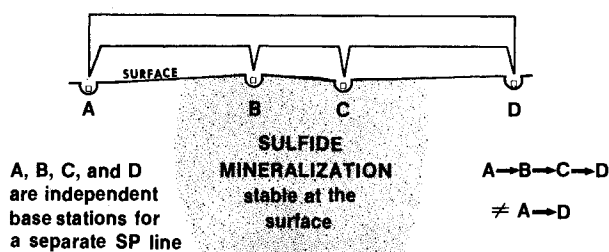


FIG. 12. Model showing the effects of locating the base station in mineralized areas.

ization indicates that current flow between the sulfide mineralization and the country rock is sensibly zero.

A number of tests of the Sato and Mooney (1960) model were made. The results were either negative or opposite to their prediction. The field data thus do not support the models presented by Sato and Mooney (1960), Sivenas and Beales (1982a), Kilty (1984), or similar models presented by others.

The potentials observed in the field appear to be a measure of the oxidation potential ΔE between the electrodes. In this context, it was found that the base-station reference electrode could not be located within the sulfide mineralization or within any near-surface reducing environment. The preliminary experimental results support the hypothesis that the observed potentials are the result of a galvanic cell established by locating the reference electrode outside the mineralized area and electrically connecting the reference electrode to a roving electrode in contact with the sulfide mineralization. In the absence of the electrodes and the connecting wire, no detectable current flows in the orebody or the surrounding country rock.

ACKNOWLEDGMENTS

The work on which this paper is based was done while I was employed by Climax Molybdenum division of AMAX, Inc. I would like to thank AMAX, Inc. for their kind permission to publish the field survey data. Particular thanks are due all of the field crews who worked so hard, often under adverse conditions in rugged terrain, to collect the data. The paper has greatly benefited from the suggestions and criticisms of Robert E. Campbell, Robert F. Corwin, Steven Fritz, Raymond Sadowski, and a number of anonymous reviewers. However, the conclusions are solely my own.

REFERENCES

- Becker, A., and Telford, W. M., 1966, Spontaneous polarization studies: *Geophys. Prosp.*, **13**, 173-188.
- Burr, S. V., 1980, A complete instruction booklet on self-potential surveying and prospecting: unpublished.
- Corry, C. E., DeMouly, G. T., and Gerety, M. T., 1983, Field procedure manual for self-potential surveys: Zonge Engineering and Research Organization.
- Corwin, R. F., 1973, Offshore application of self-potential prospecting: Ph.D. dissertation, Univ. of California, Berkeley.
- Corwin, R. F., and Hoover, D. B., 1979, The self-potential method in geothermal exploration: *Geophysics*, **44**, 226-245.
- Fedynsky, V. V., Brodovoi, V. V., and Gehamkov, V. A., 1970, Geophysics in prospecting and exploration for mineral deposits in the USSR, in *Mining and groundwater geophysics, 1967*: *Can. Geol. Sur., Econ. Geol. rep.*, **26**, 667-687.
- Fox, R. W., 1829, Some remarks on mineral veins & etc.: *Phil. Mag.*, **6**, 17-21.
- 1830a, On the electromagnetic properties of metalliferous veins in the mines of Cornwall: *Proc. Roy Soc. of London*, **2**, 411.
- 1830b, On the electromagnetic properties of metalliferous veins in the mines of Cornwall: *Phil. Trans., Roy Soc. of London*, **23**, part 2, 3rd series, 339-414.
- Garrels, R. M., and Christ, C. L., 1965, *Solutions, minerals, and equilibria*: Freeman Cooper and Co.
- Gay, S. P., 1967, A 1,800 millivolt self-potential anomaly near Hualgayoc, Peru: *Geophys. Prosp.*, **15**, 236-245.
- Hansuld, J. A., 1966, Eh and pH in geochemical exploration: *Bull., Can. Min. and Metall.*, March 1-8.
- Hulse, S. E., 1978, An investigation into the causes of steady state electrical potential differences occurring naturally on the surface of the earth: M.S. thesis, Univ. of Arizona.
- Kelly, S. F., 1924, Electrical prospecting in Canada, *Trans., Can. Inst. Min. Metall.*, **27**, 278-305; also *Bull., Am. Zinc Inst.*, **7**, 21-29.
- 1957, Spontaneous polarization survey on Noranda Mines, Quebec, 1924, in *Methods and case histories in mining geophysics (Canada)*: *Sixth Commonwealth Mining and Metall., Cong.*, 290-293.
- Kilty, K. T., 1984, On the origin and interpretation of self-potential anomalies: *Geophys. Prosp.*, **32**, 51-62.
- Kruger, F. C., and Lacy, W. C., 1949, Geological explanation of geophysical anomalies near Cerro de Pasco, Peru: *Econ. Geol.*, **44**, 485-491.
- Logn, Ö., and Bölviken, B., 1974, Self potentials at the Joma pyrite deposit, Norway: *Geoexpl.*, **12**, 11-28.
- Malmquist, D., and Parasnis, D. S., 1972, Geophysical documentation of a third-generation copper deposit in North Sweden: *Geoexpl.*, **10**, 149-200.
- Parasnis, D. S., 1970, Some recent geoelectrical measurements in the Swedish sulphide ore fields illustrating scope and limitations of the method concerned, in *Mining and groundwater geophysics, 1967 (Ottawa)*: *Can. Geol. Sur., rep.* **26**, 290-301.
- 1975, *Mining geophysics*, 2nd ed.: Elsevier Scientific Publishing Co.
- Pirson, S. J., 1971, New electric technique can locate gas and oil: *World Oil*, **173**, 69-74.
- Poldini, E., 1938, Geophysical explorations by spontaneous polarization methods: *Mining Mag.*, **59**, 278-282 and 347-352; also **60**, 22-26 and 90-94.
- Pourbaix, M., 1974, *Atlas of electrochemical equilibria in aqueous solutions*: Pergamon Press, Inc.
- Robinson, R. F., and Cook, A., 1966, The Safford copper deposit, Lone Star mining district, Graham County, Arizona, in *Geology of the prophyry copper deposits; southwestern North America*: Titley, S. R., and Hicks, C. L., Eds., Univ. of Arizona Press, 251-266.
- Sassen, R., 1980, Biodegradation of crude oil and mineral deposition in a shallow Gulf Coast salt dome: *Organic Geochem.*, **2**, 153-166.
- Sato, M., 1960, Oxidation of sulfide ore bodies, I. Geochemical environments in terms of Eh and pH: *Econ. Geol.*, **55**, 928-961.
- Sato, M., and Mooney, H. M., 1960, The electrochemical mechanism of sulfide self-potentials: *Geophysics*, **25**, 226-249.
- Semenov, A. S., 1974, *Electrical prospecting with the method of the natural electric field*, 2nd ed.: English translation available from C. E. Corry.
- Sill, W. R., 1983, Self-potential modeling from primary flows: *Geophysics*, **48**, 76-86.
- Sivenas, P., and Beales, F. W., 1982a, Natural geobatteries associated with sulphide ore deposits, I. Theoretical studies: *J. Geochem. Explor.*, **17**, 123-144.
- 1982b, Natural geobatteries associated with sulphide ore deposits, II. Field studies at the Viburnum Trend, southeast Missouri, USA: *J. Geochem. Explor.*, **17**, 145-160.
- Verink, E. D., and Parrish, P. A., 1970, Use of Pourbaix diagrams in predicting the susceptibility to de-alloying phenomena: *Corrosion*, **26**, 214-216.
- Wilckens, F., 1955, The basis of the self-potential method: *Zeits. Geophys.*, **21**, 25-40.
- Zablocki, C. J., 1976, Mapping thermal anomalies on an active volcano by the self-potential method, Kilauea, Hawaii: *Proc., 2nd UN Symp. Development Utilization Geothermal Resources, San Francisco*, **2**, 1299-1309.