

Electrochemical and electrokinetic aspects of porphyry copper systems: experiments and field observations

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ABSTRACT. — Experimental field and laboratory studies of porphyry copper systems indicate that recent electrochemical processes occur in the environment of large, vertically extended, semiconducting sulphide bodies. Vertical differences in oxygen fugacities cause specific electrochemical reactions around the sulphide mineralization, indicated by the dipole system with a negative self potential at the earth's surface near the deposits. As a result of electrochemical reactions, fluids with relatively high pH are formed at the cathode (top), while low pH fluids are formed at the anode (bottom) of sulphide bodies. Laboratory experiments show that high pH fluids move from the surroundings of the cathode towards the anode and being only partly neutralized by acidic fluids formed at the latter. The remaining acidic solution moves upwards for reasons of compensation wrapping the remaining high pH fluid. This onion-shell-like arrangement of the basic and acidic fluids around sulphide bodies is considered to maintain the potassic alteration zone and promotes sericitisation of the intermediate, quartz-sericite zone of porphyry copper systems, respectively. These two alteration zones, largely magmatic and transitional in origin, spatially coincide by and large with the presence of the two types of electrochemically altered fluids. At depth, sulphides are electrochemically oxidised to

sulphates such as anhydrite. The released Cu ions (and other electropositive ions) are captured by the electric field and do not dissipate far into the country rocks.

RIASSUNTO. — Gli studi sperimentali di laboratorio e di campagna sui sistemi di *porphyry copper* mettono in evidenza processi elettrochimici negli areali occupati da corpi solfurei semiconduttori abbastanza ampi ed estesi verticalmente. Le differenze verticali nelle fugacità d'ossigeno causano specifiche reazioni elettrochimiche attorno alle mineralizzazioni di solfuri indicate da sistemi dipolari con autopotenziali negativi nella superficie terrestre in prossimità di tali depositi.

In seguito a tali reazioni elettrochimiche, si formano fluidi con pH relativamente alto nel catodo (superficie superiore) mentre in corrispondenza dell'anodo (zone profonde) di tali corpi solfurei si generano fluidi a basso pH. Esperimenti di laboratorio indicano che i fluidi con valore di pH elevato si muovono dalle zone circostanti il catodo verso l'anodo e sono solo parzialmente neutralizzati da quelli acidi generati da quest'ultimo. Le soluzioni acide rimanenti si spostano verso l'alto per processi di compensazione avvolgendo i restanti fluidi con pH elevato.

Questa disposizione di tipo cipollare dei fluidi basici ed acidi attorno ai corpi solfurei è responsabile del mantenimento della zona di alterazione potassica e dell'innesco della

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sericitizzazione delle zone intermedie a quarzo e sericite dei sistemi di *porphyry copper*.

Queste due zone di alterazione, inizialmente magmatiche e transizionali, coincidono spazialmente con la presenza dei due tipi di fluidi alterati elettrochimicamente. In profondità i solfuri sono elettrochimicamente ossidati a solfati tipo anidrite. Gli ioni rame rilasciati (così come gli altri ioni elettropositivi) sono catturati dal campo elettrico e non si disperdono nelle rocce circostanti.

KEY WORDS: *Porphyry copper deposits, fluid flow, electric field, electrokinetics, geobattery, sericitisation.*

INTRODUCTION

Porphyry copper deposits are pluglike dikes and cylindrical plutons which may be 1 to 10 km in diameter (Gustafson and Hunt, 1975; Meyer, 1981). The ore normally occurs in rock fractures and is commonly zoned around a centre (Lowell and Guilbert, 1970; Guilbert and Lowell, 1974) with a vertical extension of several kilometres (Meyer, 1981). The epizonal environment is considered the hearth of the porphyry base metal deposit (Guilbert and Park, 1986). Exploited porphyry copper deposits represent the largest man-made open (e.g., Chuquibambilla/Chile, Bingham/USA) and underground mining operations (e.g., El Teniente/Chile) in the world.

An idealised, tectonically undisturbed porphyry copper deposit consists of a cylindrical ore shell of chalcopyrite with or without bornite within a zone of potassic alteration (Lowell and Guilbert, 1970; Titley and Beane, 1981; Beane and Titley, 1981; Guilbert and Park, 1986). This ore shell is partly overlapped by a phyllic alteration zone carrying abundant pyrite and lesser chalcopyrite (Fig. 1). Laterally, the alteration grades outwards to a propylitic zone (chlorite-epidote-carbonate) and upwards into an «advanced argillic assemblage» (Meyer and Hemley, 1967). The propylitic zone may represent either an early sheath around the potassic zone prior to the sericitic alteration or the result of weakening solutions from the

sericitic alteration. Much of the sericite-pyrite zone may also be superimposed on the K-silicate (Meyer, 1981). The sericite zone may taper out downward. It is generally accepted that the potassic, phyllic and argillic alteration reflects the interaction of host rocks with hydrothermal fluids, although some additional sericite and/or clay may also be added during supergene alteration (Sillitoe and McKee, 1996; Titley and Marozas, 1995). Most porphyry ore deposits have been once or repeatedly tectonically overprinted.

The diverse alteration processes are poorly understood (Titley, 1994) and much debated. The one-fluid concept of alteration is based on the consideration of the thermodynamic stability of the K-bearing minerals. Sericitisation of K-feldspar necessitates either a fluid with a decreasing activity ratio of K^+/H^+ at constant temperature or a fluid decreasing in temperature at constant K^+/H^+ (Fig. 2) or anything between these extremes. According to Beane and Titley (1981) changes in hydrothermal minerals are largely controlled by chemical effects and the phyllic assemblage should reflect low Na^+ , Ca^{2+} , and Mg^{2+} relative to K^+ in the fluid. Changes in H^+ concentration has not been discussed in detail, but is widely assumed.

The two-fluid model of alteration is based on hydrogen and oxygen isotope studies suggesting a magmatic fluid that produced the K-feldspar-biotite assemblage (Sheppard *et al.*, 1969, 1971). Post-mineralisation encroachment of meteoritic fluids on the central intrusion caused sericitic alteration. Initially, exogenic more or less acidic fluids, however, would render magmatic signatures due to water-rock interaction when moving toward the centre of the intrusion. Henley and McNabb (1978) proposed that a low density magmatic vapour entered the core of the intrusion and condensed to a high-salinity liquid in the carapace of the intrusion. Along the margins of the plume, condensed fluids were probably entrained into circulating ground water.

Beane and Titley (1981) summarised the properties of fluid inclusion studies as follows:

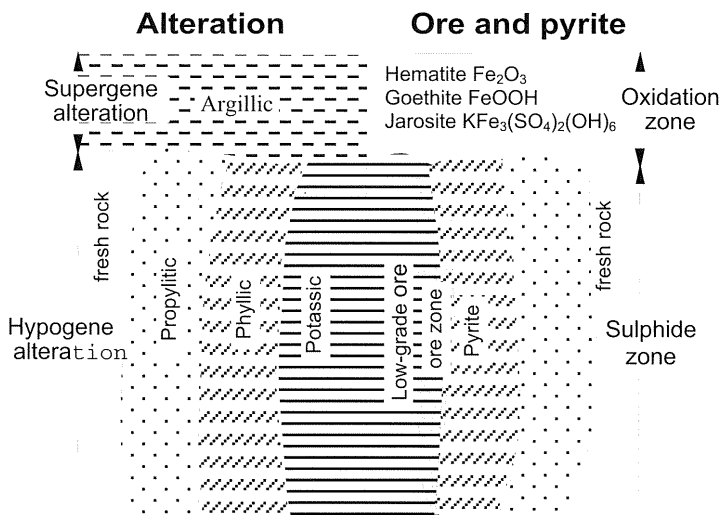


Fig. 1 – Idealised cross-section through the mineralization (right side) and alteration zones (left side) of a porphyry copper system redrawn after Lowell (1968) and Beane and Tittley (1981). **Propylitic** zone: chlorite-epidote-carbonate; **Phyllic** alteration zone: quartz-sericite; **Potassic** alteration zone: K-feldspar, biotite; **Argillic** alteration: quartz-kaolinite-chlorite; **Low grade ore** with low total sulphide contents; **ore shell**: pyrite, chalcopyrite, bornite, molybdenite; **pyrite** shell: pyrite with little chalcopyrite and bornite.

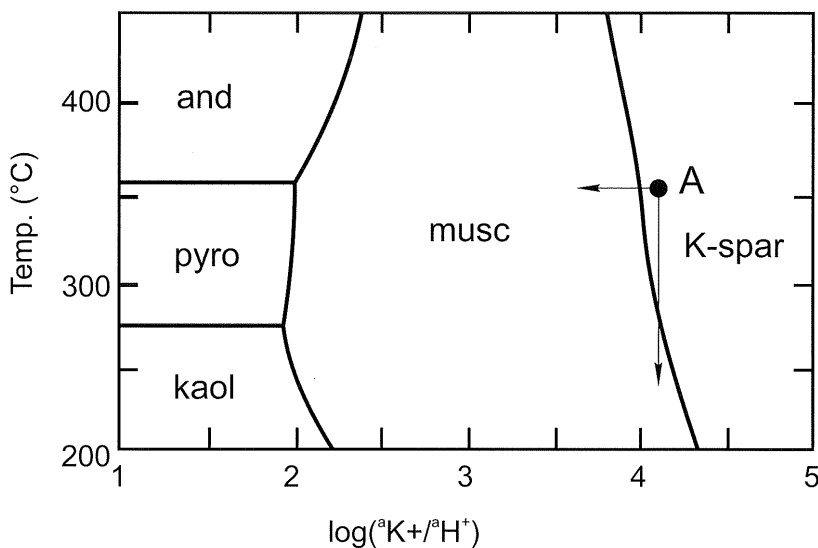


Fig. 2 – Stability of K-silicate minerals as a function of the activity ratio of K^+ and H^+ at 500 bars and quartz saturation (after Beane and Tittley, 1981). Starting from point A in the potassic zone, the arrows show that by decreasing temperature and/or decreasing log activity of the K^+/H^+ ratio sericitisation is possible. (and: andalusite; pyro: pyrophyllite; kaol: kaolinite; musc: muscovite, K-spar: K-feldspar)

(i) magmatic or early alteration fluids show high homogenisation temperature and salinity (>700°C; 30-60% NaCl-equiv.), (ii) halite-saturated fluids of intermediate temperature indicate inclusions that homogenise at 250-600°C and often indicate boiling systems, and (iii) late stage fluids are characterised by homogenisation temperatures of <450°C and salinities <20% NaCl-equiv. Guilbert and Park (1986) suggest that ore deposition took place from mesothermal boiling fluids (250-500°C, rarely 600-700°C, and 30-60% NaCl-equiv.).

The host rocks of some porphyry copper deposits (for example El Teniente and Los Bronces, both in Chile) contain large amounts of anhydrite, particularly at depth (Gustafson and Hunt, 1975; Camus, 1975; Warnaars, 1985). $\delta^{34}\text{S}$ of anhydrite and sulphide differ by 10 to 15‰ (Field *et al.*, 1983; Ohmoto and Rye, 1979). Field and Gustafson (1976) suggested that the early anhydrite-chalcopyrite-bornite assemblage with initial $\delta^{34}\text{S}$ of about 0‰ is associated with the potassic alteration, whereas the later anhydrite-pyrite-chalcopyrite assemblage with enhanced $\delta^{34}\text{S}$ between +5 and +10‰ is related to the quartz-sericite alteration.

Thus, there are several questions in particular concerning epigenetic post-ore sericitisation, which occurred later than propylitisation and potassic alteration and at low temperatures (200-350°C) and low fluid salinity. Although some supergene sericite might be formed by acidic fluids seeping from the top of the weathered ore body, the larger amounts seem to be of hypogene origin. A direct consequence of the former process would be a sericitic or argillic zone at the contact between the enriched blanket and the potassic alteration zone, which has never been reported as a significant feature. Thus, the hypogene sericite demands for an acidic fluid from depth.

CURRENT ELECTROCHEMICAL MODELS

In nature, any sulphide ore body forms a geobattery with the cathode at top and the

anode at depth (Sato and Mooney, 1960; Becker and Telford, 1965; Blain and Brotherton, 1975; Bolviken and Logn, 1975; Bolviken, 1978; 1979). Sivenas and Beales (1982a,b) defined two types of self-driving, galvanic cells:

- The oxygen concentration cell (OCC), which is considered to consist of an inert dipole electrode with difference of oxygen concentrations in the cathodic and anodic domain yielding the driving forces for the reactions; and

- the sulphide galvanic cell (SGC), in which the sulphides are dissolved at the anode, whereas, most likely, a reaction similar to that of the OCC occurs at the cathode.

In the OCC the ore body is thought to split into two half cells and to act only as an electronic conductor for the transfer of electrons from the anode to the cathode (Sato and Mooney 1960; Bolviken and Logn, 1975; Stoll *et al.*, 1995; Bigalke, 1996). In the SGC model the dipole electrode takes part in electrochemical reactions. The anodic reaction at depth is the galvanic corrosion of sulphides due to the aeration of the top of the ore body. The reaction of the dissolved oxygen in groundwater might be considered as the driving force of the cell. In nature, both types of electrode settings might occur side by side (Sivenas and Beales, 1982a). In terms of the OCC and SGC model the dipole field results from electrochemical processes, which yield a flow of H^+ ions in the fluid and electrons in the sulfide body, both heading from the anode to the cathode. The influence of also generated OH^- ions at the cathode is not considered (Bolviken 1979; Bolviken and Logn, 1975; Levinson 1980).

Contrasting the OCC model, Corry (1985) summarised experiences that contradict some fundamental assumptions made by the above cited authors. He finds that negative self potentials are bound to quartz-sericite-pyrite alterations associated with sulphide ore bodies, which is in agreement with our measurements in alteration zones of porphyry copper deposits in Chile (Timm and Möller, 2001).

Furthermore, the model cannot explain self potentials exceeding 1 Volt (Kruger and Lacy, 1949), no relation to the water table is observed, no positive pole could be detected so far, and the stability of self potentials imposes the requirement that sulphides are chemically stable in an environment within the electrical regime of measurement.

In a recent paper (Timm and Möller, 2001) published measurements of the redox-, self- and total potentials in Chuquicamata and Los Bronces mines, both in Chile. The local redox potential is interpreted in terms of local H^+ activity. The total potential is the sum of the self- and local redox potentials which are not always changing equi-directional.

Therefore, the aim of this study is to show that specific electrochemical reactions take place at both ends of the sulphide deposit generating fluids with high and low pH values at the cathode and anode, respectively, and thereby establishing a dipole field. The generated fluids of different pH values could be the cause of distinctly different alteration reactions such as those associated with porphyry copper deposits. It will be shown that (i) a constant dipole field is established, if the ore body is embedded in a environment of decreasing oxygen fugacity, and (ii) the various alteration zones differ in H^+ activity. The changes in H^+ activity are studied experimentally and in field measurements.

EXPERIMENTAL STUDIES

All sulphides are semiconducting materials and many of them (e.g. chalcopyrite and pyrite) show considerable electric conductivity. For example, between the isolated sulphide grains dispersed in non-conductive rocks in the dry open pit of Chuquicamata, Chile, the electric conductance is in the range of 10^{-3} S/m.

In order to study electrochemical processes associated with sulphide-bearing bodies, two types of experiments have been designed. The first type of experiments examines chemical

features of the electric potential field in aqueous systems. These experiments are conducted in tabular reaction cells with height:length:width of 20:30:2 cm (Fig. 3a). Chemically pure quartz sand (E. Merck) was treated with 0.3 to 1 M Na_2SO_4 solutions containing a pH sensitive indicator, for at least 2 days at a pH value of about 6.5, before it was flushed into a cell hosting two separate Pt mesh electrodes (not covered with Pt black) surrounding a polyethylene rod. The Pt mesh electrodes are connected to a DC power supply. After 2-3 days, the potential is fixed at 1.5 V with the cathode at top and the anode at bottom. Due to polarisation and electrolysis of water, OH^- and H^+ ions are generated at the electrodes and the solution turns blue (alkaline) at the cathode and red (acidic) at the anode (Figs. 3b-c). The registered electric current is in the range of about 1 μA .

The cells allow a study of the dispersion of OH^- and H^+ ions into the porous medium (about 45% porosity). After about 2 weeks, the two coloured fields visibly contact each other and neutralisation of OH^- and H^+ ions takes place (Fig. 3b). Again 2 weeks later, the upper coloured fluid field in Fig. 3c is distorted indicating that the OH^- bearing fluid generated at the cathode is replaced by neutral solution from the top as indicated by the arrows. The OH^- ions and anions of the dye characterising the fluid from the cathode slowly moves against the electric field which is only possible, if fresh solution moves from the surface of the sand package towards the electrode assemblage (Fig. 3d). Due to enhanced dispersion of H^+ ions the remaining acidic fluid starts to envelop the basic zone. The final result is that the space between the electrodes is mainly occupied by the high pH fluid which is wrapped by a shell of the low pH one.

In experiments, where three vertical sets of electrodes are arranged in the same cell but at various distances from the surface, each set develops its own system of fluid movement (Fig. 3e) at least if the distance of the electrodes in each assemblage is less than the distance between the different systems.

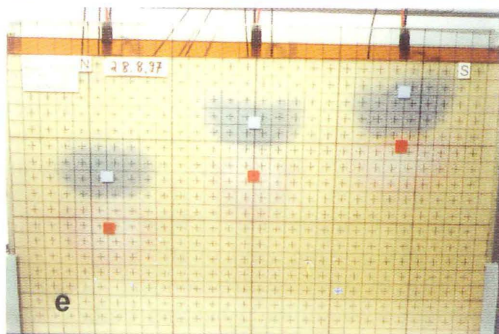
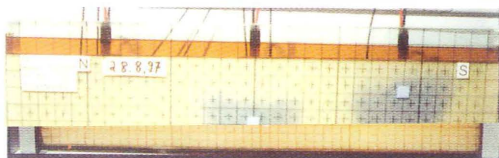
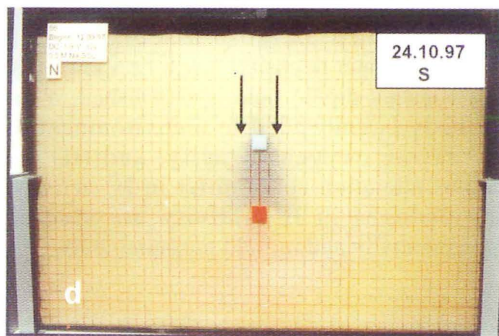
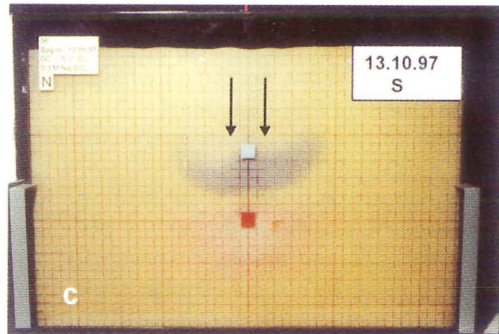
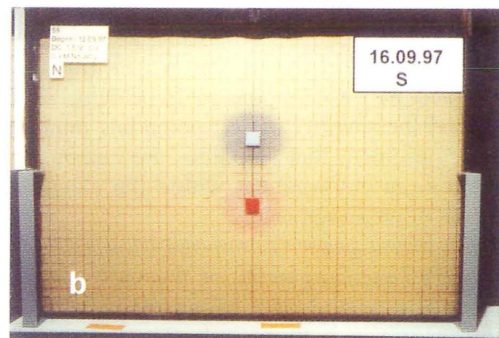
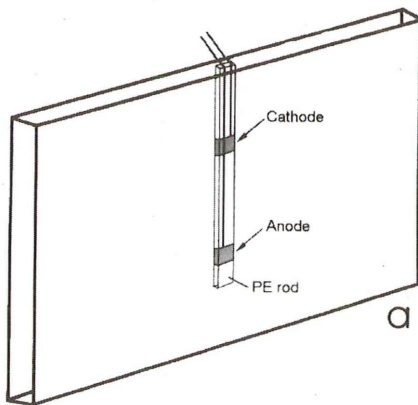


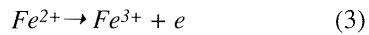
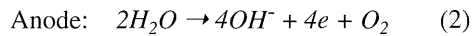
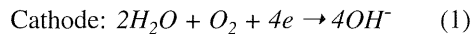
Fig. 3 – Photographic reproductions of the vertical front plate of a tabular, experimental cell (a) filled with sand and 0.3 M Na_2SO_4 solution at pH 6.5 containing a pH sensitive dye. The blue and red coloured labels in (b-d) indicate the position of the Pt-mesh electrodes, at which OH^- and H^+ ions are generated and makes the solution blue and red, respectively. After four days electromigration of ions lead to radial distributions around the electrodes (b). Four weeks later, the radial distribution is deformed and, particularly, the alkaline solution shows that it is being replaced by a fresh one from the top (c). After another six weeks, the alkaline solution is only present in the range between the electrodes (d). The time dependent distribution of the deformed, coloured fields indicate the development of induced movement of the alkaline solution across the electrode arrangement downwards (arrows), the acidic solution ascends at greater distance from the electrodes. Three assemblages of electrodes at different covers of sand are driven by the same DC voltage of 1.5 V. These three systems do not interfere with each other and develop in the same way as shown in b to c (e).

The second type of experiment simulates the action of a geobattery (Fig. 4). The pyrite electrodes are manufactured by attaching a copper wire to pyrite plates cut from the same lump of massive pyrite. This mounting is immersed in epoxy resin in order to seal all fissures and pores. After hardening of the resin, the site opposite to the fixed Cu wire is cleaned of resin by grinding. All half cells of the sulphide electrodes and the Ag/AgCl reference electrode are filled with 3 M KCl solution and are linked by agar-filled electrolyte junctions. Flushing the cells with either air or nitrogen (the latter being produced from liquid nitrogen) turn them into cathode or anode, respectively.

After about one hour, constant potentials are registered for both half cells relative to the Ag/AgCl reference electrode. Coupling the sulphide electrodes by a variable load, the electric current in each half-cell is changed from zero to maximum current densities, by which the potentials decrease and increases at the cathode and anode, respectively. When plotting the absolute anodic and cathodic current densities vs. the measured potentials

(relative to the Ag/AgCl electrode) Fig. 5 is obtained, in which the extrapolated horizontal sections represent the exchange current densities at the electrodes under equilibrium conditions (Bockris and Reddy, 1977).

A detailed inspection of the surface of the electrodes after a long-time experiment at the corrosion potential reveals that the cathode is still fresh but the anode shows brownish to red spots indicating the formation of oxidised iron compounds. This proves that oxidation processes occurred at the anode, although it was in the N₂-flushed environment. The fundamental electrode reactions could be:



Any anodically produced O₂ (reaction (2)) is immediately consumed by oxidation of other ionic species like Fe²⁺. Reaction 3 represents the direct oxidation of Fe(II). Evidence for reaction (4) could not be found.

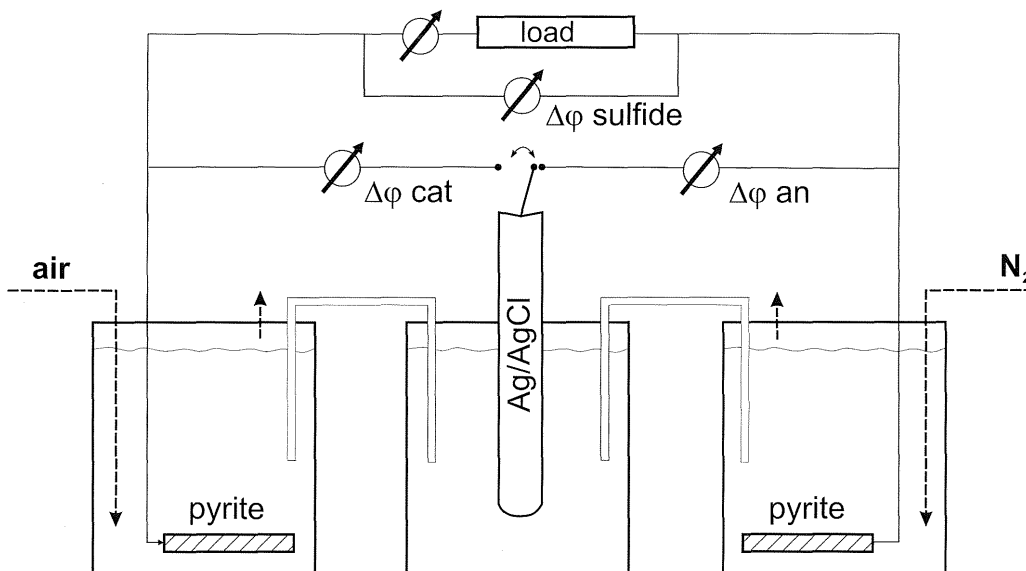


Fig. 4 – Design of a self-driving cell arrangement containing sulphide electrodes under air and nitrogen coupled to a Ag/AgCl reference electrode. The load allows the variation of the resistance between 10⁶ and 0 Ohm.

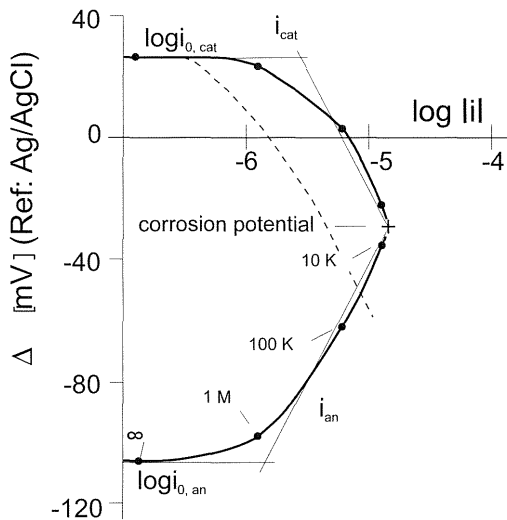


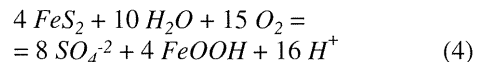
Fig. 5 – Plot of potential vs. logarithm of the absolute current densities induced by electrochemical reactions at the surfaces of the sulphide electrodes. All data are read after 30 min and can be considered to represent a transient equilibrium. $i_{0,cat}$ and $i_{0,an}$ represent the exchange current densities at the cathode and anode, respectively. The corrosion current density and corrosion potential are defined by the intersection of both trends lines. The dotted line shows the influence of decreasing exchange current densities on the trend of the cathodic potentials and on the corrosion potential (Bockris and Reddy, 1977).

MEASUREMENTS OF ELECTRIC POTENTIALS IN THE FIELD

Since the reported experiments indicate considerable differences of redox potentials between the basic and acidic solutions, the experimental results on redox potentials will be compared with field measurements of redox potentials between the zones of potassic and sericitic alteration in the dry open pit of the Chuquicamata mine, Chile.

In-situ redox potentials are measured on rock surfaces between a Pt electrode and an Ag/AgCl reference electrode (both from Mettler Toledo) placed at distances of 15 to 30 cm (Timm and Möller, 2001). The rock surface is cleaned of dust, sprayed with water, and two separated clots of wet, commercial bentonite with a pH value of 7.7 at 20°C are pasted onto

it. Into each clot a polyethylene ring with a stopper is pressed. The stopper has a hole through which the electrode is inserted. Both electrodes are slowly pressed through the clay onto the surface of the rock. The electrolyte contact is established and maintained by the wet clay. The clay-rock redox potential at the interface (from hereon termed clay potential) is varied by ionic interaction with the underlying rock. The readings started with values much higher than the final ones and decreased by 20 to 100 mV with time. Because the redox potential was measured when the changes of readings were 1 mV/min, it follows that the long-time redox potential would be lower than the registered one. The observed, slow approach to a final value might be due to ion exchange between rock and clay, reaction of oxygen with sulphide minerals at the rock's surface (eq.4), and/or changes of the oxygen fugacity in the wet bentonite (eq. 5):



$$Eh = 1.23 + 0.015 \log (fO_2) - 0.059 pH \quad (5)$$

Across bench O1 near the bottom of the very dry open pit of Chuquicamata, Chile, the potassic zone shows lower Eh values than the quartz-sericite zone (Fig. 7). Assuming constant local oxygen partial pressure during the measurements of the clay potentials and neglecting other redox active couples, eq.(5) can be used to convert measured clay potentials into pH units (Fig. 8). The pH axis is calibrated by the measured pH value of the clay of 7.7 and the theoretical slope of 0.059 mV/pH at room temperature. In both alteration zones the values scatter around specific means, yielding a potential difference of about 60 mV, which corresponds to about one pH unit at room temperature. Thus, it is qualitatively confirmed that the quartz-sericite zone shows higher Eh values than the potassic zone, which is in good agreement with the pH difference visualised in our described experiments (Fig. 3).

DISCUSSION

The porphyry copper system as a geobattery

In any galvanic cell the maximum potential difference at equilibrium is lowered under current flow, i.e. when reactions take place at both electrodes (Fig. 5). Depending on the specific conductivity of the ore body, the established potential difference is always less than the maximum value. In porphyry copper systems with their low electric conductivity, the exchange of electrons between the electrodes is hampered. In terms of Fig. 5 the working point of the geobattery might be well in the range of the horizontal segments of the $\log/i/$ vs. ϕ curves, i.e. they work near to equilibrium conditions. As shown schematically in Fig. 5, the actual potentials of the electrodes under current depend on the exchange current

densities which in turn depend on structure and composition of the electrodes and the solution-solid interface (Bockris and Reddy, 1977). Lowering the cathodic potential, e.g. under conditions of reduced exchange current density $i_{o,cat}$ (dotted lines in Fig. 5) has a positive effect on electrochemical reactions taking place at the enhanced negatively biased cathode. Under such conditions the electrochemical reduction of O_2 at the negatively charged surface is favoured by the lowered activation energy E_{η} as shown schematically in Fig. 8 (Bockris and Reddy, 1977).

In order to discuss electrochemical reactions and electrokinetic effects it is necessary to sketch an electric circuit that simulates typical electrical conditions of a porphyry copper system (Fig. 9), based on the various experimental results. Different from those

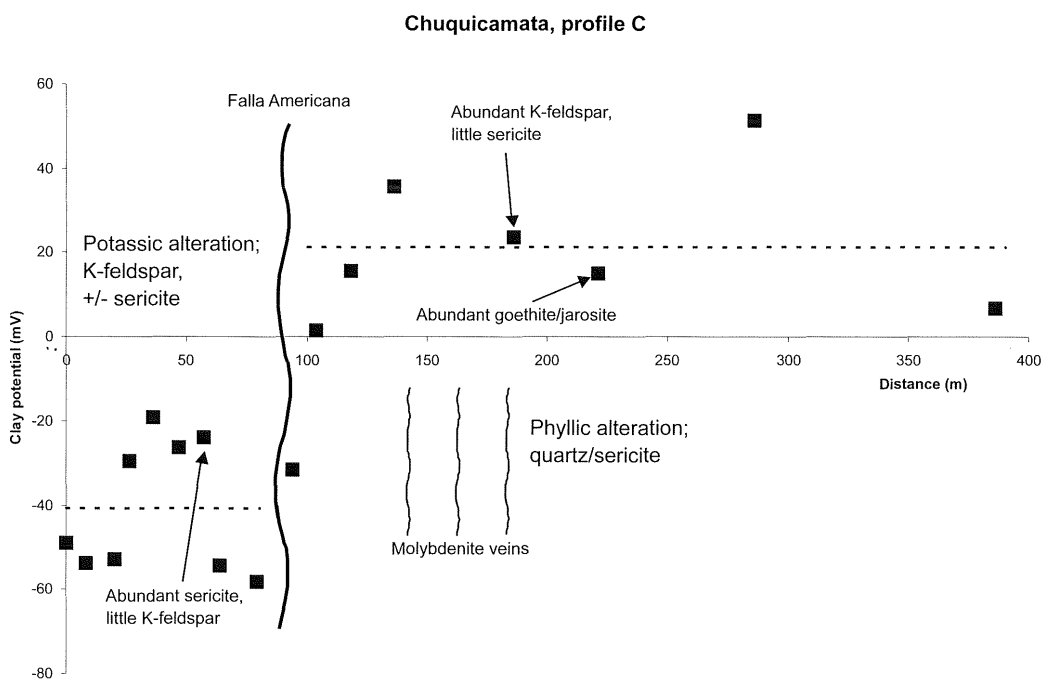


Fig. 6 – Plot of measured clay potentials across the lithologic boundary of the potassic and quartz-sericite zones at the lowermost bench in the open pit of the Chuquicamata mine. In the dry open pit of Chuquicamata the sericite zone qualitatively show the expected higher potential than the potassic zone. Dashed lines indicate the arithmetic means of the clay potentials of both zones.

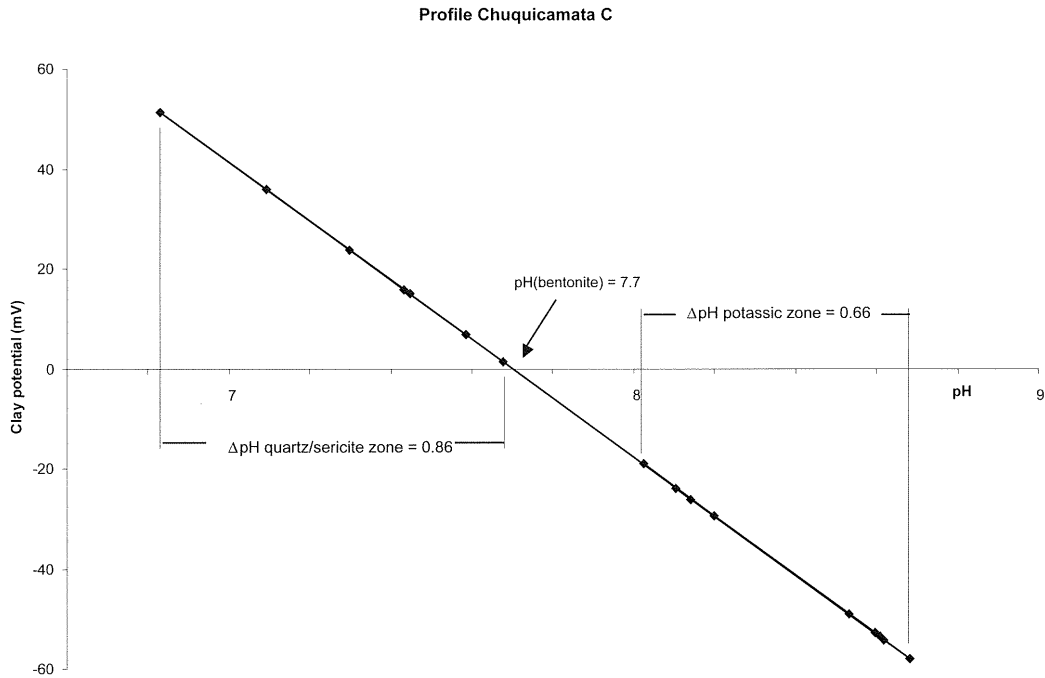


Fig. 7 – Interpretation of clay potentials in terms of pH values that are established at the clay-rock interface, assuming that no other redox process is acting than assumed in eq. (5). The pH axis is calibrated by the pH of the wet clay, which yield pH 7.7 at 20°C. The slope of the calibration line is assumed to be 0.059 mV/pH. The resultant pH at the clay-rock interface in the potassic zone is alkaline, but neutral to weakly alkaline in the quartz-sericite zone.

being already published (Sato and Mooney, 1960; Becker and Telford, 1965; Blain and Brotherton, 1975; Bolviken and Logn, 1975; Bolviken, 1978, 1979; Sivenas and Beales, 1982a,b) additionally OH^- ions are involved.

For three reasons the electrochemical process at the cathode might be the rate controlling step: (i) low solubility of oxygen in groundwater, (ii) consumption of oxygen in the weathering zone of the deposit, and (iii) the anode-reacting domain being much larger than the cathodic domain. Some of the released Cu(I) at depth might move in the electric field towards the cathode, where it is electrochemically or chemically precipitated in the «enriched blanket» together with the infiltrating dissolved copper from the weathering zone at the very top of the ore body. The electric field concentrates Cu from both sources in the cathodic domain.

Given an electric field, fluid flow is induced in porous media by electrochemical effects as shown by the reported experiments. Fluid flow is caused by two effects:

- The generated OH^- and H^+ ions at the cathode and anode, respectively, (electrolysis) have to be charge-compensated for reasons of electroneutrality of the system which is achieved by migration of hydrated ions and counterions moving in opposite directions (electro-migration), and

- the walls of all pores are electrically charged (mostly negatively) with the corresponding countercharge in the adjacent fluid, which may give rise to an unipolar current in capillaries (electro-osmosis).

By friction mainly the cations with their voluminous solvation shells drag along a water column in tiny pores. The superposition of electro-migration and electro-osmosis seems to

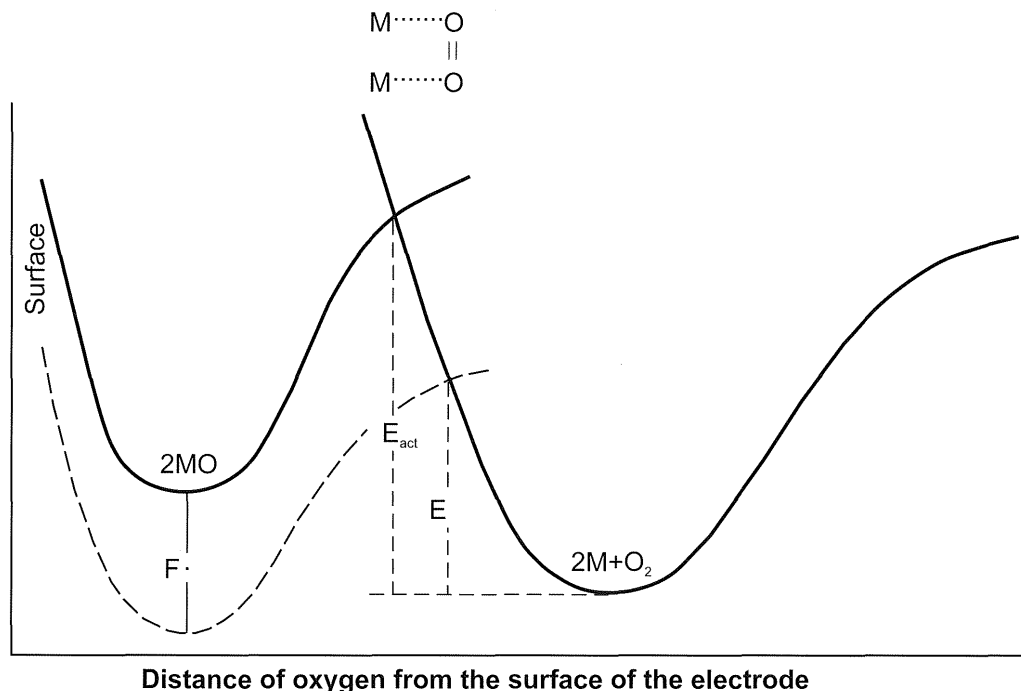


Fig. 8 – Schematic representation of the Morse curves (after Bockris and Reddy, 1977) which describe the change in potentials as a function of the distance between the reactants showing the two assumed reactions steps (i) the dissociation of oxygen bonds at the surface and (ii) the formation of metal-oxygen compounds MO at the electrode surface, where M represents any reaction centre. The overlap of the two curves define the chemical activation energy E_{act} . Because the respective curve for (ii) can be lowered by a negative overvoltage h of the surface of the reactant M, the electrochemical activation energy E_{η} for this process is much less than E_{act} in case of the purely chemical reaction. At a negatively biased surface (cathode) the reaction of chemisorbed oxygen with water in order to form OH^- ions is energetically favoured.

yield a net fluid flow from the top to the bottom at least at the low potential differences as present in natural systems. A more quantitative discussion of the electrokinetic effects will be given elsewhere. The dispersion of H^+ exceeds by far that of the slower OH^- ions. For this reason, OH^- ions dominate H^+ ions in the space between the electrodes. This controls the confined distribution of the basic fluid in Figs. 3c and d.

Chemical changes of fluids and mineralogical alterations

The chemical changes in the ambient fluids of the electrodic domains (Fig. 9) may induce alteration of the country rocks and in the post-

ore sedimentary cover. Chemical anomalies in post-ore cover have already been suggested by Bolviken (1978; 1979) who discussed «secondary redox potentials» at the earth's surface that might be applied to exploration.

The electrochemically generated alkaline fluid prevents the oxydation of the sulphide body in two ways, (i) acidic solutions infiltrating from the zone with intensive weathering are neutralised, and (ii) the residual oxygen of the infiltrating fluids are electrochemically consumed by reaction (1). As may be derived from the experiments, the alkaline fluid tends to move across the ore body downwards and partly neutralises the acidic fluid formed at depth. The remaining,

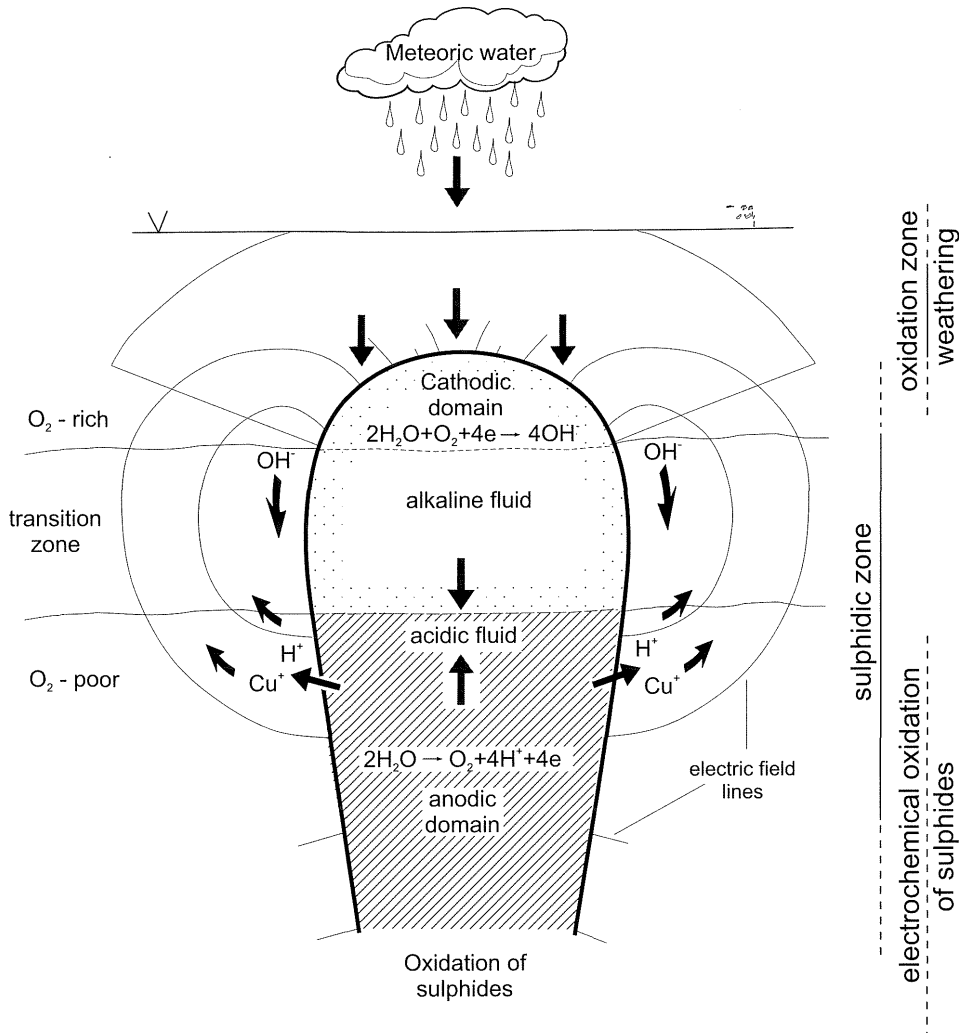


Fig. 9 – Schematic sketch of a porphyry system linking an oxygen rich and poor zone. The sulphides are part of the central body (within the bold line boundary) and act as an electron conductor. By electrochemical reactions alkaline and acidic fluids are generated at the stippled and dashed surface areas. The given electrochemical reactions represent fundamental ones but others (eqs. (3) and (4)) could also play a role. The alkaline fluid neutralises the acidic fluids from the oxidation zone infiltrating the sulphide zone. The residual alkalinity stabilises the potassic zone or reacts with the acidic fluids ascending from depth. At the bottom oxidation of sulphides occur according to eqs. (3) and (4) which might lead to formation of anhydrite.

upwards moving low pH fluid generated at the anode wraps the downwards moving, remaining high pH fluid. Across the contact zone of both fluids neutralisation occurs.

Under natural conditions the basic fluid

stabilises K-feldspar and biotite, the main components of the earlier formed potassic zone, whereas the acidic fluid favours sericitisation of K-feldspar and mica of the earlier alteration. The released K⁺ ions, like the Cu⁺ ions, are

captured by the electric field and are directed towards the cathodic domain, where they may be consumed by secondary biotitisation and formation of bornite in the potassic zone, respectively. Thus, the two pronounced alteration zones coincide with the presence of the two types of fluids resulting from essentially the same meteoric fluid but altered by electrochemical reactions at the ore body.

In the anodic domain considerable mass oxidation must occur for which the increasing contents of anhydrite with depth of porphyry systems may give evidence (Guilbert and Lowell, 1974; Gustafson and Hunt, 1975). It may be argued that most of the oxidation products are formed in magmatic or «transitional» processes as defined by Burnham and Ohmoto (1980), however, according to their reported diagram anhydrite is only in equilibrium with magnetite at temperatures below 300°C and 1 kbar. At higher temperatures only SO₂ is formed and arguing that this SO₂ forms the sulphate still leaves the question unanswered from where the necessary oxygen is derived? The described electrochemical model also yields a simple explanation for the presence of oxidation products such as anhydrite at depth. According to this idea, some of the anhydrite of the quartz-sericite zone might be epigenetic.

CONCLUSIONS

Assuming that the experimental studies simulate typical features of a natural self-driving, galvanic cell as represented by porphyry copper systems (Fig. 9) it follows:

- electric fields are established due to the presence chemical gradients of, e.g., oxygen in the earth's crust. In case of vertically extended porphyry copper deposits this leads to cathodic and anodic domains at the top and bottom, respectively,

- basic and acidic fluids are formed by electrochemical reactions across cathodic and anodic domains of the ore body, respectively, and

- fluids move along the ore zone from top to bottom.

The interaction of the fluids leads to chemical and mineralogical alteration of the host rocks. Although most of the hydrothermal alteration is magmatic to post-magmatic («transitional» after Burnham and Ohmoto, 1980) in origin, the anticipated electrochemical reactions yield obviously similar results. Since the latter only came into action after considerable erosion of the overburden of the porphyry systems, i.e. meteoric water with dissolved oxygen had access to the ore body, the electrochemically induced alteration is later than the magmatic ones. The electrochemically generated fluids, basic at top and acidic at depth, tend to conserve the earlier established hydrothermal alterations. In the more alkaline environment K-feldspar and biotite are stabilised, whereas the H⁺ ions are consumed by sericitisation of residual K-feldspar and biotite of the quartz-sericite zone and the adjacent potassic alteration yielding secondary or late sericite. Thus, the alteration is the result of both early magmatic and late electrochemical processes, the contribution of which have still to be studied in detail. It cannot be just by chance that the two pronounced alteration zones of porphyry systems are met by fluids that correspond with the mineralogical composition of the former. It rather turns out that the porphyry system as a whole is a passive, self-organising system with the remarkable tendency for conservatism of its alteration zones and metal content.

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