Redox-induced spontaneous polarization as a cause of large self potential anomalies over disseminated sulphides and other buried features

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Self potential (SP) has been used for over 150 years as a passive geophysical exploration tool but the cause of SP anomalies over sulphide ore bodies remains the subject of debate. The most prevalent theory for their formation is the dipole model (Figure 1) which argues that the difference in oxidation potential between the top and bottom of a metallic ore body results in upward movement of electrons through it, and a return current in the surrounding country rock. For reasons described below, SP dipoles should not exceed about 400 mV above sulphides or slightly more above graphite. Also, according to the dipole model, disseminate sulphides should produce no SP phenomenon at all because a continuous metallic or semi-metalically bonded conductor between the oxidants and reductants is required. Thus, the dipole model has been recognized as problematic for decades since disseminated sulphides are often reported to have large SP anomalies not uncommonly exceeding 1000 mV (e.g. Corry, 1985; Goldie, 2002).

Many numerical SP models exist but these largely describe the responses to be expected on surface due to buried polarized metallic bodies of various shapes, attitudes and depths. The models do not generally attempt to describe the cause of the polarization in the first instance and are therefore empirical. Also, since they are ultimately based on the dipole
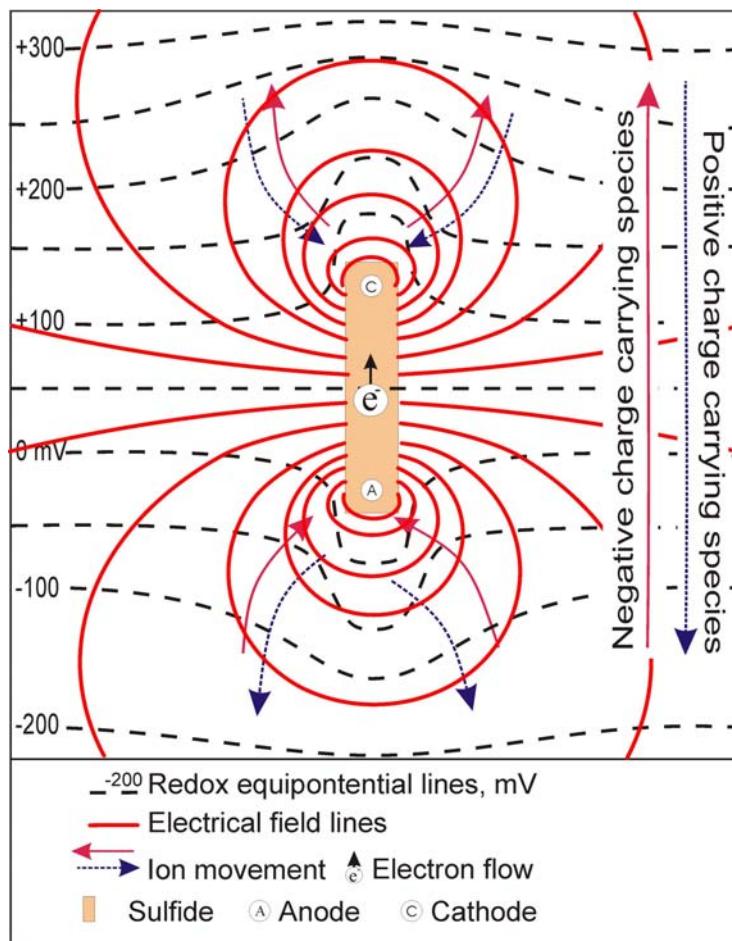

Figure 1. The dipole model. An electronic conductor in an electrolyte with a vertically increasing redox gradient develops an electrical polarity (modified after Hamilton, 1998 and Govett, 1976).

model, they are subject to its limitation, including the inability to account for responses over disseminated sulphides.

This paper proposes a new model that accounts for the presence of SP anomalies and is different from previous theories because it accounts for responses over both disseminated and massive sulphides.

The dipole model for the formation of SP over metallic orebodies

Schlumberger (1920) noted during his early resistivity surveys that sulphide bodies spontaneously generate electric currents with significant voltages, the equipotentials of which often outline the orebody. In his concise, elegant paper he proposed that SP occurs because of uneven galvanic corrosion of the sulphide as it is immersed in a groundwater electrolyte of unequal oxidation potential (*uneven* corrosion is required because without separation of oxidants and reductants, there would be no electron flux and therefore no SP phenomenon in the surrounding country rocks).

In another seminal paper, Sato and Mooney (1960) argued that SP around a single phase sulphide body cannot result from the oxidation of the sulphide itself because as the ore oxidizes, it does so locally in the upper oxidized environment and this will not result in a polarization of the ore body. Rather, the presence of SP demonstrates that the sulphide acts as a wire in an electrolyte that conducts electrons from reducing agents in the groundwater environment at depth to oxidizing agents near surface. In the groundwater around the lower part of the ore body, the presence of stronger reducing agents than the ore itself is evidenced by (i) the continued presence of the ore and (ii) by the presence of an SP phenomenon. If the groundwater at depth were more oxidizing than the ore, the entire ore body would oxidize whereas if it has an oxidation potential equal to that of the ore, the ore would oxidize locally in its upper part. In either such case, there would be no polarization of the ore body and therefore no SP.

Likewise, for the ore body to polarize, the oxidation potential of the environment surrounding the upper part of the ore must exceed that surrounding its lower part. However, if the oxidation potential near surface significantly exceeds the oxidation potential of the ore itself, as occurs in the unsaturated zone, the shallower ore will oxidize directly. Only the component of voltage that results from the difference in oxidation potential of the ore versus that of the groundwater environment at depth will contribute to the polarization of the ore body and development of SP. Sato and Mooney (1960) explain this quantitatively using the concept of "immunity domain" of ore materials. They demonstrate that ore materials with differing oxidation potentials are capable of producing specific SP voltage maxima. Graphite and sulphide bodies are capable of producing the highest voltages, which amount to approximately 800 mV. This would result in an SP anomaly on surface of about -400 mV, when referenced against a distant electrode on surface. Sato and Mooney (1960) state that this model is unable to account for SP anomalies exceeding 1 volt.

Thornbur (1985) pointed out that oxidation of the sulphide itself can result in an SP if the ore contains multiple phases with different oxidation potential. His model is very similar to Sato and Mooney's except that electrons are provided by the oxidation of a more reduced sulphide, which alters to a less reduced phase that is still electrically conductive. He cited an example in Australia where the upper several hundred metres of a pyrrhotite-rich ore body has phase-converted to pyrite due to such a process.

Redox-induced spontaneous polarization

Despite its limitations, the dipole model is widely accepted and in specific cases is well supported by field observations. However, it does not account for SP responses over disseminated sulphides or any other deposit where the SP voltage exceeds 400 mV. Corry (1985) reported SP responses over porphyry deposits that commonly exceed 500 mV and Goldie (2002) reported sustained SP anomalies that in some cases exceed 10,000 mV above silicified gold mineralization at Yanicocha in Peru.

SP responses exceeding 750 mV are not only unexplainable by the dipole model; they exceed the theoretical upper limit of all single-cell aqueous electrochemical cells. A cell with a total voltage over 1500 mV (750 mV per electrode) exceeds the electrochemical limits of water stability and will result in its decomposition to hydrogen at the cathode and oxygen at the anode. The presence of water in all SP systems therefore limits the overall voltage of a single dipole conductor. As mentioned, voltages are further limited by the nature of the conductor.

The dipole model relies on differences in oxidation potentials from one end of the conductor to the other. For a number of years exploration geochemists have been describing redox gradients that range from millimetres to kilometres in scale. The Earth's crust represents a large-scale redox gradient that is oxidizing upward (Bolviken, 1979). As predicted by the dipole model, electronic conductors within this tend to polarize and develop a negative pole on their upper end (Bolviken and Logn, 1975; Govett, 1976). More recently, 'reduced chimneys' have been described over ore bodies and other buried reduced features (e.g. Hamilton et al. 2004a & b; Hamilton and Hattori, *in press*) that are associated with very strong redox gradients, both horizontally and vertically. The color-transition between oxide caps and underlying sulphides that are commonly observed over porphyry-type ore systems are visible expressions of strong redox gradients.

We argue that disseminated sulphides, or any other polarisable substances, that occur within strong redox gradients will polarize with a negative pole developing in the oxidizing (positive) redox direction (Figure 2). In a process that is exactly analogous to that of the dipole-model, each isolated sulphide grain develops an SP cell around it, driven by the slight oxidation-potential difference between each end of the grain. The voltage developed by each grain dipole would be miniscule but grains that are end-on are the equivalent of batteries stacked in series and therefore the voltages are additive.

Unlike the dipole model, there is no theoretical upper limit to the voltage that could be developed in such a system and as a result, where conditions are ideal, overall voltages
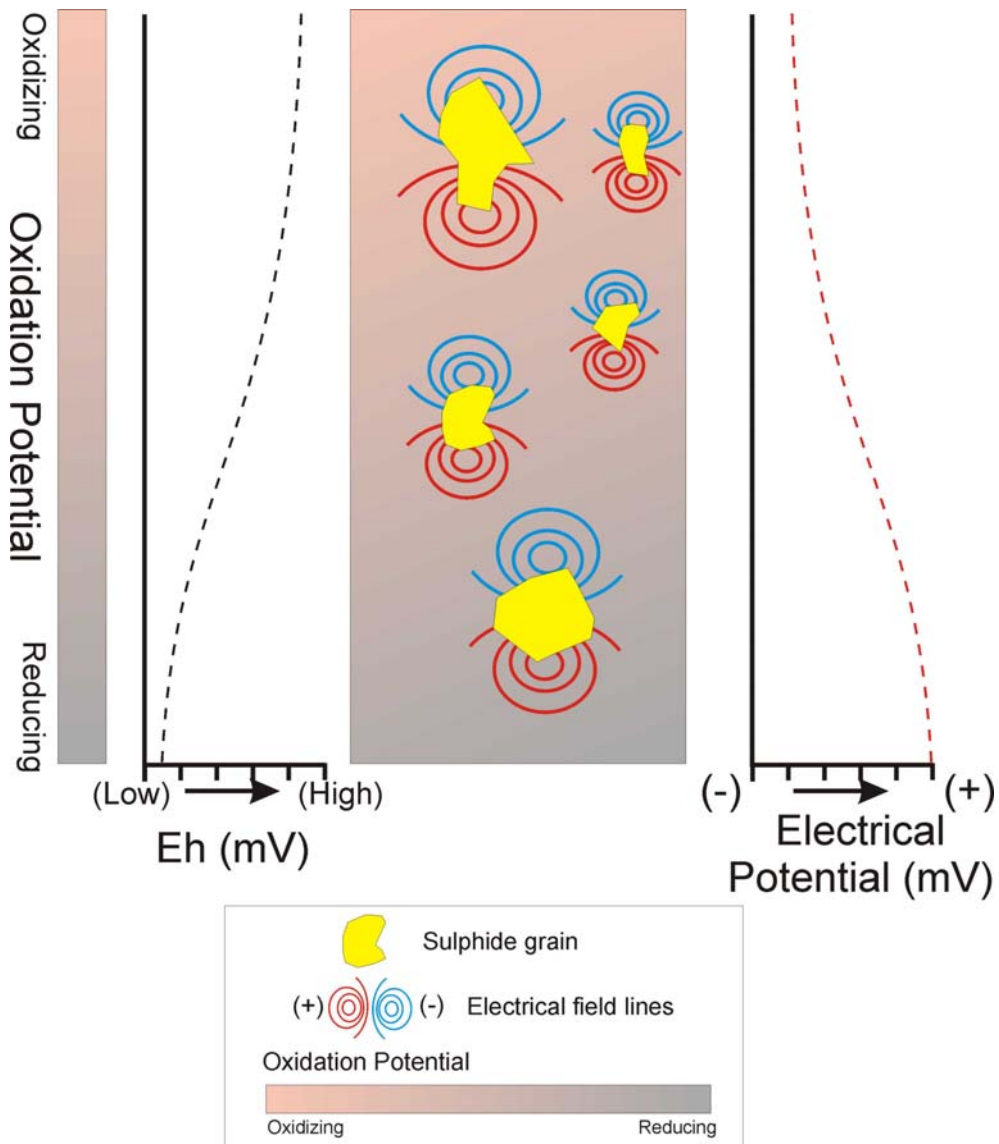
Figure 2. Development of electrical dipoles around individual sulphide grains in a strong redox gradient. The voltages of end-on grains are additive, imparting a net electrical potential across the redox gradient, the strength of which is dependent on the strength of the redox gradient, the composition of the sulphide and the abundance of grains influenced by the gradient.

exceeding several volts could easily be achieved. The most ideal conditions would occur where disseminated minerals with metallic or semi-metallic bonding exist in unusually strong redox gradients, and where the redox conditions are not sufficiently oxidizing to directly attack the minerals. Conditions such as these may occur at the base of oxide caps over porphyry deposits. Graphite flakes, sulphide grains and native gold could all contribute to SP responses provided they occur in a redox gradient. The dipole model is actually a special case of redox-induced spontaneous polarization in which a single massive conductor polarizes in a large-scale redox gradient.

There is also evidence that subtle SP responses can develop in the redox gradient without the presence of metallic grains. We previously argued (Hamilton and Hattori, *in press*)

that an SP response over an accumulation of H_2S in groundwater is due to mutual alignment of redox-active polar ions in solution with their negative poles pointing in the positive redox direction. Nyquist and Corry (2002) reported SP responses over an organic-waste plume from a tomato factory and these may be related to such a process. We are currently testing the possibility that bacteria may be involved in the generation of SP responses, either or both by catalyzing the redox reactions that help to establish the redox gradient or perhaps more actively as a mechanism for autotrophs to secure a flux of redox-active ions as a source of metabolic energy.

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