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# Studies on the Surface Characters of Minerals (2) : The Distribution of Tarnish Colours on the Crystal Surface of Pyrite

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## Studies on the Surface Characters of Minerals. 2. The Distribution of Tarnish Colours on the Crystal Surface of Pyrite.

By

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*With Plate XI.*

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It was early known that the tarnish colours on the surface of minerals and metals are produced by the interference layer on the surface. It was W. Haidinger<sup>1)</sup> who first found the existence of a certain difference in the distribution of tarnish colours in different crystallographical orientations. J. Hausmann<sup>2)</sup> thoroughly studied the phenomenon and observed the differentiation of the natural tarnish colours on (100) and (111) of a crystal of galena. He elucidated the fact that the interference layer in question was mainly made up of oxides or hydroxides resulting from the chemical attack of the surrounding medium.

If a polished surface of a mass of ore consisting of various sulphide minerals be etched by a suitable reagent, certain minerals retain their brightness while others are more or less tarnished or etched. J. Lemberg,<sup>3)</sup> and lately Mac Leo,<sup>4)</sup> have recommended the utilisation of this difference in the etching or colouring velocity of the microscopical discrimination of minerals.

The latter author, and lately W. Schneiderhöhn<sup>5)</sup> have tried to explain this phenomenon partly by the action of the electric current which is produced by the difference in the potential of various minerals against

the solution.

The differentiation of colouring due to the difference in the crystal individuum may also be observed on a properly etched surface of a polished pure metal, for instance, on a block of pure copper. The same statement holds true with a mass of pure pyrite or of pure chalcopyrite which causes sometimes a confusion in the microscopical identification. However, this fact informs us that there must exist a certain electro-chemical difference even in the different orientations of a single crystal individuum.

H. Bäckström<sup>6)</sup> has suggested that there must exist an electric current between the cubic and octahedral faces of magnetite crystals when they are immersed in a suitable solution and are connected electrically, because these two faces have different solubilities against the solution.

Mac Leo in his brilliant work,<sup>7)</sup> gives a full explanation to the differentiation of tarnish colour in a single crystal. According to this author, tarnish colours may sometimes be produced by the action of local currents. In the case of a single crystal, the most labile face coincides with the most positive one, and vice versa, the velocity of the chemical reaction must be largest at the most labile surface, hence the latter ought to be most rapidly tarnished.

The investigations of the present writer<sup>8)</sup> have revealed that, in the case of pyrite the ions which carry the electricity are the  $\text{SH}^-$  ions and not the  $\text{Fe}^{++}$  ions so that the most labile surface on which the sulphur atoms are most easily ionized, becomes always the positive electrode. This is evident since the potential is proportional to the surface density of the free crystalline bond of the  $\text{S}_2$  atom groups. So far the result coincides with Mac Leo's theorem, but we must be careful to distinguish the "velocity of tarnishing" from that of chemical corrosion; so far as the phenomena are concerned with the electric action, the most labile surface seems to be most seriously corroded, but the tarnish colours are most easily produced on the most stable surface.

Theoretically considered, a local current is produced by a chemical action between the  $\text{SH}^-$  ions and  $\text{H}^+$  ions upon the surface. At the anode surface, where the potential is lowest, the  $\text{SH}^-$  or  $\text{OH}^-$  ions discharge

whereby the oxidation takes place, while at the cathode surface, where the potential is highest, the  $H^+$  ions discharge and unite with the sulphur atoms forming the  $SH^-$  ions and the reduction occurs there.

The FeS atom groups which are produced on the cathode surface may be dissolved away by the solution when the latter is sufficiently acidic. Therefore, the cathode surface is liable to remain always fresh and bright even though it be corroded seriously, but the anode surface is covered by the interference layer, which is often insoluble and protects the surface from further reactions.

It follows from the above consideration that the more labile surface must have the smaller velocity of tarnishing. The natural evidences in the distribution of tarnish colours, which will be described presently, seem to prove this statement in an eloquent manner.

### **The Distribution of Natural Tarnish Colours.**

A microscopical examination of the natural tarnish colours on a crystal face of pyrite would at once reveal that in many cases, every crystal face is not uniformly coloured. A regular differentiation of colour may sometimes be recognizable along with the striation as is shown in Fig. 1 in Pl. XI. This may well be explained by the difference in the surface stability between the crystal faces of different indices.

In many cases, however, a single crystal face is so very irregularly coloured that it does not appear to show any regular differentiation; fresh surfaces having no tarnish colour are irregularly patched in the coloured part in which the distribution of colours is also haphazard.

W. Haidinger<sup>9)</sup> has tried to explain this irregularity by an assumption that the condition of formation was not favourable, for instance, the concentration of the solution was not uniform. However, a close observation of numerous specimens of pyrite from Sagi, Akatani, Sennin and a few other localities has shown that the above-mentioned irregularity is only an apparent one; any "irregular" distribution may still be explained by the local difference in the surface stability, and that it would have produced any kind of "irregular" distribution even when the concentration of the

solution had been uniform.

In many specimens, some bright, fresh part is left along with cracks or scars of the crystal as may be seen in Figs. 1 and 2 in Pl. XI. Edges, walls etc. of a mechanical crack are naturally irregular in form; their skins are formed by minute atomic surfaces of several different indices, mostly complex in their symbols. Consequently they are unstable as compared with the natural crystal faces of simpler indices. In other words, their surface densities of the free crystalline bond are generally larger at these irregular surfaces than the others. A local current ought to flow from these surfaces to the neighbouring natural faces through the crystal body. The  $\text{SH}^-$  or  $\text{OH}^-$  ions in the solution discharge at the stable surface and may produce the interference layer, while the  $\text{H}^+$  ions attack the unstable surfaces of the crack, fissure, and their vicinity, the corroded surface remaining always fresh and bright.

In an alkaline or a neutral salt solution, the above reaction is often weaker than in the acid solution, but the result is essentially the same as in an acid solution. As a matter of fact, a careful observation would at once prove that the differentiation of the tarnish colour of the above type is very common in pyrite especially in those occurring from the oxidized zone of mineral deposits.

A still more interesting case is shown in Figs. 3, 4 and 5 in the same plate in which more or less deep depressions are formed. The inside of the depression is invariably fresh and bright while the outside is beautifully coloured. In this case, the local current must have been produced first by the presence of a certain unstable point which formed the cathode, while the surrounding natural face acted as the anode. The digging action of the current at the cathode may be considered to have proceeded until at last the spot is so markedly enlarged and deepened that its diameter may sometimes reach a millimeter or more.

In one case, the writer has observed a quartz crystal at the bottom of a depression which was situated on a tarnished (210) face. The contact surface between the pyrite mass and the quartz grain ought to have been inevitably irregular and hence more unstable than the face

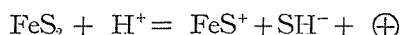
(210), and this difference in the surface stability might have been the starting-point of the local current.

In some cases, crystal edges and corners remain fresh and bright while the neighbouring surfaces are tarnished as may be seen in Figs. 5 and 6 in the same plate. This may also be explained by the presence of various unstable surfaces in these portions. The more seriously corroded are these, the more liable to produce the local current if the crystal be an electro-conductor.

### Summary and Conclusion.

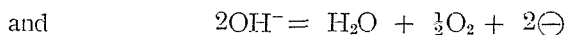
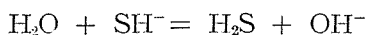
In many pyrite crystals, the distribution of tarnish colours may be explained by the electro-chemical change caused by the local current which is, in turn, produced by the local difference in the surface density of the free crystalline bond of sulphur atoms.

At the bright and fresh part of the surface, which formed the cathode, the reaction



continued to occur, forming more and more labile surfaces and thus promoting the intensity of the local current.

At the tarnished or oxidised part, which served as the anode, the reactions



etc.,

took place and the original stable surface was rendered more stable by the protective action of the oxygen-bearing crust.

Therefore, so far as the phenomenon is concerned with the electro-chemical reaction, it is the stable surface that displays various tarnish colours, while the unstable surface always remains fresh and bright though it may be corroded vigorously. Since any scars, cracks, edges or any other imperfect part of the surface are relatively unstable as compared with the perfect crystal faces, the former tend to remain untarnished and the latter are liable to be coloured.

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Kyoto Imperial University.

October 1, 1925.

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Fig. 1.

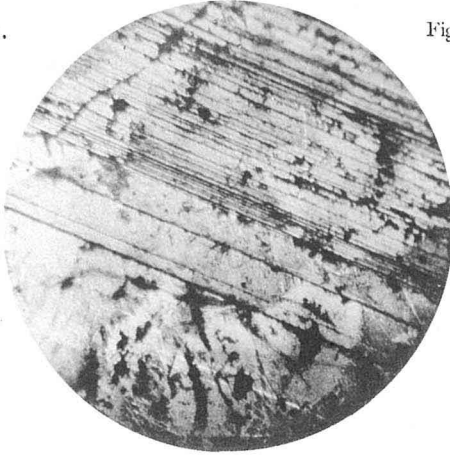


Fig. 2.



Fig. 3.



Fig. 4.

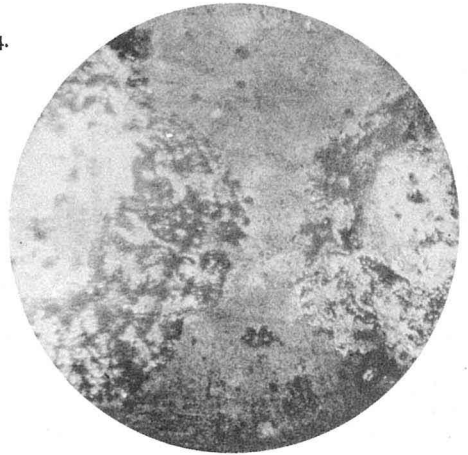


Fig. 5.

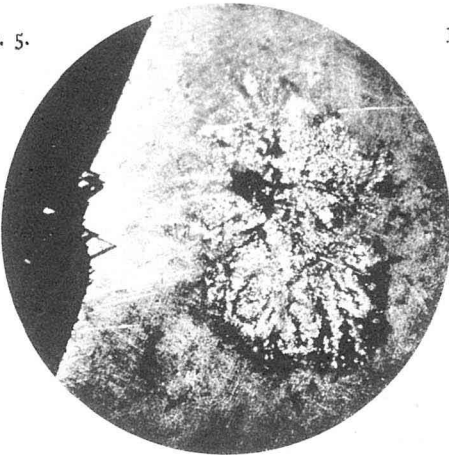


Fig. 6.

