

Studies on the Surface Characters of Minerals.
3. A simple Method for
the Determination of the Surface Stability
of Some Minerals.

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When a crystal of pyrite is immersed in an acid solution, numerous leptonological surfaces of the former assume their proper potentials. An equilibrium is soon established between the ionization pressure of sulphur atoms on the one hand, and the mutual attraction of SH^- ions and the positively charged surface on the other.

If the solution is allowed to stand still, the local current in the crystal body will soon be minimalized, and the system will remain practically unchanged. If, however, the positive charge of the crystal be continually removed and the H^+ ions be forced against the surface, the current may continue to flow; the H^+ ions will unite with the SH^- ions as soon as the latter are produced, and hydrogen sulphide gas will consequently continue to evolve.

The writer has contrived this method and has found that it renders the examination of the local difference in the surface stability simple and easy. The method will be reported in this paper.

Experimental Method

A crystal of pyrite was immersed in a solution of some 0.15 normal

of hydrochloric acid at room temperature. The crystal in this condition does not effervesce noticeably. A pencil of metallic zinc which is wholly covered with grease or paraffin except the very small area of the pointed terminal, is prepared. This pencil, too, when dipped into the above solution, does not effervesce noticeably on account of the smallness of the exposed area.

However, the crystal surface suddenly begins to effervesce as soon as the pointed end of the pencil is touched to the crystal body, but the effervescence stops short at the instant when the contact is released.

The degree of effervescence differs according to the place on the surface with which the pencil comes in contact. If the pencil be touched to a smooth cubic surface, for instance, the effervescence is generally very weak, but it is remarkably strong if the contact point be on some irregular surface such as is produced by the fracturing of the crystal.

The effervescence does not occur equally on the whole surface; certain special places such as the crystal edges or corners, cracks, scars, etc. especially give off a larger amount of gas. An analysis of the evolved gas showed that it consisted mainly of hydrogen sulphide and hydrogen.

In order to examine whether there exists any definite relation between the amount of gas evolved and the position of the contact, the following experiments were carried out:

About 200 ccm. of 0.15 normal HCl solution, saturated with H_2S , was placed in a suitable dish in which a well-formed crystal of pyrite was also sunk. An inverted glass funnel whose tubular part led to a capillary glass tube was placed over the crystal. The inner diameter of the capillary was previously calibrated. The funnel and the capillary were first filled with the solution by suction, and then the pencil of zinc was touched to the desired locality of the crystal for a definite length of time during which the crystal was firmly supported by a glass rod.

The capillary was so small that the evolved gas bubbles were entirely checked at its lower end. After a definite length of time, the pencil was removed; the small gas bubbles adhering to the crystal were completely removed by means of a small feather brush; all the gas which was col-

lected at the bottom of the funnel was brought to the proper part of the capillary by suction and the length of the gas filament was read by means of an attached scale paper.

Many blank tests showed that the amount of hydrogen evolved from the zinc pencil in the assigned length of time was entirely negligible within the limit of the experimental error, hence the correction due to this was not necessary.

Result of Experiment

The results are represented in the following tables in which the relative amount of the evolved gas in each experiment is expressed by the length of the gas filament *L*. The duration of the contact was confined to one minute.

Table 1.
Experiment Series 1.

Exp. No.	<i>L</i>	Contact Surface
1	29.6	irregular surface
2	9.5	(100)
3	3.7	"
4	4.2	"
5	3.8	"
6	21.5	irregular surface
7	7.5	(100)
8	5.8	"

Table 2.
Experiment Series 2.

Exp. No.	<i>L</i>	Contact Surface
1	2.5	(III)
2	1.5	"
3	1.3	"
4	1.1	"
5	0.7	"
6	0.6	"

7	2.7	(III)
8	0.9	〃
9	8.5	irregular surface
10	10.4	〃
11	8.9	〃
12	14.0	〃
13	11.2	〃
14	4.0	〃
15	9.2	〃
16	<u>0.8</u>	〃
17	12.5	〃
18	12.5	〃
19	12.8	〃

Table 3.
Experiment Series 3.

Exp. No.	L	Contact Surface
1	4.2	(III)
2	3.5	〃
3	1.5	〃
4	6.5	〃
5	1.6	〃
6	0.8	〃
7	2.2	〃
8	5.5	〃
9	3.2	〃
10	20.2	irregular surface
11	6.0	〃
12	8.8	〃
13	8.5	〃
14	13.5	〃
15	6.8	〃
16	20.0	〃
17	8.8	〃
18	13.0	〃
19	18.4	〃

Table 4.
Experiment Series 4.

Exp. No.	L	Contact surface
1	1.2	(111)
2	0.3	"
3	0.8	"
4	0.3	"
5	0.3	"
6	0.2	"
7	1.2	(100)
8	4.5	"
9	5.4	"
10	2.2	"
11	<u>20.0</u>	"
12	9.5	"
13	7.8	"
14	2.8	"
15	<u>7.4</u>	irregular surface
16	20.0	"
17	27.5	"

In each crystal, there seems to exist a certain difference in the gas evolution according to the kind of the contact surface. Of course the exact nature of the contact surface is unknown even under a microscope, and the terminal of the zinc pencil is in no way a geometrical point so that it may touch several leptonological surfaces at the same time. Therefore, certain abnormal values such as those underlined in the tables may be often obtained which very likely do not correspond to the values for the desired surfaces.

The absolute amount of gas evolution may be a function of the area of the surface in action, the degree of their perfection and stability; here we are only able to recognize roughly the relative abundance of the gas evolution in various surfaces of each crystal individuum, and we can generalize the result as follows:

The gas evolution is very slight when the contact surface is a more

or less perfect octahedral surface; somewhat more abundant in a cubic surface; it is remarkably large if the contact surface is an irregular one such as a fracture.

Exactly the same conclusion can be obtained from the similar experiment with galena, though, in this case, the cubic cleavage is so very perfect that really an irregular atomic surface can hardly be obtainable, still there must be numerous edges of the minute cubes on the fractured surfaces, and especially some vicinal faces in them. Therefore, a certain difference in the relative stability between a smooth (100) and an "irregular" surface might be expected.

In the following experiment, two galena crystals from Kamioka having a rounded portion which is considered to be the result of chemical corrosion was employed. They had also smooth cubic cleavage surfaces so that the relative abundance in the gas evolution could be conveniently measured. The results are given in the following tables :

Table 5.
Experiment Series 5.

Exp. No.	L	Contact Surface
1	1.4	(100)
2	2.0	"
3	2.6	"
4	2.8	"
5	2.4	"
6	2.8	"irregular" surface
7	3.0	"
8	4.8	"
9	3.5	"
10	3.4	"
11	3.5	"

Table 6.
Experiment Series 6.

Exp. No.	L	Contact Surface
1	0.3	(100)
2	0.2	"
3	0.3	"
4	0.3	"
5	0.3	"
6	0.8	"irregular" surface
7	0.8	"
8	0.9	"
9	0.8	"
10	1.0	"

That the above general rule also applies here requires no further explanation.

Discussion

In the above experiments, the positive charge of the crystal¹⁾ must have found its way to flow in the negatively charged zinc pencil through the contact portion of the two. This, in turn, must have accelerated the ionization of the zinc from the pencil. The zinc ions thus produced may expel the hydrogen ions around the pencil, and those hydrogen ions may strike the crystal surface to unite with the SH^- ions. The zinc ions may directly reach the surface, but the result is the same as in the case of the hydrogen ions for in both cases the evolution of hydrogen sulphide and the formation of zinc chloride will result, provided the solution is sufficiently acidic. At any rate, an electric current will flow from crystal to zinc, zinc to solution, and return from the solution to the crystal.

This current may, of course, flow through all the surface of the crystal when it is immersed in a solution, but its passage should mainly be confined to the vicinity of the contact portion, for the resistance ought to be smallest there. As a matter of fact, the corrosion is serious around the contact spot. However, there is another factor which control the amount of the flow of current. The edges, cracks, scars, or irregular

1) That the crystal is positively charged in this condition was already proved in this series of investigations (cf. this Memoirs, Series B. Vol. I, No. 4, p. 320)

fractures, etc., must be in higher potential than the smooth crystal face, i. e., the SH^- ions must accumulate more densely on these irregular surfaces which have the larger surface density of the free crystalline bond than the surfaces of simpler crystallographical indices. Therefore, the electrical resistance must be smaller at these places than on the remaining surfaces. And it is also a matter of fact that the evolution of hydrogen sulphide is more vigorous at these places than on the other even when the contact portion is situated on a smooth crystal surface.

When the contact portion lies on an irregular surface, the voltage of the current ought to be generally large, hence the effect on the ionization of zinc is also large; a large amount of current flows, and its chemical action is also large.

On the contrary, when the contact position lies on a smooth crystallographical face of very stable nature, the ionization of zinc is not markedly accelerated; the voltage of the current is small and the chemical action is also small. This explains the difference in the gas evolution according to the difference in the contact position.

In short, the ionization of zinc and that of the crystal surface effect each other mutually and accelerate each other so that the difference in the stability of the contact surface manifests itself in the amount of gas evolution in an exaggerated manner.

Iron monosulphide which is formed by the action of the H^+ ions upon pyrite may readily be dissolved by an acid solution, giving H_2S gas, whereby the positive charge of the FeS^+ atom groups is left on the crystal. Hence the above effect is redoubled also from this reason.

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