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RELATIONS BETWEEN THE CRYSTAL-STRUCTURE OF MINERALS AND THEIR BASE-EXCHANGE CAPACITY

C. H. EDELMAN

(Wageningen, Holland)

With regard to their base-exchange capacity, three groups of minerals are to be distinguished :---

| Strong base exchange. several zeolites montmorillonite beidellite halloysite | } group | Moderate base exchange several zeolites micas chlorites felspars Al-bearing amphi- boles and pyro- xenes busito | Low or no base exchange apophyllite kaolinite pyrophyllite talc Al-free amphiboles and pyroxenes |
|---|---------|--|---|
| | | leuche | Kyanne |

This distinction is not yet based on a comparison under identical circumstances of material of known grain size or surface, but gives a rough qualitative idea of the observations to be found in the literature.

The minerals of the second and third groups may show a stronger base-exchange if their surface is characterised in a high degree by the so-called *meta-structure* (Wiegner), while drastic grinding leads to the same result (Kelley).

In this paper we intend to prove that the ideal lattices of the several mineral-groups show differences which correlate with the adsorption properties found in an empirical way. That these differences in structure are the real causes of the differences in the adsorption-capacity will be made probable.

These differences can be best illustrated with the aid of the structures of kaolinite, muscovite and halloysite. Kaolinite and

halloysite are characterised by layer-lattices, consisting of layers which are only bound to each other by weak forces. In each layer the valencies are out-balanced.

The consequences of this building-principle are: bad crystalgrowth parallel to the C-axis and perfect cleavage parallel to the planes (001), which planes separate the layers. With the micas this situation differs, as in this mineral-group the separate layers are bound with Kions. The cleavage of the mica goes over these K-ions.

The cleavage-planes of kaolinite can show two configurations of ions.

1. An oxygen-sheet, bound to Si, arranged in a hexagonal pattern.

2. A hydroxyl-sheet, bound to Al, also arranged in a hexagonal pattern.

It must be noted that the edges of the cleavage-planes of kaolin and other minerals can never be out-balanced in detail, so that unsaturated valencies, which can cause all kinds of adsorption phenomena, should be present.

As the ideal surface of kaolinite does not seem to render possible a base-exchange, we must come to the conclusion that the ion-configurations 1 and 2 are little sensitive to kations under normal laboratory conditions.

The same applies to the cleavage planes of pyrophyllite which only show the configuration 1.

When observing the possible cleavage-surfaces of the halloysitestructure, we meet with 3 configurations.

1. A sheet of O-ions, bound to Si;

2. A sheet of OH-ions, bound to Al;

3. A sheet of OH-ions, bound to Si.

As the activity of halloysite with regard to kations is relatively strong, and the configurations 1 and 2 in the kaolin-structure are not active, the activity can, regarding this structure, only lie in the OHgroups which are bound to Si. That under normal conditions the activity of OH-groups, which are bound to Al will be weaker than that of the OH-groups which are bound to Si, is easy to understand.

One could say that halloysite behaves like a real acid.

The base-exchange of the minerals of the second category is the result of quite another property, which is best illustrated by the behaviour of muscovite.

In the ideal case of $KAl_2(AlSi_3)O_{10}(OH)_2$ the muscovite shows complex layers $Al_2(AlSi_3)O_{10}(OH)_2$ consisting of several sheets strongly bound together by common O-ions and represented by the scheme :---



These complex layers are linked by K-ions in 12-fold position.

The distribution of the K is completely regular, but according to the opinion of prominent crystallographers this cannot be the case with the Al in the tetrahedron-layers; the distribution of the Al in this layer must be statistical. From this it follows that, strictly speaking, the K-ions are not equivalent as regards the forces that bind them to the lattices. The cleavage of the micas goes over the K-ions, so that after cleavage the K must be equally distributed over both halves. Statistically the K-ions are for two-thirds of their valency bound to the half to which they remain attached, whereas the open space statistically gets one-third of the negative free valency.

Deviations from the statistical average cause spots that retain larger and others that retain smaller free valencies, so that favourite and less favourite spots for base-exchange must occur.

It is evident that the ideal surface of muscovite fragments must show quite different properties from the monotonous balanced surface of kaolinite and pyrophyllite. Besides this active (001) surface the micas also will have their incomplete outbalanced edges with all inherent consequences.

With the felspars, cleavage also goes over the K-ions, so that in some respects compatible phenomena appear. A remarkable feature is that Al-free amphiboles and pyroxenes, notwithstanding their content of bases, belong to the third category, whereas the Al-containing members of these families undoubtedly exchange bases.

It seems that the surface of minerals becomes activated through the presence of Al in tetravalent position as compared with allied minerals which do not possess this property (Van der Meulen).

Contrary to the minerals that have been under discussion hitherto it has not been possible to find in the structure of montmorillonite proposed by Hofmann any correlation with the remarkable adsorption phenomena of this mineral. The cleavage of this mineral, which, as well as kaolinite, is characterised by a true layer-lattice, exclusively shows configurations of type 1 of p. 98 (oxygen-sheet bound to silica). This surface must be considered to be inert. Consequently the baseexchange of the montmorillonite cannot be explained from the proposed structure. Nor is it possible to understand the linear swelling of montmorillonite, for this can only be caused by a strong polarising effect of the interior surfaces.

This polarising effect is difficult to explain by the inert O-surface.

It seems, however, that the structure of Hofmann is open to discussion, and a final opinion on the possibility whether the adsorptionproperties of minerals can always be considered in connection with their crystal-structure cannot be given until a revision of the montmorillonite structure has been established.

A more complete treatment of this subject in collaboration with Dr. P. van Campen will be offered for publication to the Zeitschrift für Kristallographie.