

The loss of weight at 120°C. is negligible, although the mineral decrepitates noticeably at higher temperature indicating that water may be occluded within the crystals.

Spectrographs of the antlerite indicate the presence of small amounts of silicon, aluminum and titanium, probably in the form of oxides and included under the insoluble matter in the above analyses. Traces of calcium, iron and silver are also present in quantities too small to be detected by other analytical methods (less than 0.01 per cent).

In the same collection of specimens from Chuquicamata, chalcantinite and natrochalcite were also found, the latter in distinct crystals of the type recorded by Palache and Warren, and in such abundance that it is probably one of the important ore minerals.

The recent recognition of antlerite as occurring in this deposit, evidently in large amounts, suggests that much of what has been called brochantite may really be antlerite, since the two minerals are similar in general appearance and their qualitative chemical reactions are the same.

THE FORM OF REPLACEMENT CRYSTALS

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Epidote crystals introduced during the replacement of a rock mass¹ have been found elongated parallel to the *c* axis, a direction along which elongation of epidote is very rare. The sections contain a great many of these epidote crystals which are mostly microscopic in size, but in every case the elongation was found to be parallel to the *c* axis rather than along *b*, the common direction of elongation. The development of such a rare crystal form under replacement conditions warrants an explanation since it may make clear certain features of replacement processes.

The mechanism of replacement² and the probable nature of the introduced material will not be discussed here beyond a few brief comments pertinent to the subject of this paper.

The positions occupied by material favorable to the reaction with the introduced substance no doubt determined the positions

¹ Observed in thin sections of rocks from Courtland, Arizona, in the possession of Professor L. C. Graton, Harvard University.

² The Mechanism of Replacement and Recrystallization: Ernest E. Fairbanks, *Econ. Geol.*, forthcoming article.

in which the epidote crystals developed. The material introduced may have entered chiefly by diffusion through amorphous grain boundaries, or along cleavage planes, or directly through the crystal lattice itself. The velocity of such diffusion should be greatest through amorphous grain boundaries, less along cleavages and least through a crystal lattice. Replacement, especially at its inception, is commonly observed along grain boundaries working into the replaced mineral along cleavages.

Replacements appear to be volume for volume in nature, as pointed out by Lindgren. Changes taking place *within* the crystal lattice should serve to explain such relationships. Upon first thought it might appear as though the introduction of material into a rock mass would tend to produce an increase in volume. Such introduction is, undoubtedly, attended by loss of material as a result of a diffuse cycle which is initiated by the entrance of the foreign material into the rock mass.

In the case of a portion of the rock material reacting with the introduced substance it would appear as though volume relations should vary. It is known, however, that the molecular volume of a compound is not, as a rule, the sum of the atomic volumes of its component elements, a notable contraction usually occurring on the combination of the elements. This contraction is due to the difference in the crystal structures of the solid elements and the solid compound. Therefore, it would appear as though an actual decrease in volume should occur as a result of replacement in some cases. A compensating influence is afforded by attendant increase in volume similar in magnitude to that of the decrease as a result of the production of solid solutions. The substitution of atoms, as shown from X-ray study, involves a distortion of the crystal lattice. The crystal lattice of a solid solution continues to possess the lattice of the solvent up to a certain concentration of solute producing an expansion of the lattice, which, in the case of 8 per cent Mg replacing Al, amounts to an increase from 4.05 to 4.10 Å.

If the foregoing facts are significant in the control of volume relationships, a relation should be expected between the two rare cases (1) when an increase in volume takes place on combination, and (2) when a decrease in volume is produced by atom substitution during solid solution formation.

Volume relations are not necessarily preserved under near surface replacements indicating that pressure is an important factor in the preservation of volume relationships.

Passing over the subject of volume relationships with this brief hint regarding the nature of the process, we have yet to consider the factors which tend to produce unusual crystal elongation.

Crystallization velocities vary at various crystal faces.³ Normally the velocity along the *b* axis of epidote is the greatest. In the presence of foreign material adsorption⁴ of such material may also be greatest upon the faces developed at the extremities of the *b* axis. Now adsorption of foreign material is known to impede the crystallization velocity (C.V.). If this inhibition reduces the velocity along *b* until it is less than along the *c* axis, the result will be that the crystal will grow more rapidly along *c* and thus become elongated as found in the study of the thin sections.

The mechanism of the inhibiting effect of adsorbed material upon the C.V. may be given briefly as follows: molecules or atoms form an adsorption layer upon a surface of a crystal lattice. The molecules or atoms of such layers are not permanently attached but are considered to constantly shift away from the lattice and back. The retention of molecules requires time and during this period some other surface may be building more rapidly. Hence a change in original velocities may be produced.

The attractive force of an atom is a factor which likewise may be important in producing changes in C.V. Adsorption layers may be as thick as 20 or 50 molecules in some instances, while in other cases it may have the thickness of a single molecule. The distance to which this attraction can extend is a debatable subject.

Considering epidote through its entire period of formation we would expect foreign material to be adsorbed upon some surface of the unit-cell the moment such a cell is formed, providing conditions which favor adsorption are satisfied. Here we are dealing with anisotropic media and adsorption can affect the crystallization velocities of the crystal axes while such action is impossible if the media remains isotropic.⁵

³ The Effect of Various Factors Upon the Velocity of Crystallization of Substances from Solution: John D. Jenkins, *J. Am. Chem. Soc.*, **47**, No. 4, April 1925, pp. 903-922. Jenkins determined the velocities of crystallization by means of two methods, (1) a rapid refractometric method and (2) a thermometric method.

⁴ Adsorption is here considered to be a manifestation of both the causal factors of chemical combination and true solution i.e., molecular attraction and the kinetic motion of the molecules, chemical combination being entirely due to the attractive forces between the atoms or molecules, while true solution is a manifestation of the tendency of the thermal agitation of the molecules to produce a chaotic mixture.

⁵ Further discussion of crystal modification with special attention to the mechanism as given by Valetton is being prepared for a future article.

Only a small quantity of foreign material need be adsorbed to control the crystallization. Analyses of various epidotes show a varying amount of impurities. The greater portion of this foreign material was occluded during the process of crystallization and was not added by the process of adsorption.

The elongation of epidote crystals along the *b* axis is believed to be satisfactorily explained as a result of the reaction of introduced material with rock material amenable to such reactivity. During the process of crystallization, due to adsorption of foreign material, the growth of the crystals along the *b* axis is retarded to a greater extent than along the *c* axis.

Lindgren's⁶ contention, that replacement is essentially a process of adsorption and super-saturation, receives, then, additional support from the foregoing observations, with regards to the importance of adsorption.

⁶ Mineral Deposits, p. 26, New York, 1919.

A NEW THEORY OF THE COMPOSITION OF THE ZEOLITES. PART IV

(Continued from page 152)

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5. THE COMPOSITION OF HEULANDITE AND RELATED ZEOLITES

Doelter¹ has collected 47 analyses of heulandite and three more have been published since the date of his compilation. However, many of these are too old to be of high quality, and some were made on impure material. In heulandite, as in other zeolites, the ratio between Al_2O_3 and $\text{RO} + \text{R}_2\text{O}$ is very nearly constant and very nearly unity. Excluding therefore a few analyses because this ratio is unsatisfactory, the "superior" analyses of heulandite are the following:

Doelter's Nos. 11, 19, 23, 25, 37, 38, 40, 41, and 47.

A. L. Parsons:² Heulandite from Digby Cut, Nova Scotia.

K. H. Scheumann:³ Heulandite from Beruford, Iceland.

¹ Hdb. Mineralchemie, II, 3, (1921), p. 171.

² U. Toronto Studies, Geol. Ser., 14, (1922), p. 52.

³ Ber. Sachs. Akad. Wiss., Leipzig, LXXIII, (1921), p. 1; Zeit. Kryst., LVII, (1923), p. 657.