development of asystolic periods of more than 5 seconds' duration. The vagus was stimulated periodically during an infusion of 0.1 to 1  $\mu$ g of norepinephrine per kilogram per minute. After 5 to 10 minutes, vagal stimulation permitted ventricular escape with much less slowing of the sinus rate. The reversal of the reservine effect by norepinephrine implies that the effect of reserpine to reduce ventricular rhythmicity is the result of catecholamine depletion.

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5 October 1960

## **Crystal Structure Refinement of Reedmergnerite**, the Boron Analog of Albite

Abstract. Ordering of boron in a feldspar crystallographic site  $T_1(0)$  has been found in reedmergnerite, which has silicon-oxygen and sodium-oxygen distances comparable to those in isostructural low albite. If a simple ionic model is assumed, calculated bond strengths yield a considerable charge imbalance in reedmergnerite, an indication of the inadequacy of the model with respect to these complex structures and of the speculative nature of conclusions based on such a model.

Recent conclusions important to the interpretation of the mineralogy and petrology of alkali feldspars have been presented by Ferguson (1). Evidence supporting the new theory is taken in part from the results of crystal-structure analyses of low and high albite (2) as to (Al, Si)-ordering in tetrahedral sites  $T_1$  (0),  $T_1$  (m),  $T_2$  (0), and  $T_2$  (m), and from the resulting charge balance calculated for these sites when a simple ionic model is assumed. Determination by x-ray diffraction methods of (Al, Si)-distribution in feldspar crystals must necessarily be indirect because of the near equivalence in x-ray scattering power of aluminum and silicon. A recently described min-

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eral, reedmergnerite (3), NaBSi<sub>3</sub>O<sub>8</sub>, is isostructural with albite, NaAlSi<sub>3</sub>O<sub>8</sub>, and the elements boron and silicon can readily be distinguished by x-ray techniques. Furthermore, aluminum and boron have many chemical and structural similarities in crystals, both elements occurring coordinated by a tetrahedron of oxygens, with boronoxygen distances of 1.46 to 1.48 A (4) and aluminum-oxygen distances of 1.75 to 1.79 A(5). It seemed probable that comparison of albite and reedmergnerite structures would help to clarify the (Al, Si)-distribution problem and provide additional information about charge balance assumptions. Accordingly, a detailed crystal-structure investigation of reedmergnerite has been completed, in which we started with the known low albite parameters (2).

Thirteen cycles of least-squares analysis of 2753 three-dimensional data for reedmergnerite have been carried out on a Burroughs 220 digital computer; the full matrix associated with the normal equations was used. A residual factor

$$R \equiv \Sigma \mid \mid F_{obs.} \mid - \mid F_{calc.} \mid \mid / \Sigma \mid F_{obs.} \mid$$

of 11 percent has been obtained, excluding data recorded as zero. Reedmergnerite contains the typical feldspar framework found in low albite (2); the refinement shows that boron is wholly contained in site  $T_1$  (0), and that the framework is distorted as compared to that in albite, so that the smaller boron-oxygen tetrahedra can be accommodated. The resultant shrinkage in framework accounts for an average 4-percent reduction in dimensions of the reedmergnerite cell as compared with those of the albite cell (3). The silicon-oxygen distances in reedmergnerite (Table 1) compare so closely with those reported for low albite (2) that considerable doubt is cast on the validity of (Al, Si) assignment from small variations in these bond distances, according to the relationship proposed Table 1. Some interatomic distances for reedmergnerite and low albite (2).

	second	
I	nteratomic dis	tances (A)
Re	edmergnerite	· · · · · · · · · · · · · · · · · · ·
(all	$\pm$ 0.01 A)	Low albite
$T_{1}(0)$	) tetrahedron	
(B or Al)- $O_{A}(1)$	1.47 <sub>a</sub>	1.762
(B or Al)- $O_{\rm R}(0)$	1.48	1.702
(B or Al)- $O_c(0)$	1.44	1.762
(B or Al)- $O_{\rm D}(0)$	1.47 <sub>a</sub>	1.74
Av.	1.468	1.74 <sub>2</sub>
$T_1(m$	) tetrahedron	
Si-O <sub>1</sub> (1)	1.58	1.59
$Si-O_{\mathbf{p}}(m)$	1.60	1.62
$Si-O_{c}(m)$	1.60,	1.55 <sub>8</sub>
$Si-O_{\rm D}(m)$	1.62	1.583
Av.	1.60,	1.59
$T_2(0$	) tetrahedron	
Si-O.(2)	1.62-	1.61。
$Si-O_{P}(0)$	1.57.	1.62,
$Si-O_{c}(m)$	1.63	1.64
$Si-O_{\rm D}(m)$	1.62	1.64
Av.	1.61	1.63
$T_{2}(m$	) tetrahedron	
Si-O.(2)	1.65	1.64
$Si O_n(m)$	1.61	1.59-
$Si-O_{\alpha}(0)$	1.61	1.61.
$Si-O_{\rm p}(0)$	1.60	1.61,
Av.	1.62.	1.61
(	Oxvgen-Na	0
0.(1) 24	8, 2, 50,	2.61- 2.68-
$O_{1}(1) = 2.4$	2 39	2.36
$O_{\mathbf{n}}(0)$	2.40	2.46
$O_{\alpha}(0)$	(3.44)	2.88
$O_{\alpha}(m)$	2.84	(3.24-)
$\mathbf{O}_{n}(0)$	2.37	2.46-
$O_{\rm p}(m)$	2.85	(2.99-)
<b>C</b> D()	2	(2.2.2.7)

by Smith (5) and used in the study of albite (2).

The sodium atoms in reedmergnerite are located in the cavities within the feldspar framework. Anisotropic temperature motion of the sodium atoms has not yet been fully investigated, but the isotropic temperature factor B is 1.23  $A^2$ , in marked contrast to the maximum B of 0.78  $A^2$  found for the other atoms in the structure. The coordination of oxygen atoms about sodium in reedmergnerite is comparable to that found in albite for the five closest oxygens (Table 1), but some

Table 2. Bond strengths contributed by (B or Al)<sup>3+</sup>, Si<sup>4+</sup> and Na<sup>+</sup> to  $O^{2-}$  atoms in tetrahedral groups of reedmergnerite and low albite (2). (a)  $T_1(0) = B$  (reedmergnerite), Al (low albite), remainder = Si; Na coordinated by five closest oxygens (reedmergnerite, Table 1), by six closest remainder = 51, Var Gordaniade by investigates (Aygens (recamergnerite), Al (low albite), remainder = Si; Na coordinated by seven oxygens (Table 1). (c) Al-Si distribution taken as follows:  $T_1(0) = 0.72$  Al,  $T_1(m) =$  Si,  $T_2(0) = 0.20$  Al,  $T_2(m) = 0.09$  Al, remainders = Si; Na coordinated by six oxygens (Table 1). (d) Al-Si distribution as in (c); Na coordinated by seven oxygens (Table 1).

Tetrahedral site	Bond strength						
	Reedmergnerite		Low albite				
	( <i>a</i> )	<i>(b)</i>	<i>(a)</i>	<i>(b)</i>	(c)	( <i>d</i> )	
$T_{1}(0)$	7.80	7.56	7.83	7.71	8.02	7.90	
$T_1(m)$	8.15	8.31	8.08	8.18	8.03	8.13	
$T_{2}(0)$	8.15	8.31	8.08	8.18	7.93	8.03	
$T_2(m)$	7.90	7.78	8.00	7.93	8.00	7.93	
$\Sigma[\Delta]$	0.60	1.28	0.33	0.72	0.12	0.33	

changes occur among oxygens more distant than 2.6 A from sodium. These changes require that sodium in reedmergnerite be considered as either fiveor sevenfold coordinated, in contrast to the sixfold coordination assigned to sodium in low albite (2). When bond strengths to the oxygens in reedmergnerite are calculated over each tetrahedral site, on the basis of a simple ionic model, and compared with those so determined for albite (2), a charge imbalance is found in reedmergnerite (Table 2) that at best is almost double any found for albite. In our opinion such calculations serve merely to underline the inadequacy of the ionic model in treating the complex feldspar structures. This study strongly suggests that any new theory dependent on results from such a model should be considered speculative until more experimental evidence becomes available (6).

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30 August 1960

#### **Detection of Boundary Films**

Abstract. Results, obtained with a photoelectric refractometer and sucrose solutions, indicate that a concentrated surface layer rapidly builds up when sucrose solutions are allowed to stand under conditions where evaporation can occur from the surface. The phenomenon is similar to the formation of a cool boundary film which has recently been shown to occur on the surface of the ocean.

Ewing and McAlister have recently reported experiments showing the existence of a cool boundary film on the surface of evaporating water (1). We have observed a similar phenomenon during investigations carried out to develop a photoelectric refractometer for use in the sugar industry. The effect is particularly marked when the U-bend type of refractometer first described by Karrer and Orr (2) is used. This consists of a U-bend of solid glass rod



Fig. 1. Graphs of refractive index, as determined by the U-bend photoelectric refractometer, against time. Curve A was obtained when the U-bend was introduced into a freshly stirred sucrose solution; curve B was obtained when the U-bend was introduced into the sucrose solution which had been allowed to stand for 1 minute. After 11 minutes, this solution was stirred with an ordinary laboratory-type stirrer.

down one limb of which parallel light is shone. The intensity of the light emerging from the other limb, which is easily measured photoelectrically, is dependent on the refractive index of the medium in which the curved part of the U-bend is immersed.

Typical results are shown in Fig. 1, which is a graph of the refractive index indicated by the photocell output against time. These particular results were obtained with a rod 8 mm in diameter bent into a U with a radius of 2.5 cm at the curved end. The solution used was a pure, aqueous sucrose solution of concentration 67 percent by weight; the measurements were made in a darkened room at a temperature of 24°C and a relative humidity of 75 percent.

Curve A shows that when the dry Ubend is immersed in the freshly stirred solution, the refractive index is almost constant. If, however, the sucrose solution is allowed to stand for 1 minute before the U-bend is introduced (curve B), the indicated refractive index is initially higher but begins to drift downwards; if the solution is then stirred. the indicated refractive index drops rapidly to a constant value equal to that found in a freshly stirred solution.

The explanation of these effects appears to be that when sucrose solutions are allowed to stand under conditions where surface evaporation can occur, a boundary film of concentrated solution builds up; this film adheres to the U-bend when it is passed through the surface but can be dispersed by mild agitation. This explanation is similar to that given by Ewing and McAlister for their experiments, although we have postulated a concentration rather than a temperature gradient; to ascribe the phenomenon to temperature effects alone would require the surface film to be some 20°C cooler than the bulk of the liquid.

The effect is so marked with sucrose solutions probably because the diffusion constant for sucrose solutions diminishes rapidly at high concentrations (3). In agreement with this, the effect is small at moderate concentrations of sucrose but is larger than that shown in Fig. 1 when molasses is used. It is of some interest that the boundary film can build up so quickly when a sugar solution is handled in the atmosphere; the need for care in carrying out precision refractometry with concentrated sugar products is clear.

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SCIENCE, VOL. 132