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# Authigenic analcite in the Golden Valley Formation southwestern North Dakota

Marvin J. Furman University of North Dakota

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Authentic Analcite in the Golden Valley Formation (?),

SouthWestern North Dakota

by

Marvin J. Furman

Bachelor of Science, St. Lawrence University 1965

# A Thesis

Submitted to the Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Master of Science

Grand Forks, North Dakota

July 1970

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Department: Geology

Degree: Master of Science

In presenting this thesis in partial fulfillment of the requirements for a graduate degree from the University of North Dakota, I agree that the Library of this University shall make it freely available for inspection. I further agree that permission for extensive copying for scholarly purposes may be granted by the professor who supervised my thesis work or, in his absence, by the Chairman of the Department or the Dean of the Graduate School. It is understood that any copying or publication or other use of this thesis or part thereof for financial gain shall not be allowed without my written permission. It is also. understood that due recognition be given to me and to the University of North Dakota in any scholarly use which may be made of any material in my thesis.

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# ACKNOWLEDGEMENTS

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# TABLE OF CONTENTS





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LIST OF TABLES

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# LIST OF FIGURES



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Authigenie analeite constitutes up to about 60 parcent of a massive, arkosic sandstone exposed on major buttoe in the North Dakota Bidlands. The analcito constitutes up to about 60 percent of a thin analcimolite bed at the top of the arkose unit. The analcite occurs as spherulites in the interstices of the arkose and as a cement in the analcimolite. Three types of spherulites are recognized: (1) spherulites with an internal radial structure; (2) spherulites with a massive center and a peripheral radial structure; and (3) spherulites lacking an internal radial structure or having a poorly-defined intermal structure. The spherulites occur individually and as coalesced masses. Analcite in the arkose and analcimolite is silica-poor.

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Detrital minerals associated with the analcite include quartz, Natiligioclase, K-feldspar, and illite. Sericite is associated with and ofte in the arkose, and may also be authigenic. The analcite is Loust abundant at the base of the arkose unit and increases upward. The abundances of analcite and the detrital feldspars are inversely **Autubody** 

**苹果是在这一个人的一个小时间的小时间,我们在我们的时候,我们在我们的时候,我们在我们的时候,我们在我们的时候,我们的时候,我们就会在我们的时候,我们的时候,我们也没有,我们的时候,我们就能把我们的时候,我们也没有想到这样的** 

Amisite composition, distribution with respect to the felascars, presence of sericite, and the absence of a vitroclastic texture, sugpost-dime analcite in the arkose was derived from post-depositional dimoducion of the feldspars. It is proposed that analcite in the artes and analoimolite were derived from different, but similar, persat materials.

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# MODES OF OCCURRENCE OF ANALOTTE

Analcite is classified as a mamber of the zeolite group, although in structure, chomistry, and (igneous) paragenesis it has close affinities with the feldspathoids (Deer, et al., 1963). The composition of analcite is generally expressed as NaAlSi<sub>2</sub>O<sub>6</sub>  $nH_2O$ . There are, however, variations in composition, in which potassium substitutes for sodium, and sodium and aluminum substitute for silicon (Wilkinson, 1968).

Analcite occurs in igneous and sedimentary rocks. It is a primary mineral of late formation in some intermediate and basic ignecus rocks. It also forms in the late stages of crystallization of some hydrothermal solutions. In sedimentary rocks it occurs as icositetrahodral crystals, spherulites, and most frequently as replacements of volcanie glass shards.

<u>olar Salar Salar</u>

Proposed origins for analcite in sedimentary rocks are by:  $(1)$ alteration of volcanic glass by hydrolysis (Bradley, 1929; Deffeyes, 1959); (2) direct precipitation from surface waters (Van Houten, 1962) (3) reaction and alteration of other alkali zeolites (Goodwin and Surdam, 196?); (4) reaction between saline waters and clay minerals (Keller, 1992); and (5) reaction and alteration of primary tectosilicate ministralis (May, 1966).

Zsolites are among the most common authigenic silicate minorals in sadimentary rocks (Hay, 1966), usually forming in sediments as a prodwot of diagenetic processes. Diagonesis, generally, is defined as the . Autheal and chemical adjustment of the sediment after deposition, ro-

mitting in changes in composition and texture. Dispensate to remunicted to lower temperatures and productes to distinguish it from motomorphism. A number of minoralogical changes mark the transition from diagenesis to low-grade metamorphism, among which is the replacement of analcite by albite and quartz (Turner, 1958).

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Pettijohn (1957) includes in diagenesis the processes of cementation, authigenesis, diagenetic differentiation, intrastratal solution, and compaction. Cementation is the precipitation of mineral matter in the voids of a clastic sediment, resulting in induration of the sediment to a rock. Authigenesis is the result of reaction among the constituents of a sediment after deposition, with the formation of new minorals or overgrowths on others already present. It is an attempt to establish an equilibrium mineral assemblage. However, diagenetic reletions, responsible for the elimination of unstable minerals, seldom roach completion because of the low temperature conditions (Packham and Crock, 1960). A typical diagenetic mineral assemblage, therefore, is a casequilibrium assemblage, consisting of detrital "reactant" minerals (or metastable authigenic minerals) and "product" authigenic minerals. Diagenic differentiation is the redistribution of materials within a sediment. Intrastratal solution is a chemical attrition by solutions adving on the constituents of a rock after deposition. Compaction rethes or aliminates interstitial voids in a sediment, generally in-Internative of the second of burial.

# SCOPE AND PURPOSE OF STUDY

Zeclites are considered to be possible indicators of physical and

chemical conditions in diagonesis and Low-grade metamorphism. Their importaneo has boen evaluated by chamining their natural occurrences; from which environmental parameters have been inforred. The inforred parameters have then been evaluated and more rigorously defined in experimental studies. Notable contributions to this approach have been made by Coombs (1954) and Coombs,  $\mathfrak{g}_{\mathbb{Z}}$   $\mathfrak{g}_{\mathbb{Z}}$ . (1959).

Various aspects of the conditions under which zeolites crystallize have been recognized through extensive examinations of natural occurrences. This study is another contribution to the overall analysis. A major occurrence of analcite in a single rock unit was selected for study. Occurrences of analcite with respect to associated detrital and authigenic minerals, distribution in the rock unit, and composition have boen investigated.

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# PREVIOUS INVESTIGATIONS

In North Dakota analcite was first reported in Tertiary rocks associuted with uranium (Beroni and Bauer, 1952). Other occurrences in Tertiary rocks have been reported in South Dakota and Montana (Wanless, 1922; Rozendal, 1956; Denson, et al., 1959; Denson and Gill, 1965). These cocurrences have been attributed to the alteration of associated pufficeous materials.

# DESCRIPTION OF STUDY AREA

The study area, in southwestern North Dakota, is situated between 102º to 104º W longitude and 46° to 48° N latitude. It includes iso-Lated buttes in Golden Valley, Billings, Stark, Slope, and Dann Coun-

ties (Fig. 1). The area covers approximately 150 square miles. Buttes, consisting of nearly horizontal bods of sand, silt, and clay, rise 400 The topography of the area, to which the to 600 feet above the plain. term "Badlands" is applied, is due mainly to stream and rain erosion. The area is drained by the Little Missouri River and its tributaries.

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Figure 1.

# Reference Map



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#### . MEI'HODS OF INVESTIGATION

# SAMPLING

Tertiary rocks in southwestern North Dakota have been sampled to determine the occurrence of authigenic analcite. A total of 252 spot samples were taken. Analcite could not be distinguished in hand speci-. men and was identified by **x-ray** diffraction analysis. This required sampling to be carried out in two stages. First, reconnaissance sampling was undertaken to determine the distribution and major occurrences of analcite-bearing rocks. The analcite-bearing rocks were then sampled in detail. Factors influencing the choice of sample localities included · the coourrence of complete sections, outcrops showing variations in lithology, and sedimentary structures. Sections more than ten feet thick were spot. sampled at five-foot intervals from the top of the unit. Sections less than ten feet thick were sampled at the base, middle and top. Selected oriented samples were taken from sedimentary structures. Areal locations and stratigraphic positions of samples cited in this paper are given.in the appendix and Figure 1.

## ANALYTICAL PROCEDURES

#### General

The analcite-bearing rocks were examined in thin section to determine the characteristics, occurrence, and textural relationships of the detrital and authigenic minerals. X-ray diffraction methods were used for qualitative and semi-quantitative mineral analysis. Grain-

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size distribution was determined by sieve and pipette analysis.

## Petrographic Preparation

The majority ot analcite-bearing rocks used for thin sectioning were friable and required special treatment. The samples were cut into slabs measuring approximately  $1 \times 3/4 \times 1/8$  inches and impregnated using a technique.developed by Renton (1965).

## Petrographic and Optical Measurements

Thirty-one thin sections were examined.. An ocular micrometer was used for grain-size measurements. Grain shape was estimated by visual comparison with a. roundness-spbericity chart (Krumbein and Sloss, 1963). Index of refraction was determined by the Becke line method. The composition of plagioclase in thin section was determined by Wahlstrom's procedure (1960). Extinction angles, measured with respect to aPpropriate cleavage planes, were plotted on a determinative curve from which the molecular percent of anorthite was read (Wahlstrom, 1960, pp. 120-125). Extinction angles were measured from the trace of  ${010f}$ in fragments cut paralled to  $[001]$ , from the trace of  $[010]$ in sections cut normal to { 001} and **{01cj,** and from the trace of the {010} plane in sections showing albite twinning or {010} cleavage.

# X-Ray Diffraction Analysis

Procedures for X-ray Diffraction Analysis--194 samples were selected for routine qualitative and semi-quantitative x-ray diffraction analysis. A sample measuring approximately 6 X 4 X 4 inches was crushed and a 20 gram sub-sample was taken. The sub-sample was ground

in a 8000 Spex Mixer/Mill in Spex vial 8001 for seven minutes. A second sub-sample of 150 mg. was taken and ground in Spex vial 5004 for an additional seven minutes. One gram of the sample was then back-loaded in a cylindrical, rotating sample holder. The following machine conditions were used:

X-Ray Generator (Phillips Constant Potential 50 KV-50 ma). X-Ra.y Tube. (Machlett Cu Tube-Short Anode) *37* KV-18 ma. Diffractometer (Phillips High Angle)

l degree 2 *Q* scan speed.

l degree divergence and anti-scatter slit.

Ni filter.

Detector (Phillips Scintillation-Transistorized) 1.0 KV.

Circuit Panel (Phillips 12206/53), Bristol. Recorder.

PHA, width  $3.5V$ , level  $6.0V$ .

Linear scale.

l second time constant.

 $2 \times 10^3$  counts per second.

*30* inches per hour chart speed.

Minerals were identified by peak position and relative intensity on the diffractogram. Diffractograms of reference minerals and the ASTM File were used for reference.

Modal compositions were semi-quantitatively determined by the method developed by Alexander and Klug (1948) and modified by Leroux, <u>et al</u>.  $(1953)$  and Karner (1968). The weight fraction of a given mineral component was calculated from the expression:

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x_1 = \frac{1}{(1)} \cdot \frac{4 \cdot \frac{4}{5}}{4 \cdot 1}
$$

where,

 $X =$  weight fraction of component  $1$ .

- $\mathcal{M}_i^{\mathcal{F}}$  = mass absorption coefficient of component 1.
- $\mathcal{M}_{\epsilon}^*$  = mass absorption coefficient of bulk sample.
	- $I =$  intensity diffracted at a definite Bragg angle 20 by crystalline component 1 in the bulk sample.
	- $(I)$  = intensity diffracted at a definite Bragg angle 20 by pure • crystalline component 1.

The equation expresses the weight fraction of a mineral component in the bulk sample as a ratio of the peak intensity of the mineral component to the peak intensity of a pure standard mineral, corrected for ab. sorption. Leroux, <u>et al</u>. (1963) further established the following re-<br>lationship to experimentally determine the absorption correction:

$$
\frac{M_{s}^{2}}{M_{s}^{2}} = \frac{P_{s} \log T_{s}/T_{o}}{P_{o} \log T_{i}/T_{e}}
$$

where,

- $P_i$  = apparent density of a pure sample of component 1.
- $Z_s$  = apparent density of a sample containing weight fraction X of component 1.

 $T_a$  = intensity of incident x-ray beam.

 $T<sub>S</sub>$  = intensity transmitted by sample containing weight fraction X of component 1.

 $T_1$  = intensity transmitted by pure component 1.

Measurements were made of the peak intensity of a given component in the bulk sample and corresponding intensity of the pure component. The peak intensity of the component in the bulk sample was determined by the difference between the peak height and background intensity. Values for the mass absorption coefficients of the minerals were taken from Tatlock (1966) or calculated from the data of Klug and Alexander (1954). The values used for the calculation of the weight fractions are given in Table 1. The results of these analyses are given in Tables  $9$ ,  $10$ ,  $11$ , and  $12$ , and Figures  $9$  and  $14$ .

# Precision and Accuracy of Semi-Quantitative X-Ray Diffraction Mineral Analysis--Expressing the results of the analyses as semi-

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quantitative rather than quantitative implies a lesser degree of accuracy. Error has been introduced by using standards for measurement of 100 percent peak intensity that are not from the sample (standards



Clay fraction standard separated from samples

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taken from U. N. D., Department of Geology Reference Collection). As the properties of the mineral components of the sample depart more from the norm of the standards, the results become more semi-quantitative. The range of composition and crystallinity of the minerals in the sample **is narrow** and does not vary systematically. The introduced error, therefore, is approximately constant. The data has been used only for comparison within itself, and in this respect is considered valid. .

Niskanen (1964) investigated the accuracy and precision of' direct quantitative x-ray diffraction analysis. The mean error of an analysis of a synthetic mineral mixture was within two percent. However, the accuracy of an actual rock analysis was considerably poorer, with a mean error of approximately ten percent.

The variables affecting the reproducibility of data obtained by the previously described technique are: (1) inconsistencies in the measurement of peak intensities; (2) variations in packing the unoriented powder and the degree of preferred orientation in the powder; and  $(3)$  variations in the grain size of the powder due to inconsistencies in grinding. To evaluate the affect of these variables on the reproducibility of the data eight samples were selected and scanned three times after unloading, remixing, and repacking. The standard deviations of the computed weight fractions of the individual minerals in the bulk sample are given in Table 2.

· The minimwn limit of detectability of a mineral component·in the bulk sample is largely a function of the crystallinity of the substance (Klug and Alexander, 1954). A poorly crystallized mineral may be a

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major component of a sample, but may not yield a significant peak. Generally, a peak was considered significant and the intensity was measured, if the peak was approximately three standard deviations of the height of the background peaks above the lower boundary of. the background trace. If a peak did not fulfill the above conditions, but was still considered present, the minerals was reported as a trace amount. The amount of a mineral that was reported as a trace varies with the substance. The amount of a mineral reported as undetected or trace, therefore, may range from complete absence to the maximum values in Table J.

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# Determination of Analcite Composition

Fifteen samples were selected to determine analcite composition. The samples represent the vertical and lateral extent of analcitebearing rocks in the Golden Valley Formation {?). The procedure used for this analysis was developed by Saha (1959; 1961). It is based on variation of the {639) peak position of analcite with varying unit cell



composition. The composition is expressed as the silica ratio:  $2 \text{ SiO}_2/\text{Na}_2$ <sup>0</sup> +  $\text{Al}_2\text{O}_3$ . Silicon was added as an internal standard. The sample was scanned through *78.5°* to 76.0° 28 at 0.25 degrees per minute, using a chart speed of 15 inches per hour. The previously described diffractometer was used. The angular difference between the (639) peak of analcite and the (JJl) peak position of silicon was plotted on Saha's (1959) determinative curve, from which the silica ratio was read. Each sample was seamed three times and an average value was used. The average of the standard deviations of the replicate analyses is 0.04.

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A predominantly monomineralic specimen  $(4775)$  allowed easy concentration of analcite for indexing. The sample was crushed and enriched by flotation. The decanted fraction, dried, was ground with a mortar and pestle by hand for ten minutes. Quartz was added as an internal standard to detect peak shift due to misalignment or instrument response. The sample was scanned through  $80^{\circ}$  to  $2^{\circ}$  20 at 0.25 degrees per minute, using a chart speed of 15 inches per hour.

# Clay Mineral Analysis

Four samples of analcite-bearing arkose were selected for a detailed identification of clay minerals by x-ray diffraction. The samples were disaggregated by crushing and  $>$ 40 fraction was separated by sieving. Smaller fractions were separated by settling in an aqueous suspension.

Oriented and random mountings were prepared. Oriented mountings of  $4\mathcal{M}$ , 2 $\mathcal{M}$ , and  $\langle 1\mathcal{M}$  fractions were prepared by sedimentation from an aqueous suspension on a glass slide. The suspension was dried at room temperature. Random mountings were prepared of  $7 \lambda_{\mathcal{A}}$ , and  $4 \lambda_{\mathcal{A}}$ fractions by passing the sample through a sieve and allowing it to fall on a laquer-coated slide. The oriented samples were treated following Gaudette's (1965) procedure. Samples were heated to 500° C. for one hour and exposed to an ethylene glycol atmosphere for 72 hours. Glycolated and unglycolated pellets were also prepared. **A** one gram sample of the clay fraction, backed by two grams of cellulose, were compressed in a hydraulic press at eight tons pressure for fifteen seconds.

Randomly mounted specimens were scanned through J8° to 20° 29 at a rate of l degree per minute. Oriented samples were scanned through  $50^{\circ}$  to  $2^{\circ}$  20 at a rate of 1 degree per minute. The analyses were conducted on the previously described diffractometer. The results of these analyses are discussed on pages Jl and 32.

### Grain Size Analysis

Twenty-seven samples representing the lateral and vertical extent of. the analcite-bearing arkose were selected for grain size analysis.

The samples were disaggregated by crushing as recommended by Folk (1964). Sand-sized and smaller grains were separated by sieve analysis. The sand-sized grains were divided into the basic divisions of sand-sized material of the Wentworth Scale. The silt-clay fraction was differentiated using North Dakota Geological Survey Procedure A-65 (Clayton, 1965). The results of these analyses are given in Table 8 and Figure 11.

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 $\begin{minipage}{.4\linewidth} \textbf{TABLE 4} \end{minipage}$ 

GENERALIZED SECTION OF FORMATIONS EXPOSED IN THE AREA OF ANALCITE-BEARING SEDIMENTARY ROCKS IN SOUTHWESTERN NORTH DAKOTA



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described and named by Leonard (1908; 1911). Leonard and Smith (1909) differentiated the Fort Union "Formation" into the Tongue River and Sentinel Butte Members. Royse (1967a) has redefined the Tongue River and Sentinel Butte as formations.

The Tongue River Formation, generally, rests conformably on the Ludlow and Cannonball Formations of the lower Fort Union Group (Denson and Gill, 1965). A local hiatus, however, is recognized at the Tongue River-Cannonball contact **(A.** Cvancara, Department of Geology, University of North Dakota, personal communication, 1970). The Tongue River Formation is composed of fine- to medium-grained, cross-bedded sandstones, shales, clays, claystones, and lignites. Published measurements of the thickness of the Tongue River Formation vary widely. The author considers Royse's figure for thickness (1967a), of approximately 300 feet in southern Golden Valley County, the most accurate. The Tongue River Formation is exposed in Golden Valley, Billings,-Slope, Stark, Dunn, McKenzie, Williams, and Morton Counties, North Dakota (Royse, 1967b) •

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# Sentinel Butte Formation

The Sentinel Butte Formation rests conformably on the Tongue River Formation. It consists of clays, shales, lignites, and sandstones interbedded with sands, siltstones, claystones, and marls. Reports on the thickness of the Sentinel Butte Formation, like the Tongue River Formation, vary widely. The Sentinel Butte Formation is exposed on major buttes in Golden Valley, Billings, and Slope Counties, North Dakota and along the Missouri Escarpment (Royse, 1967b).



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#### TABLE 5 MINERALS IDENTIFIED IN SAMPLES TAKEN IN RECONNAISSANCE STUDY

\*Refer to Appendix and Figure 1 for areal and stratigraphic positions of cited specimens.

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TABLE 3 (continued)

Specimen	Quartz	Plagioclase Feldspar	Potassium Feldspar	Analcite	Calcite	Dolomite	Clay	Volcanic Glass	Muscovite
5987	$\dot{\mathbf{X}}$	$\pmb{\chi}$	$\pmb{\mathsf{X}}$				$\pmb{\mathsf{X}}$		$\mathbf X$
4745	$\pmb{\mathsf{X}}$	$\pmb{\chi}$	$\mathbf X$		$\pmb{\chi}$			$\pmb{\chi}$	
4744	$\mathbf{x}$	$\pmb{\chi}$	$\mathbf x$				$\pmb{\chi}$	$\mathbf{x}$	

TABLE 3 (continued)

#### PETROGRAPHY OF ANALCITE-BEARING ROCKS

# MINERALS

#### QUARTZ

Quartz is a constituent of all the analcite-bearing rocks examined. It occurs as anhedral, detrital grains. The grains occur both individually and as composites of individual grains.

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The individual grains range in sphericity from  $0.3$  to  $0.5$  and average 0.4. The roundness ranges from 0.1 to 0.9 and averages 0.2. The grains have moderate to strong undulatory extinction. They range in diameter from 0.1 mm to 0.3 mm and average 0.2 mm.

The composite quartz grains consist of aggregates of individual grains joined at sutured contacts. The composite grains range in diameter from 0.2 mm to 1.7 mm and average 0.5 mm. The individual grains comprising the aggregates have slight to moderate undulatory extinction, and have approximately the same dimensions as the individual quartz grains described above.

The grains occur in the sediment embedded in the cement or matrix. The grains are commonly embayed (Fig. 2).

#### FELDSPAR

Detrital plagioclase and potassium are both present in the analcite-bearing arkose. The plagioclase ranges in composition from  $A_{120}$  to  $A_{120}$  to  $A_{145}$ . However, due to possible ambiguity in determining the sign of extinction angles, the plagioclase maybe as albitic as  $An_{\eta}$ . The grains are anhedral and range in diameter from 0.1 mm

Figure 2. Detrital quartz grain. Arrows point out embayed edge. The quartz grain is embedded in argillaceous matrix. **X** JOO Crossed Nic9ls Specimen 4670

Figure 3. Detrital albite grain. Arrow points out pitted edge. The albite grain is embedded in argillaceous matrix. **X** JOO Crossed Nicols Specimen 4670







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$32$ <br>to 1.0 mm and average 0.4 mm. The sphericity ranges from 0.3 to 0.9 and averages 0.6. The roundness ranges from 0.1 to 0.9 and averages 0.3.

The potassium feldspar occurs as microcline and possible orthoclase. The microcline bas been identified by the characteristic crosshatched twinning. The grains identified as orthoclase, however, may be untwinned microcline. The grains range in diameter from 0.1 mm to 1.6 mm and average 0.8 mm. Grain roundness ranges from 0.1 to 0.5 and averages  $0.3$ . The sphericity ranges from  $0.5$  to  $0.9$  and averages  $0.7$ .

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The detrital feldspars, like the quartz, are commonly embayed  $(Fig. 3)$ .

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Detrital chert occurs as anhedral grains ranging in diameter from 0.2 mm to 0.4 mm. There are also isolated and very minor occurrences of spherically shaped, possibly authigenic, chert grains.

### ANALCITE

Analcite occurs as spherical and sub-spherical grains ranging in diameter from 0.1 mm to 0.5 mm and averaging 0.2 mm. Three types of grains are recognized: (1) grains with a radial internal structure  $(Fig, 4); (2)$  concentrically-structured grains with a massive center and a peripheral radial structure (Fig. 5); and (3) grains without an internal structure or a poorly-defined internal. structure (Fig. 6).

Thia mode of occurrence of analcite fits the definition of the term "spherulite" as used by Pettijohn (1957, p. 96). Spherulites are defined as minute, sub-spherical, radial bodies which have formed in

situ, and which coalesce to form packed polyhedra.

The spherulites with poorly-defined or absent internal structure are the most abundant. Spherulites with radial structure are the next most abundant, followed by the concentrically-structured spherulites.

Analcite is generally thought to be isometric. However, the Maltese cross interference figure on the radial spherulites and the slight birefringence indicates that the analcite is anisotropic. The optical behavior of the spherulites is dependent on the optical properties of the analcite, the state of elastic strain of the individual crystallites, and the relative crystallite orientation. The slight birefringence has been variously attributed to loss of water, strain, or to ordering of the Si, Al atoms in the structure (Deer, et  $a1.$ , 1963). Coombs  $(1955)$  has recognized a modification of analcite that is birefringent and biaxial. Departures from the isometric lattice dimensions are not detectable, a1though weak anomalous reflections may appear.

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X-ray diffraction powder data for the Golden Valley (?) analcite (specimen  $4775$ ) are given in Table 6. In contrast to the reference data for analcite (ASTM File--7-363, 7-340, and 19-1180) there are a number of minor reflections absent. Most of the absent reflections are in the high angle region **(28)40°).** In the low angle region **(29<40°)**  three reflections are absent:  $(411, 330)$ ,  $(420)$ , and  $(530, 433)$ . This is similar to Crook's (1967) observations, in which the (411, JJO), (600, 442), ~ (200') refiections were noted to be weak **or** absent. In addition,  $(721)$ ,  $(811)$ , and  $(1051)$  reflections were recognized, but do not correspond to any reflection in the reference data. The significance of these reflections is·not immediately apparent. The possibil-

Figure 4. Analcite spherulite with internal radial structure. The internal structure is identified by the Maltese cross interference figure. The partially included detrital grain is quartz. The birefringent rim is sericite. X 600 Crossed Nicols Specimen 4672

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Figure 5. Analcite spherulite with a massive center and a peripheral radial structure. Dotted line outlines the massive center. The spherulite is embedded in a sericitic matrix. X 600 Crossed Nicols Specimen 4672





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Distorted, coalesced, analcite spherulites. These Figure 6. spherulites do not show any internal structure. Argillaceous matrix (illite ?) outlines the spherulite X 300 Crossed Nicols Specimen 4672 shapes.

Coarse-grained illitic matrix (sericite). Black areas Figure  $7.$ are analcite. X 600 Crossed Nicols Specimen 4672





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ity of an unrecognized mineral impurity in the sample, however, must be considered.

The composition of analcite is given in Table *7.* The extremely fine-grained, polycrystalline nature of the analcite spherulites precluded an accurate determination of the index of refraction.

### CLAY MINERALS

lllite, and possibly kaolinite, are the only clay minerals that have been identified in the analcite-bearing rocks. Two textural modifications of the clay minerals have been recognized in thin section. A fine-grained variety occurs in the interstices of the arkose. A coarse-grained variety also occurs in the interstices of the arkose (Fig.  $7$ ), and replaces detrital quartz and feldspar. It also occurs as inclusions in the analcite spherulites (Fig. 8). The coarsegrained variety consists of interlocking, platy flakes. This fits the ' description of authigenic illite outlined by Carrigy and Mellon (1964 ). The coarse-grained illite replacing quartz also fits the description of authigenic muscovite given by Rex (1966). Coarse-grained illite is generally referred to as sericite (Pettijohn, 1957). Sericite, however, is intermediate in composition between the "ideal" composition of illite and muscovite (Grim, 1968; Reesman and Keller, 1967).

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Velde and Hower (1963) have proposed distinguishing between illite polymorphs in sediments as a method for identifying authigenic illite. Attempts to identify the illite polymorphs in various size fractions of the analcite-bearing arkose were not conclusive. The critical peaks for identification of individual polymorphs are very closely spaced (Grim,  $1968$ ). The peaks obtained from the samples were broad and dif-

fused, and individual peak positions could not be positively identified.

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Figure 8. Sericite inclusions in an analcite Birefringent rim around spherulite Spherulite is adjacent to detrital embedded in argillaceous matrix. **icols** Specimen 4672 spherulite. is also sericite. quartz grain and X 600 Crossed



X-RAY DIFFRACTION POWDER DATA FOR ANAICITE (SPECIMEN 4775) TABLE 6.

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TABLE 7. COMPOSITION OF ANALCITE

### ROCK TYPES

### ARKOSE

The minerals composing the arkose are quartz, chert, Na-plagioclase, K-feldspar, analcite, and illite. Chert is a minor constituent and is included as part of the quartz content. Fine-grained illitic matrix and sericite occupy the interstices of the arkose.

The modal composition of the arkose is given in Figure *7.* Quartz is generally the most abundant mineral component. Analcite is usually the next most abundant mineral. The average analcite content is approximately 30 percent. The analcite ranges from complete absence to a maximum of approximately 70 percent. The feldspars are relatively minor constituents. The sum of the plagioclase and potassium feldspar contents, on the average, does not exceed more than 20 percent of the composition of the rock. Potassium feldspar is the more abundant variety. Sericite occurs sporadically and is generally a minor component. However, it may comprise as much as 30 percent of the rock.

The classification of the rock as an arkose is based on the amount of feldspar, total clay, and rock fragments present. Metamorphic quartz grains are the rock fragments. These components, re-computed to 100 percent, have been plotted on Folk's (1964) classification diagram (Fig. 10). The majority of the points are in the arkose and subarkose categories. "

The arkose is texturally immature and poorly sorted. Grain sized data of the arkose are presented in Table 8. The arkose is characterized by a relatively high standard deviation. The grain-size mode is

# Figure 9.

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# Modal Composition of Analcite-Bearing Arkose

Data from samples cited in Tables 9, 10, 11, and 12.



at the very fine sand-coarse silt boundary of tho Wentworth size classification. All samples analyzed show positive skewness toward the finer grain sizes. In a plot of the sand-silt-clay content of the arkose, the majority of the points fall in the sand corner (Fig. 11). The grain-size distribution has a narrow range.

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. Detrital quartz and feldspar make up the framework of the arkose. The grains are unoriented in the matrix. A small percentage of the quartz and feldspar grains are in contact.

The interstices of the arkose are occupied by analcite and illite. Analcite occurs as individual spherulites in the matrix or as aggregates of spherulites. In the aggregates the original spherical shape is distorted to a polyhedral shape (Fig.  $6$ ). The spherulites range widely in diameter. Fine-grained illite and coarser sericite frequently outline the individual spherulites in the aggregates (Fig. 6). The spherulites range from undistorted individuals in the matrix, to where the matrix between the spherulites in the aggregates has been reduced to a veinlet remnant. Matrix may not always be present at the boundaries of the distorted spherulites.

Analcite and sericite frequently occur together in the arkose. Sericite often occurs as unoriented inclusions in the spherulites. Spherulites in the sericite matrix may have indistinct boundaries. Coarse sericite grains, where in contact with spherulites, are oriented with their long axes tangential to the spherulites (Fig. 12).

Spherulites occasionally occur in contact with detrital quartz and feldspar grains and are distorted. The spherulites may partially or wholly include the detrital grains.

Figure 10.

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Mineralogic Classification of Analcite-Bearing Arkose (After Folk, 1964). Plotted points represent analyzed samples.



# TABLE 8



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\*Refer to Appendix and Figure 1 for stratigraphic and areal locations of cited specimens

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TABLE 8 (continued)

Figure 11. Grain-Size Distribution of Analcite-Bearing Arkose

Plotted points represent analyzed samples.

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There are some differences in analcite content of the arkose in its lateral extent. The modal compositions of the arkose from the different buttes are given in Tables 9, 10, ll, and 12. Arkoses from Slide and Chalky Buttes have the lowest average analcite content, approximately 15 percent. Arkoses from Sentinel and Flat Top Buttes have approximately the same average analcite contents, 30 percent. Arkose from Bullion Butte has the highest average analcite content, approximately 40 percent.

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The analcite-bearing arkose, compared to the modal compositions of "typical" arkoses (Pettijohn, 1957), is notably deficient in potassium and plagioclase feldspars.

### ANALCIMOLITE

The minerals composing the analcimolite are analcite, quartz, and illite. Analcite is consistently the predominant mineral component. The term analcimolite is applied to a rock type in which analcite is the principle mineral constituent. The analcite content ranges from approximately 40 percent to 80 percent and averages approximately 60 percent. The modal composition of the analcimolite is given in Figure 14.

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Quartz grains form the framework of the analcimolite. The grains have high sphericity and low roundness, and have an average diameter of 0.17 mm. Analcite does not occur as spherulites as it does in the arkose, but occupies the interstices of the analcimolite as the cementing material. Analcite in the analcimolite appears to be massive, but a red stain outlines what might be individual grains (Fig. 13).

# Figure 14. Modal Composition of Analcimolite.

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Data from samples cited in Tables 11 and 12.



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The average diameter of these possible grains is 0.08 mm. Analcite composing the analcimolite has approximately the same composition as analcite in the arkose. Illite is present as irregular masses in the analcite.

There is some variation in the analcite content of the analcimolite in its lateral extent. Analcimolite from Slide Butte has the highest average analcite content, approximately 70 percent. Analcimolite from Chalky Buttes has the lowest average analcite content, approximately 50 percent. Analcimolite from Bullion Butte has an average analcite content of approximately 60 percent. The modal compositions of the analcimolite from the different buttes are given in Tables 11 and 12.

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Figure 12. Coarse sericite flakes oriented tangential to the periphery of spherulites. Black area area analcite spherulites. X 600 Crossed Nicols Specimen 4670

Eigure 13.

Texture of Analoimolite. Parallel Light  $Z$  150 Specimen 4775



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\*Refer to Appendix and Figure 1 for stratigraphic and areal locations of cited specimens.<br>\*\*Mineral contents expressed as parts per ten<br>\*\*\*Mineral not detected

\*\*\*\*Mineral detected only in trace amount

Specimen	Quartz	Plagioclase	K.Feldspar	Analcite	Muscovite (sericite)	Total Clay	Total	
5981	3.2	0.8	0.7	1.7	3.1	T	$-9.5$	
4689	2.7	1.3	1.2	2.0	$\bullet$	2.5	9.7	
4693	4.4	1.0	1.0	1.3	T	2.0	9.7	
4682	4.7	T	1.2	4.7	T	T	10.6	
4686	3.4	T	0.9	3.9	T	2.0	10.2	
4707	3.4	0.4	0.9	1.7	T	2.5	8.9	$\infty$
4679	3.8	0.4	1.7	3.7		Т	9.6	
4688	4.9	1.0	0.9	2.1	T	2.0	10.9	
7014	5.3	T	0.7	4.2	1.3	$\mathbf T$	$11.3$ .	
7015	3.9	0.4	0.5	1.9	2.6	2.0	11.3	

TABLE 9 (con't.)



## TABLE  $10$



MODAL COMPOSITION OF ANALCITE-BEARING ROCKS ON FLAT TOP BUTTE T. 139 N., R. 104 W., GOLDEN VALLEY COUNTY

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MODAL COMPOSITION OF ANALCITE-BEARING ROCKS ON BULLION BUTTE T. 137 N., **R.** 102 W., BILLINGS COUNTY

TABLE 11

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MODAL COMPOSITION OF ANALCITE-BEARING ROCKS ON SLIDE AND CHALKY BUTTES T. 139 N., R. 101 W., SLOPE COUNTY

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### DISCUSSION

### MINERAL ASSOCIATIONS

The association and significance of the following materials, with respect to the occurrence of analcite, will be dealt with in turn: volcanic glass, quartz, plagioclase, potassium feldspar, and sericite.

### Analcite-Pyroclastic Association

Pyroclastic materials containing volcanic glass are in close' proximity to the analcite-bearing rocks of the Golden Valley Formation (? ). Ash beds are present above and below the analcite-bearing rocks , on Sentinel, Flat Top, and Chalky Buttes.

The recognized genetic relationship between analcite and volcanic glass warrants consideration of the tuffaceous material as precursor to the analcite. A survey of the occurrences of analcite believed to have originated from pyroclastic materials shows that the vitroclastic texture is commonly preserved (Bradley, 1928; 1929; Bramlette and Posnjak, 1933; Ross, 1941; Coombs, 1954; Deffeyes, 1959; Gulbrandsen and Cressman, 1960; Brown and Thayer, 1963; Terrugi, 1964; Loughnan, 1966; Ijima. and Utada, 1966; Robinson, 1966; Wilkinson and Whetten, 1967 ). This texture is not present in the arkose of analcimolite, suggesting that the analcite in these occurrences has not been derived from volcanic glass.

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Whetten and Coombs (1967) have proposed a genetic classification of sedimentary analcites based on composition. Annlcites originating from siliceous volcanic glasses are silica-rich. The Si/Al ratio of



Group A-Silica-rich analcites formed from siliceous volcanic glass by inferred reaction with saline waters.

Group B--Analcites occurring in a burial metamorphic environment. Group C--Silica-poor analcites inferred to be formed by direct precipi-

tation or by reaction of highly alkaline water with sediment. Ar--Composition of analcite in arkose; An--Composition of analcite in analcimolite.

Figure 15. Classification of Analcite Based on Composition (After Whetten and Coombs, 1967)

the Golden Valley(?) analcite is low, 2.0 to 2.4. Analcite of this low Si/Al composition is generally considered to have originated by direct precipitation from highly alkaline waters, or by reaction of such waters with clay minerals **or** other sedimentary materials (Fig. 15).

### Analcite-Quartz Association

· Detrital quartz is present in all of the analcite-bearing rocks examined. There is no apparent relationship in the distribution of quartz and analcite in the analcite-bearing rocks. The detrital quartz in the analcite-bearing rocks is embayed. The embayments are interpreted as the effects of dissolution by reaction with interstitial water. There is no textural indication of analcite replacing the quartz.

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The majority of natural, fresh, surface waters are undersaturated with respect to amorphous silica, but supersaturated with respect to quartz. However, the corroded condition of the quartz suggests that a solution in contact with the sediment, at some time in the history of the sediment, was undersaturated with respect to quartz.

### Analcite-Feldspar Association

There is a well-defined relationship in the distribution of analcite and the detrital feldspars. A plot of analcite versus plagioclase contents of the analcite-bearing arkose shows a decrease in plagioclase with an increase in analcite (Fig.16). Curves have been calculated by the method of least squares for the point distributions in Figures

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Figure 16. Scatter Diagram of Analcite-Detrital Plagioclase Data taken from specimens cited in Tables 9, 10, 11, and 12.


Figure 17.

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Scatter Diagram of Analcite-Detrital Potassium Feldspar<br>Data taken from specimens cited in Tables 9, 10, 11, and<br>12.



16, 17, and 18. The curves are the best possible fits for the trends of the point distributions and give the highest correlation coefficients. The calculated curve in Figure 18 defines the point distribution as curvilinear. The curve is used only to define qualitatively the point distribution. There is a similar curvilinear relationship

16, 17, and 18. The curves are the best possible fits for the trends of the point distributions and give the highest correlation coefficients. The calculated curve in Figure 18 defines the point distribution as curvilinear. The curve is used only to define qualitatively the point distribution. There is a similar curvilinear relationship between analcite and potassium feldspar (Fig. 17).

The curvilinear distribution of the previously described relationship can be explained by the vertical distribution of analcite, plagioclase, and potassium feldspar in the section (Fig. 21). The analcite content increases upward in the section. Correspondingly, the. feldspar content decreases upward in the section. The significance of the vertical distribution of these minerals has been statistically tested. The unit has been divided into a lower 30 foot section and an upper 30 foot section. The statistical significance of the differences between the mean mineral contents of the upper and lower halves of the section have been computed. Table 13 gives the confidence levels at which differences in the mean mineral contents in the upper

TABLE 13.--Confidence Levels at which the Hypothesis  $\overline{x}_{230} \neq \overline{x}_{30}$ .<br>can be accepted as Significant

Mineral	$\overline{X}$ 30	$\overline{X}$ < 30	Confidence Level
Analcite	$4.3$ ppt.	$2.3$ ppt.	99.5%
Plagioclase	$0.2$ ppt.	$0.5$ ppt.	99.5%
K-Feldspar	$0.7$ ppt.	$0.8$ ppt.	70

and lower halves of the section can be accepted **as** significant. The calculated rcgrossion curves show the vertical distribution of the

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minerals to also be curvilinear.

It is concluded, from the distribution relationships, that analcite has been derived from the detrital feldspars. This conclusion is supported by the results of mineral synthesis experiments, in which analcite has been produced in reactions between albite and water (Friedman, 1951; Fredrickson and Cox, 19.54; Morey and Chen, *1955;* Sand, Roy, and Osborn, 1957; Morey and Fournier, 1961). Textural relationships in the arkose indicate that analcite is not directly replacing the feldspars. The analcite occurs as distinct spherulites. There is no penetration or embayment of the feldspars by analcite.

The equilibrium conditions for the reaction between analcite and albite have been experimentally investigated. Campbell and Fyfe (1965) determined the temperature and pressure of equilibrium for the reaction:

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NaAlSi<sub>2</sub><sup>0</sup>6<sup>\*H</sup><sub>2</sub><sup>0</sup> + Si<sub>0</sub><sub>2</sub><sup> $\rightarrow$ NaAlSi<sub>3</sub><sup>0</sup><sub>8</sub> + H<sub>2</sub><sup>0</sup></sup>

At conditions of low  $P_{H>0}$  the reaction is at equilibrium at approximately 190° C. At temperatures less than 190° C. analcite is stable relative to albite.

Silica activity can displace the equilibrium temperature (Campbell and Fyfe, 1965). The corroded condition of the detrital quartz and feldspar suggests that the silica activity of the solution may be a significant factor in controlling the analcite-feldspar relationship. If a solution is saturated with respect to amorphous silica, the dissolution of albite will be depressed (Fyfe and McKay, 1962). Under such conditions albite·would be stable relative to analcite at temperatures less than 190° C. The corroded quartz, however, suggests

Figure 18. Vertical Distribution of Analcite, Plagioclase, and Potassium Feldspar. Data taken from specimens cited in Tables 9, 10, ll, and 12.

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that the solution was undersaturated with respect to quartz. Consequently, the albite was probably easily dissolved in the solution.

Hess (1966 ) has approximated the fields of stability of minerals in the system  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  at 25<sup>o</sup> C., on the basis of the composition of the solution in equilibrium with the minerals (Fig. 19). The single hachured area in Figure 19 represents the composition of natural lake and river waters (data from Livingstone, 1963). The surface water compositions are outside the stability field of analcite. The double hachured area is the composition of a solution in contact with analcite (Hay and Moiola, 1963). This solution is assumed to be in equilibrium with analcite, and representative of a solution from which analcite would crystallize. The arrow is a crude, hypothetical, approximation of the change in composition of fresh surface water to produce a solution from which analcite would crystallize. The origin of the arrow has been purposely placed to the left of the - Log  $[SiO<sub>2</sub>] = 4$  isopleth, the solubility of quartz. The corroded condition of the detrital quartz, as previously discussed, suggests that the original solution was undersaturated with respect to quartz. The proposed solution from which analcite would crystallize, as inferred from Hess's (1967) diagram, was undersaturated with respect to silica, alkaline, and had a high  $Na<sup>+</sup>$  concentration. It has been pointed out that solutions of this composition usually do not exist at the surface of the earth. However, after burial the reaction of interstitial water with the mineral components of the sediment, in the relatively closed system that would be produced by burial, could easily establish solutions of the required concentration. As the quartz and

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Figure 19.

Isoplethic section at  $\log \frac{K^+}{H} = 4$  of phase diagram for the system  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}^2\text{O}_2-\text{H}^2\text{O}_3$  (after sitess, 1966). Single hachured symbol represents range in composition of lake and river waters. Double hachured symbol represents the composition of a solution in equilibrium with analcite. See text for discussion.

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feldspars dissolved, the solution composition moved to the right with increasing silica concentration. The compositipn would also move upward, as indicated by the arrow, since the dissolved feldspars would add to the cation concentration and increase the pH of the solution. The pH, however, would be maintained at moderate alkalinity. As the silica concentration of the solution increased due to dissolution of the quartz and feldspars, the solubility of the feldspars would be depressed. Thus, the silica acts as a buffer. The potassium feldspar. probably reacted similarly, except that it is less soluble than sodium plagioclase (Keller,  $\underline{et}$  al., 1963). According to Hess's (1967) scheme, therefore, when the solution reaches a critical concentration of  $\left[ N a^+ \right]$  ,  $\left\{ H^+ \right\}$  , and  $\left[ SiO_2 \right]$  , analcite would crystallize.

This. reasoning is supported by data presented by Harris (1967), in which it has been shown that pore waters in a contemporary fluvial sediment have a higher silica concentration than the overlying surface water.

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This approximation of an environment that would crystallize analcite has been inferred from the relative distributions of the minerals, and the condition of the coexisting minerals. There are undoubtedly other governing factors. However, their influence is not immediately apparent or they cannot be evaluated by only a study of the natural mineral occurrences. Some of these probable factors are the influence of the groundwater recharge system, the biological activity, and the interdependence among the various dissolution-precipitation reactions.

It is therefore proposed that analcite crystallized from interstitial solutions in the rock, from constituents derived from the dis-

solving feldspars. The dissolution and precipitation reactions probably took place at a relatively shallow depth of burial. The texture of the arkose suggests that it did not undergo extensive compaction. A very small percentage of the coarse elastic grains forming the framework of the arkose are in contact. Most of the compaction probably took place in the argillaceous matrix.

The vertical distribution of analcite and feldspar in the unit is attributed to the removal of the interstitial water, the reaction media, with increasing depth of burial. Thus, the dissolution of the feldspars was impeded, halting the reaction sequence.

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### Analcite-Sericite Association

Sericite occurs in the arkose as a matrix surrounding the analcite and as unoriented inclusions in the analcite spherulites. The textural relationship suggests that the sericite formed prior to the analcite. or at least prior to the formation of the spherulites. The oriented, coarse sericite grains at the periphery of the spherulites suggest that they have been pushed aside as the spherulites grew. Some of the sericitic matrix was probably included by the spherulites as they formed.

The possible significance of the analcite-sericite association in the arkose, is that sericite has been produced, along with analcite, in minerals synthesis reactions between albite and water (Morey and Chen, 1955; Morey and Fournier, 1961). Sericite, like analcite, crystallizes from alkaline solutions (Hemley, 1959). Thus, sericite and analcite may be products of the same environment and an interdopendent

reaction.

#### FORMATION OF SPHERULITES

Spherulitic crystallization has been recognized in igneous, metamorphic, and sedimentary rocks. Three origins for spherulitic structures are proposed:  $(1)$  crystallization from a colloid;  $(2)$  segregation of disseminated mineral matter; and (3) crystallization from supersaturated, high polymer solutions. The applicability of these origins to the analcite spherulites are considered.

Spherically-shaped bodies are generally thought to have crystallized from a colloid (Rust, 1935). However, the textural criteria that has been generally interpreted as characteristic of colloidal crystal-.1 lization has been critically reviewed (Roedder, 1968). It has been demonstrated that the textural features, colloform shape, syneresis cracks, concentric banding, and radial structures, do not necessarily result from colloidal crystallization.

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The textural relationships among the individual spherulites also suggest that they did not crystallize from a colloid. Colloids have high water contents and crystallization involves dessication and contraction. The mutual interference and distortion of the spherulites suggests expansion and coalescence. The orientation of the coarse sericite grains to the periphery of the spherulites also suggests an increase in volume. **As** the spherulites grew they pushed the sericite grains aside, orienting them. It is concluded, on the basis of these considerations, that the spherulites did not crystallize directly from

a colloid.

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A colloidal phase, however, may possibly have been an intermediate stage. Experimental studies (Fredrickson and Cox,  $1954$ ) on the solubility of albite produced a gel from which analcite crystallized. The analcite, however, crystallized as a single crystal and not as a spherulite.

Pettijohn (1957) and Ramberg (1958) attribute the development of accretionary forms, such as spherulites, to differentiation. It is proposed that mineral assemblages are most stable when segregated. This is based on the assumption that the rock mass will have a lower free energy, and will therefore be more stable, if the mineral is segregated rather than disseminated. This explanation adequately accounts for the occurrence of the spherulites. It has not, however, been experimentally verified.

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Spherulitic crystallization from a supersaturated, high-polymer solution has been theoretically considered (Sears, 1963) and experimentally investigated (Bassett, et al., 1963; Magill, 1965). Spherulites are recognized to be the usual mode of crystallization of high polymers (Sears, 1961).

The formation of a spherulite, rather than a single crystal, is a function of the critical radius of nucleation (Sears, 1961). There has been little investigation of the nucleation and polymerization of silicates in"solution. Consequently, there is little basis for evaluation of the conditions which might crystallize spherulites or single crystals. The type of spherulitic structure that develops from a spherulitic nucleus is determined by the conditions under which growth, as

distinct from nucleation, occurs (Sears, 1961; Magill, 1965). The observed differences in the analcite spherulite structures, therefore, may be due to changes in conditions during growth (eg. solution concentration, temperature).

Microscopic examination has revealed only limited information that could be used to infer the origin of the spherulites. Modifications in the spherulite structures suggests that there may have been some differences in the conditions governing spherulite growth, or that the spherulites may have undergone varying degrees of recrystallization after formation. Observed textural. relationships indicate that direct crystallization of the spherulites from a colloid is unlikely. However, there is little basis to distinguish between differentiation or crystallization from a supersaturated, high-polymer solution as possible origins for the spherulites.

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### RELATIONSHIP OF ANALCITE OCCURRENCES IN THE ARKOSE AND ANALCIMOLITE

The compositions of nalacite in the arkose and analcimolite vary within a narrow range (Fig. 20). Analcite in the arkose is slightly more siliceous than analcite in the analcimolite. The average composition of analcite in the arkose is  $4.39$ . The average composition of analcite in the analcimolite is  $4.08.$ 

The composition of analcite in sedimentary rocks is a function of the parent material from which it has been derived, and the composition of the solution from which it crystallized (Whetten and Coombs, 1967; Ijima and Hay, 1968). The analcite in the arkose and analcimo-

lite are silica-poor (see Fig. 15).

Analcite in the arkose and analcimolite have different textural appearances. Analcite in the arkose occurs as spherulites and in the analcimolite it occurs as a matrix devoid of structure. The analcimolite has a smaller detrital mineral fraction than the arkose.

The analcimolite rests on the analcite-bearing arkose. The analcite content of the arkose increases upward in the section. The analcimolite appears to be a culmination of the increasing analcite content of the unit (see Fig. 14). It has been demonstrated that analcite in the arkose has been derived from the detrital feldspars. However, there is no evidence to warrant extending this relationship· to the analcimolite. The contact between the arkose and the analcimolite is sharp. There is no indication of interaction between the two rock types.

On the basis 0£ compositional similarities between analcite in the arkose and the analcimolite, it is concluded that they came from similar parent materials (see Fig. 15; Explanation; Group C). Proposed origins for analcimolite-like rocks that appear applicable to the Golden Valley (?) analcimolite are by direct precipitation from solution (Van Houten, 1962) and by crystallization of gels from alkaline springs (Eugster and Jones, 1968). There is no evidence to indicate that the formation of analcite in the arkose and analcimolite was either dependent or independent.



#### RELATIONSHIP OF ANALCITE DISTRIBUTION TO THE POST-EOCENE UNCONFORMITY

Denson (written communication to W .J. Stone, 1970) has defined the regionaJ. distribution of analcite: "In our experience, the occurrence of analcite is restricted largely to the rocks directly underlying the regional unconformity at the base of the Oligocene and Miocene. In the Williston Basin analcite can and does occur in all formations transected by this unconformity." The tentativeness of this observatior is stressed, since the mineralogy of the rocks in the Tertiary sequence has not been completely examined in detail. The Tertiary rocks in which analcite does appear are the arkose and analcimolite assigned to the Golden Valley Formation and the sands of the Sentinal Butte and Tongue River Formations.

The significance of the restriction of analcite to rocks below the post-Eocene unconformity is not immediately apparent. The absence of analcite in these rocks may reflect climatic changes or differences in the mineral composition and physical properties (eg. porosity, permeability) of the sediment. These possibilities, however, are speculative, and should be considered as largely tentative until there has been a more detailed examination of the mineralogy of the rocks above the post-Eocene unconformity, to determine the validity of Denson's observation.

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- 1. Analcite occurs in two distinct rock types, arkose and analcimolite. Analcite constitutes up to about 60 percent of tho arkose and up to 80 percent of the analcimolite.
- 2. The analcite-bearing rocks are possibly late Eocene in age, and have been tentatively included in the Golden Valley Formation.
- :,. The analcite occurs in the arkose as spherulites. Three types of spherulites are recognized: (1) spherulites with a radial internal structure; (2) spherulites with a massive center and a peripheral radial structure; and  $(3)$  spherulites with no internal structure, or a poorly-defined internal structure. Proposed origins for the spherulites are by diagenetic differentiation or by crystallization from a supersaturated, high polymer solution. The analcite is least abundant at the base of the arkose unit, and increases upward. The abundances oi' the analcite and the detrital feldspars are inversely related. It is proposed that analcite in the arkose crystallized from alkaline, interstitial solutions, undersaturated with respect to silica and with high  $Na<sup>+</sup>$  concentration. The required constituents were derived from feldspars dissolving in the interstitial solutions. Sericite occurs with the analcite in the arkose as a possible associated alteration product.

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 $4.$  Analcite cccurs in the analcimolite as a cement. Proposed origins. for the analcimolite are by precipitation from surface waters, or by crystallization of gels from alkaline springs.

5. Analcite in the arkose and analcimolite is silica-poor. Analcite in the arkose, however, is more siliceous than analcite in

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the analcimolite.

APPENDIX

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# APPENDIX

## AREAL LOCATIONS AND STRATIGRAPHIC POSITIONS OF SPECIMENS CITED IN TEXT (Numbered Localities Refer to Figure 1)





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