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INTERNAL STRUCTURE OF SILICATE MINERALS THAT GELATINIZE WITH ACID*

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ABSTRACT

A list of silicate minerals that are reported to gelatinize on being treated with acid was compiled and arranged according to a classification based on the internal structures of the minerals. From an examination of this data it is concluded that the following classes of minerals will gelatinize, if they are vulnerable to acid attack.

1. Those minerals containing silicate radicals of small molecular weight, namely orthosilicates, pyrosilicates, and possibly silicates containing ring structures of three silicon atoms.
2. Those minerals with large continuous silicon-oxygen networks that will disintegrate into units of low molecular weight.
    (a) Disilicates containing appreciable ferric iron in the silicon-oxygen sheets.
    (b) Minerals of the silica type with three-dimensional networks that contain aluminum in the ratio of at least two aluminum atoms to three silicon atoms.

Minerals that separate insoluble silica, instead of gelatinizing, upon being treated with acid, are characterized by silicon-oxygen structures of large dimensions that do not disintegrate into small units under acid attack. These are SiO_3 chains, Si_4O_{11} double chains,

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Si_2O_5 sheets not containing large amounts of ferric iron replacing silicon, and three-dimensional networks having an aluminum content less than the ratio of two aluminum atoms to three silicon atoms.

The exceptions to these rules are briefly discussed.

INTRODUCTION

Before the discovery of the methods of x-ray analysis, various attempts[1] were made to deduce the constitution of the silicate minerals by chemical means. Minerals were subjected to the action of acids, alkalies and other reagents, and from their different behaviors different types of structure were inferred, many of which have been found to be inadequate or erroneous through the more direct x-ray methods of analysis that were subsequently developed.

Now that there is a fairly detailed knowledge of the internal structure of the major groups of silicate minerals, it becomes of interest to reverse the process of study and to examine the chemical properties of these minerals in the light of their known constitution. Various physical qualities such as hardness, cleavage, twinning laws, and optical properties, have already been qualitatively or quantitatively explained in terms of the internal structures. The restricted chemical composition of some of the silicates and the greatly varied composition of others, which can undergo isomorphous replacements, are now seen to be a consequence of specific requirements of the various crystal structures. Among the few examples of a dynamic chemical property of the silicates that has been correlated with their structure are the base-exchange relations of the zeolites,[2] and the water-absorbing behavior of the clay minerals.[3]

In this paper, the property possessed by a number of silicate minerals of gelatinizing on being treated with acids will be considered in terms of their structure. This property seems especially suitable for examination because it has been noted among many different types of silicate minerals, and it so directly involves their fundamental silicon-oxygen frameworks.

The hypothesis is presented that in order for a mineral to gelatinize, its siliceous structure must be of such a nature that, when attacked by an acid, it will break down into units of small molecular weight not containing more than some small maximum number of silicon atoms.

The nature of the liberated silica is not viewed here with the care or the aim that Tschermak[4] had in mind, when he tried to identify various silicic acids which he believed were given off by the silicate minerals on

[1] For a review of these attempts, see Doelter, C., *Handbuch der Mineralchemie,* **2** (1), 61–109 (1914). Clarke, F. W., *U. S. Geol. Survey, Bull.* **588** (1914).

[2] Taylor, W. H., *Proc. Roy. Soc.* (London), **A 145,** 80 (1934).

[3] Hendricks, S. B., and Jefferson, M. E., *Am. Mineral.,* **23,** 863 (1938).

[4] Tschermak, G., *Sitz. Akad. Wiss. Wien., Math.-Naturw. Klasse, Abt.* **1,** 217 (1906).

acid treatment. Silicate minerals that are not attacked, or only slightly attacked by acids, are not considered in this paper except where decomposition may be expected from their group relations or from their composition. Neither are those silicates considered that contain additional acid radicals as major constituents (spurrite, thaumasite, etc.).

METHOD OF TESTING MINERAL POWDERS

The silicate minerals that are decomposed by acid treatment may be placed in one of two classes, following Brush and Penfield[5] (pp. 108 and 109) but reversing their order, namely:

(1) Those that separate insoluble silica without forming a jelly.
(2) Those that form a jelly (gelatinization).

That it is possible to discriminate between these two classes with practical precision is shown by the fact that this discrimination is required in the well known determinative scheme of Brush and Penfield. Their method of treating the minerals with hydrochloric or nitric acids might be adopted as a reference standard for the purposes of this discussion, although it is usually not necessary to continue the boiling until only 1 ml. of solution remains. Their method of treatment is as follows:

> (p. 278) " . . . treat one or two ivory-spoonfuls[6] of the *finely powdered* material in a test tube with from 3–5 c.c. of hydrochloric acid, and boil until not over 1 c.c. remains."

(1) For those minerals that separate insoluble silica without forming a jelly (without gelatinization), they state: (p. 281)

> "When the powder is first shaken up with the cold acid the liquid will generally appear milky, owing to the fine, suspended material; when boiled, however, the liquid becomes translucent, although the separated silica prevents it from becoming perfectly clear. After a little experience one can usually decide from appearances whether the insoluble material is *separated silica* or the *undecomposed mineral;* . . . "

The mineral is decomposed but is not completely soluble to a clear filterable solution; the presence of separated silica is characteristic. This separated silica is variously described in the literature as being slimy, gelatinous, pulverulent, flocculent, or sandy; or to form a skeleton of silica, a deposit of silica, or to separate the silica in scales. A comparison

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[5] Brush, G. J., and Penfield, S. L., *Determinative Mineralogy and Blowpipe Analysis.* 16th ed., Wiley, New York (**1898**).

[6] In order to place the reaction on a somewhat more quantitative basis, some tests were made as to the quantity of ground mineral sample in an "ivory spoonful." Using an ivory spoon (kindly loaned by Prof. Switzer of Yale) of the type and size illustrated in Fig. 42, p. 41, of Brush and Penfield, it was found that such a spoonful, the bowl of the spoon measuring about 13 by 5 mm. and about 1 mm. deep, contained from 0.04 to 0.05 ml. of 100-mesh mineral powder when neither heaped nor levelled off. For a mineral of sp. gr. 2 to 3, the sample weighed about 0.10 to 0.15 gram; for sp. gr. of 3 to 4, the sample weighed about 0.15 to 0.20 gram.

of the character of the separated silica from several minerals of class 1 does not indicate any necessity for such distinctions. In fact, some of the terms are misleading. Thus both apophyllite and chabazite are stated by Dana to yield "slimy silica" and xonotlite to yield "pulverulent silica," but comparative tests made on these minerals indicated no such essential difference between the separated silicas.

The character of the "separated silica" varies slightly for different minerals. It usually appears isotropic under the microscope (chabazite, wollastonite, pectolite, sturtite) with a refractive index of about 1.45. For apophyllite, the separated silica appeared birefringent. For some minerals the separated silica sharply retains the size and shape of the original mineral grains whereas for other minerals the grains tend to spread and fray out.

(2) For those minerals that form a jelly, Brush and Penfield state: (p. 278)

> "The mineral should go wholly into solution, unless difficultly soluble, and when the volume becomes small the contents of the tube should *thicken*, owing to the separation of *gelatinous silicic acid*."

It is obvious that the expression "separation of gelatinous silicic acid" means the *formation of a jelly*.

The procedure to be followed is explained in greater detail by Brush and Penfield on page 109. In making such tests it is well to follow the caution to mix the ground sample first with 1 ml. of water before adding the acid, in order to prevent caking. For 2 or 3 ml. of acid, 1 ivory spoonful is ample. For some minerals tested—nepheline, hemimorphite, olivine, tephroite, leucophoenicite—it was not necessary to "boil until not over 1 c.c. remains." On gentle heating, the minerals readily dissolved and formed a stiff jelly with very little diminution of total volume of liquid.

The specifications of class (2) "Those that form a jelly," under standard conditions—1 ivory spoonful of at least 100 mesh powder with 3 ml. acid—may then be defined as follows: Completely soluble to a clear filterable solution which when gently heated and allowed to stand for a short time (nepheline, for example) or if necessary, boiled with consequent reduction of volume of liquid (olivines), becomes thick from the development of gelatinous silica, so rigid that nothing runs out when the test tube is inverted.

Minerals that gelatinize easily, such as nepheline, hemimorphite, tephroite, readily set to a non-filterable rigid gel on gentle warming if 2 ml. concentrated hydrochloric acid is added to the mineral powder already shaken with 1 ml. of water. Perhaps it would set similarly in the cold if allowed to stand sufficient time. The mineral and liquid should be continuously agitated for a while to prevent "setting" of mineral grains at the bottom of the tube. This is easily done by holding the tube at its upper end between the thumb and index finger of one hand and gently tapping the bottom of the tube with a finger of the other hand.

Other minerals, such as olivine, are less easily decomposed and may require boiling and consequent reduction of volume of liquid. Undecomposed mineral may remain in the bottom of the tube even if the solution sets to a rigid gel.

Minerals of class 2 may be described as decomposed by acid with gelatinization, if the term gelatinization be restricted to mean that a rigid jelly is formed.

The expressions "separation of gelatinous silicic acid," "formation of gelatinous silica," "gelatinizes," "affords a jelly," found in the literature usually imply the formation of a rigid jelly. The phrase "separation of gelatinous silica" however is ambiguous as it may be interpreted as yielding masses of gelatinous silica without the solution setting to one rigid mass of jelly. Thus the action of acid on the two minerals, leucophoenicite and alleghanyite, of very similar composition, may be described for both minerals as yielding a "separation of gelatinous silica," but whereas leucophoenicite readily sets to a rigid jelly, repeated tests on various samples of alleghanyite failed to yield a rigid jelly although masses of gelatinous silica readily separate. In the terminology here used leucophoenicite is decomposed by acid with gelatinization whereas alleghanyite is decomposed by acid without gelatinization, although masses of gelatinous silica separate out.

Thus, although the decomposable minerals may be grouped into two classes for practical reasons, the division may not be altogether sharp and definite and transitions may exist. The filtered solution of a mineral of class 1, which does not gelatinize, that is, does not set to a rigid jelly, under the conditions described, might possibly, on sufficient reduction of volume, result in a jelly-like mass due to the small quantity of silica that went into solution though the bulk of the silica separated out as insoluble.

Compilation of Data

A list of minerals that gelatinize has been compiled mainly from the tables in the book by Brush and Penfield and from the extensive tables in the Geological Survey Bulletin by Larsen and Berman.[7] In the latter, a distinction is made between silicates that "gelatinize" and those that are "soluble in HCl." The writer has assumed that these two expressions are equivalent. Whether on addition of an acid there is immediate

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[7] Larsen, E. S., and Berman, H., *U. S. Geol. Survey, Bull.* **848** (1934).

gelatinization or whether the solution must be evaporated for the jelly to appear is largely a matter of concentration of acid and the volume of acid applied to a given weight of the mineral. Therefore, minerals indicated as showing either behavior have been included in the compilation. Because the expression "soluble in HCl" is used loosely by some authors to mean simply that the mineral is decomposed by acid, without implying anything as to the nature of the silica which is separated, special care was taken with minerals that were so described to compare the data from several sources.

The compiled list of minerals was first classified according to the scheme outlined by Berman.[8] Then the major divisions were rearranged in accordance with Bragg's classification,[9] in which the orthosilicates are considered first, as this arrangement is more convenient for this discussion. Berman is careful to point out that although the major structural types of silicate minerals have been recognized through *x*-ray studies, the actual number of species that have been completely analyzed is small, something like 10–15 per cent of the total number. He frankly admits "the probability that a considerable number of minerals will be found, when more structural data are available, to have been misplaced in the classification." Some of the anomalies to be noted later may arise from such misplacements. In spite of the uncertainties, however, Berman's classification is a valuable extension and application of the new structural principles, and it greatly facilitated the present study.

The various type structures that form the basis of modern classifications of the silicate minerals are illustrated in the following cut from Berman's paper, and his numbering of the figures is followed in this paper.

The following table should be carefully compared with the one given by Berman. All minerals that are absent from the table are not reported to gelatinize. They are undecomposed by acid or only slightly decomposed, are decomposed with separation of silica, or, for a few minerals, have no data as to their behavior towards acid given for them. Some discrepancies encountered in comparing the various sources of information are noted in the footnotes to the table, and a few other discrepancies are discussed at different places in the text.

In noting the minerals that do not appear in the table because of their non-decomposition, or only slight decomposition by acid, a rough correlation between non-decomposition and internal structure soon becomes apparent. Brush and Penfield[10] have remarked that "orthosilicates are more soluble in acids than metasilicates and polysilicates." However,

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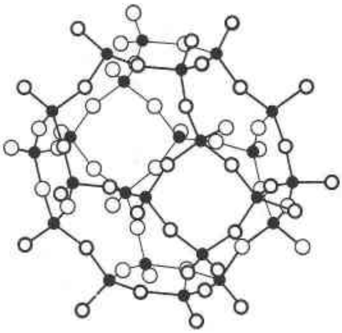
[8] Berman, H., *Am. Mineral.*, **22**, 342 (1937).

[9] Bragg, W. L., *Atomic Structure of Minerals.* Cornell Univ. Press (**1937**).

[10] *Loc. cit.*, p. 108.



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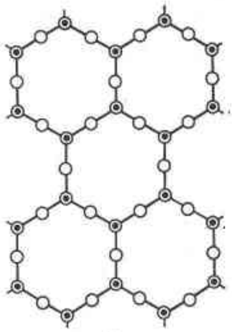

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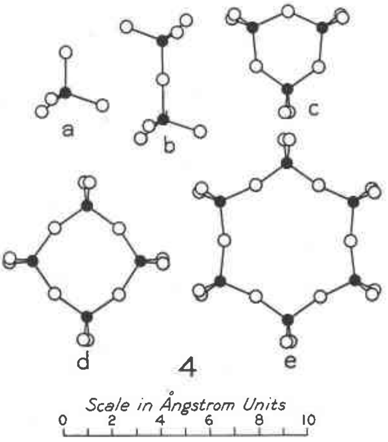

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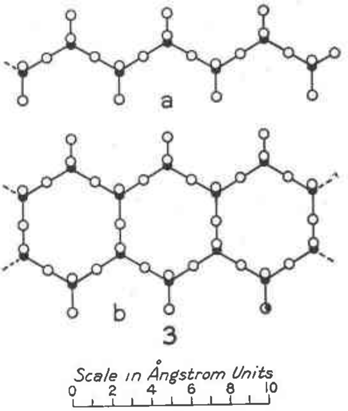

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Linkages of silicon-oxygen tetrahedra. Black, silicon, with or without aluminum; white, oxygen. After Bragg.

Fig. 1. One example of the Silica type, SiO_2; three-dimensional linkage.

Fig. 2. One example of the Disilicate type, Si_2O_5; two-dimensional linkage.

Fig. 3. Metasilicate type; (a) SiO_3, single-chain linkage; (b) Si_4O_{11}, double-chain linkage.

Fig. 4. (a) Orthosilicate type, SiO_4; independent tetrahedra. (b) Pyrosilicate type, Si_2O_7; paired tetrahedra. (c) Ring-linkage, Si_3O_9. (d) Ring-linkage, Si_4O_{12}. (e) Ring-linkage, Si_6O_{18}.

The gelatinizing minerals have silicon- (and aluminum-) oxygen linkages shown in the following figures.

Figure 1, with the amount of aluminum that replaces silicon equal to, or exceeding the ratio of, two aluminum atoms to three silicon atoms.

Figure 2, with a large amount of ferric iron replacing silicon.

Figures 4*a*, 4*b*, and possibly 4*c*.

Minerals that separate insoluble silica, instead of gelatinizing, have linkages shown in Figs. 1, 2, 3*a*, and 3*b*, except for the compositions noted above for Figs. 1 and 2.

The data on the behavior of the ring linkages, 4*c*, 4*d*, and 4*e*, are meager.

factors other than the internal structure, such as the nature of the bases, are important in determining whether a mineral is decomposed or undecomposed,[11] so this matter is considered here as a separate problem.

About 350 silicate minerals are considered in Berman's paper. In rough figures, 35 per cent of these gelatinize, 20 per cent are decomposed with separation of silica, and 45 per cent are undecomposed or only slightly decomposed by acid. The gelatinizing minerals, therefore, comprise an appreciable proportion of the total number.

A CLASSIFIED LIST OF GELATINIZING MINERALS

ORTHOSILICATES

Olivine group
  Forsterite
  Olivine
  Hortonolite
  Knebelite
  Fayalite
  Tephroite
  Roepperite
  Glaucochroite
  Monticellite
  Larsenite
  Calcium larsenite

  Larnite
  Merwinite

Phenakite group
  Willemite
  Troostite
  Trimerite[1]
  Dioptase

Humite Group
  Chondrodite
  Humite
  Clinohumite

Hodgkinsonite group
  Hodgkinsonite
  Leucophoenicite

  Gageite[2]

Garnet group
  Andradite
  Titanium garnet
  Hibschite

  Sarcolite

Allanite series
  Allanite
  Nagatelite[3]

Zircon group
  Thorite
  Uranothorite

Woehlerite group
  Rosenbuschite
  Woehlerite
  Hiortdahlite
  Johnstrupite

  Rinkite
  Rinkolite
  Mosandrite[4]
  Låvenite
  Britholite
  Hellandite
  Lessingite
  Abkumalite

Datolite family
  Datolite
  Homilite
  Gadolinite

Misc. orthosilicates
  Ilvaite
  Eulytite
  Agricolite

[11] For example, beryllium, when it is the dominant base in a mineral, greatly influences the behavior of the mineral toward acid. In the orthosilicate phenakite group and the pyrosilicate hemimorphite family, only phenakite, Be_2SiO_4, and bertrandite, $Be_4Si_2O_7(OH)_2$, are undecomposed, and thereby stand conspicuously apart from the other members which are all attacked by acid.

SUBSILICATES

- *Kentrolite group*
  - Kentrolite
  - Melanotekite[5]
- Beckelite
- *Misc. subsilicates*
  - Cappelenite
- *Uranium silicates*
  - Uranophane
  - Sklodowskite
  - Kasolite
  - Soddyite

PYROSILICATES

- *Thalenite group*
  - Thalenite
  - Cerite
  - Rowlandite
- *Melilite group*
  - Melilite
  - Akermanite
  - Gehlenite
- Hardystonite
- *Barysilite group*
  - Barysilite
  - Ganomalite
  - Nasonite
- *Hemimorphite family*
  - Hemimorphite
  - Clinohedrite
  - Cuspidine
  - Custerite
  - Molybdophyllite
- *Misc. pyrosilicates*
  - Rankinite

RING STRUCTURES

- Catapleiite[6]
- Eudialyte (eucolite)

CHAIN STRUCTURES

- *Wollastonite group*
  - Alamosite
- *Calcium metasilicate family*
  - Hillebrandite
  - Jurupaite
  - Afwillite
- *Misc. metasilicates*
  - Cenosite
  - Ussingite

DISILICATES

- *Clay group*
  - Volchonskoite
  - Nontronite
- *Talc group*
  - Nepouite
- *Friedelite group*
  - Zeophyllite[7]
  - Gyrolite[8]
- *Misc. non-aluminum disilicates*
  - Okenite
- *Leptochlorite group*
  - Thuringite
  - Cronstedtite
  - Aphrosiderite
- *Vermiculite group*
  - Griffithite
- *Mica group*
  - Lepidomelane[9]
- *Misc. disilicates*
  - Ganophyllite

SILICA TYPE

Feldspar group
- Celsian
- Anorthite

Nepheline group
- Nepheline
- Kaliophilite
- Kalsilite
- Eucryptite

Cancrinite group
- Cancrinite
- Microsommite
- Davyne

Sodalite group
- Sodalite
- Hackmanite
- Noselite
- Hauyne
- Lazurite
- Helvite
- Danalite

Zeolite family
- Stilbite group
- Phillipsite[10]

- Gismondite

- Levynite

Thomsonite group
- Thomsonite
- Faroelite
- Gonnardite
- Ashcroftine

Natrolite group
- Natrolite
- Mesolite
- Scolectite
- Edingtonite

Misc. zeolites
- Laumontite

Silicate minerals unclassified by Berman.

- Allophane
- Greenalite
- Lovchorrite
- Pilbarite
- Tritomite
- Yttrialite
- Tscheffkinite
- Zebedassite
- Cebollite
- Roeblingite
- Orientite
- Fraipontite
- Bulfonteinite
- Yeatmanite
- Silicomagnesiofluorite

The discrepancies noted below and in different places in the text may be more apparent than real, because of the possible loose usage of the expressions "decomposed by HCl" and "soluble in HCl." The writer has interpreted the former expression to mean "decomposed by HCl with separation of silica," and the latter to be synonymous with "gelatinizes with HCl," but this may not have been the meaning intended by the various authors.

[1] Trimerite is reported as soluble in HCl by Larsen-Berman; as decomposed by HCl without gelatinization by Brush-Penfield.

[2] Gageite is reported as decomposed by HCl by Larsen-Berman; as dissolved at once in warm dilute nitric acid by Palache, *U. S. Geol. Survey, Prof. Paper* **180,** 111 (1930).

[3] Nagatelite is reported as soluble in HCl by Larsen-Berman. In the original description it is said to be easily decomposed by HCl leaving a white flocculent residue—Iimori et al., *Sci. Pap. Inst. Phys. Chem. Res. Tokyo,* **15,** 83 (1931).

[4] Mosandrite is reported as soluble in HCl by Larsen-Berman; as decomposed without gelatinization by Brush-Penfield.

[5] Melanotekite is reported as decomposed by HNO_3 by Larsen-Berman; as not giving a good jelly by Brush-Penfield.

[6] Catapleiite is reported as gelatinizing by Larsen-Berman; as decomposed by HCl without gelatinization by Brush-Penfield.

[7] Zeophyllite is reported as gelatinizing by Larsen-Berman; as soluble in HCl with the separation of flocculent, slimy silica by Hintze, *Handbuch der Mineralogie*, Ergänzungsband, Lief. **4,** 747 (1937).

[8] Gyrolite is reported to gelatinize with HCl by Brush-Penfield; easily soluble in dilute acids by Doelter, *Handbuch d. Mineralchemie*, **2** (1) 470 (1914); decomposed by HCl by Larsen-Berman.

Berman suggests that gyrolite and centrallassite may be identical, but all authorities agree that centrallassite is decomposed by HCl without gelatinization.

[9] Lepidomelane is said to gelatinize by both Brush-Penfield and Larsen-Berman; as easily decomposed by HCl, depositing silica in scales by Dana, *System of Mineralogy*, 6th ed.

[10] Phillipsite is reported as gelatinizing by Larsen-Berman; as decomposed by HCl without gelatinization by Brush-Penfield.

DISCUSSION

Orthosilicates. Figure 4*a.*

As a working hypothesis for the following discussion, it is assumed that in order for a mineral to gelatinize its siliceous structure must be of such a nature that, when attacked by an acid, it will break down into units of small molecular weight not containing more than some small maximum number of silicon atoms. Under this hypothesis, it follows that minerals containing discrete SiO_4 groups, which might be pictured as being dislodged from the mineral and going into solution as simple orthosilicic acid, H_4SiO_4, would most readily gelatinize. This would account for the ready gelatinization that characterizes minerals of the olivine, phenakite, humite, hodgkinsonite, woehlerite and datolite groups. All together, forty-nine species of the orthosilicate type are reported to gelatinize.

There are conflicting data for the behavior of trimerite, gageite, nagatelite, mosandrite and melanotekite, as noted in the footnotes to the table. Norbergite of the humite group is definitely stated, in the original description[12] to be soluble in warm HCl with the separation of silica. This behavior is anomalous for an orthosilicate.

As mentioned in the section on method of testing mineral powders, alleghanyite separates a mass of gelatinous silica but does not form a rigid jelly.

Garnets are also a potential source of gelatinous silica, because of their content of discrete SiO_4 groups. However, nearly all garnets are only slightly affected by acid, and the only varieties that are notably

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[12] Bygden, A., in Geijer, P., *Geol. För. Stockholm, Förh.*, **48,** 84 (1926).

attacked to give gelatinous silica are andradite and the titanium garnets. Andradite is the first of several examples that show the weakening influence of ferric iron when it replaces aluminum in a silicate structure. The high content of ferric iron (17–23% Fe_2O_3) in the titanium garnets is probably also reponsible for their gelatinization. The garnetoid mineral, hibschite,[13] is soluble in HCl, which shows that the substitution of water for silica likewise weakens the garnet structure toward acid attack.

Subsilicates

The nature of the silicate groups in the subsilicates, kentrolite, melanotekite, beckelite, cappelenite, and in the uranium silicates, is unknown. Probably independent SiO_4 groups are present. The gelatinization of these minerals, under the working hypothesis, points to discrete units involving only a few silicon atoms or to larger networks that would disintegrate into smaller units under acid attack. Melanocerite is the only mineral among the subsilicates that separates insoluble silica.

Pyrosilicates. Figure 4b.

That the pyrosilicate group or radical containing two silicon atoms will undergo gelatinization is abundantly illustrated by the soluble members of the thalenite, melilite, barysilite and hemimorphite groups. All together, there are sixteen gelatinizing minerals of the pyrosilicate type. Murmanite of the hemimorphite family and astrophyllite, both reported to be decomposed with a separation of silica, stand as exceptions.

With this pyrosilicate unit, and all of the other condensed silicate structures which arise from mutual sharing of oxygen among adjacent silicon atoms, the reasonable assumption is made that the silicon-oxygen binding, -Si-O-Si-, among these adjacent silicons is strong enough to resist any attack by acids. The integrity of these condensed structures is also illustrated in the prevailing belief that no major physical weakness of a crystal, such as a prominent cleavage, readily transects such structures.

Ring structures. Figure 4c.

If Berman's postulate that eudialyte and catapleiite have closed silicon-oxygen rings containing three silicon atoms is correct, these minerals would offer examples of a condensed silicate unit of such dimensions gelatinizing. The evidence from catapleiite is marred by a discrepancy noted in the footnote to the table. On the other hand, steenstrupine, whose constitution is also interpreted by Berman as involving

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[13] Belyankin, D. S., and Petrov, V. P., *Am. Mineral.*, **26**, 450 (1941).

Si_3O_9 rings, is reported to be "entirely decomposed by acids," and apparently not gelatinizing.

Chain structures. Figures 3a, 3b.

Silicon-oxygen structures of considerable dimensions are first encountered in the classification at this point. There is a sudden drop in the number of minerals that are attacked by acids. As illustrated in Figs. *3a* and *3b*, the chain structures are narrow in width, but extend continuously along their length. Minerals made up of such large structures would not be expected to gelatinize.

The amphiboles, pyroxenes (with the exception of johannsenite), the members of the rhodonite series of the pyroxenoid family, and the miscellaneous pyroxenoids are undecomposed, and therefore can offer no evidence as to the behavior of the chain structures under effective acid attack. Johannsenite[14] is completely decomposed by acid with separation of silica.

Among the hornblendes aluminum substitutes for silicon in the chain up to a maximum amount of one aluminum to three silicons,[15] i.e., up to a composition, $AlSi_3O_{11}$, for the amphibole chain. Apparently a substitution of this nature and magnitude does not lower the resistance of these minerals towards acids. A high content of ferric iron (15–30% Fe_2O_3), associated with but not incorporated in the silicon-oxygen chains, is without marked effect as shown by the non-decomposition of aegirite, acmite, riebeckite, and crocidolite.

Members of the wollastonite group and some members of the calcium metasilicate family separate silica, and this would be in accord with the concept of the integrity of the silicon-oxygen chains.

Wollastonite is reported in most references as separating insoluble silica, but is said in Rutley's *Mineralogy*[16] to gelatinize. This supposedly single species has been resolved into a triclinic modification (wollastonite) and a monoclinic modification (parawollastonite).[17] The behavior of these two modifications towards acid seems deserving of further study because of Barnick's conclusion[18] that their internal structure is made up of Si_3O_9 rings rather than SiO_3 chains.

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[14] Schaller, W. T., *Am. Mineral.*, **23**, 575–582 (1938).

Results obtained by W. T. Schaller (personal communication) indicate that for members of the isomorphous series between johannsenite, diopside, and hedenbergite, the degree of attack by acid is proportional to the quantity of manganese present.

[15] Warren, B. E., *Zeits. Krist.*, **72**, 493 (1930).

[16] Rutley's *Elements of Mineralogy* by H. H. Read. 23rd ed., London (**1936**).

W. T. Schaller has found that wollastonite from Potash Sulphur Springs, near Hot Springs, Arkansas, gelatinizes readily.

[17] Peacock, M. A., *Am. Jour. Sci.*, **30**, 495–529 (1935).

[18] Barnick M., *Naturwissenschaften*, **23**, 770–771 (1935).

There are conflicting data on the behavior of searlesite.[19] J. J. Fahey of the Geological Survey Chemical Laboratory, who recently analyzed a specimen of searlesite from Sweetwater County, Wyoming, reports that[20] "searlesite decomposes when boiled for 15 minutes with 1:1 HCl, leaving a siliceous skeleton which retains the form of the original crystal fragment. Treatment with cold 1:1 HCl for 24 hours causes only a partial decomposition of the mineral." This is the behavior one would expect of a mineral having an extensive silicon-oxygen condensed structure.

The concept of the integrity of the silicon-oxygen chains throws into prominence those minerals of this part of the classification that are said to gelatinize: alamosite, hillebrandite, jurupaite, afwillite, cenosite, and ussingite. Alamosite with its simple composition, $PbSiO_3$, is outstanding among these exceptions. The question may be raised whether the formula of hillebrandite should not be written as $Ca_2SiO_4 \cdot H_2O$ and the mineral classified among the orthosilicates.

Disilicate type. Figure 2.

The condensed silicon-oxygen structure, which forms the basis for this part of the classification, extends continuously in two directions, forming a sheet-like framework. This framework bestows on platy minerals, such as the micas and the clays, their peculiar physical and chemical properties. Treating biotite and phlogopite with acids to obtain plates of hydrated silica is a well known laboratory experiment among students of mineralogy. As with the chain structures, a large number of minerals of the disilicate type are insoluble in acid.

Aluminum can freely substitute for silicon in the sheet structure, giving a continuous series of composition for the structure of Si_4O_{10}, $AlSi_3O_{10}$, $Al_2Si_2O_{10}$, and Al_3SiO_{10}, the last composition being approached in seybertite and xanthophyllite of the clintonite group. This considerable entrance of aluminum into the two dimensional silicon-oxygen sheet apparently does not cause any corresponding change in the behavior of disilicate minerals toward acids. This appears remarkable in light of the marked weakening effect that aluminum shows in the three dimensional silicon-oxygen networks to be discussed later.

A glance at the list of minerals of the disilicate type which are reported to gelatinize reveals that a high content of ferric iron is a feature common to some of them. The weakening effect of ferric iron on silicate structures, already noted with andradite and the titanium garnets, is indicated. However, an additional necessary condition would seem to be that the

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[19] Larsen, E. S., and Hicks, W. B., *Am. Jour. Sci.*, **38**, 437 (1914). Foshag, W. F., *Am. Mineral.*, **19**, 268 (1934).

[20] Personal communication.

ferric iron must be in the silicon-oxygen sheet itself to promote the disruption of this sheet into smaller units. Ferric iron within the sheet structure has been recognized in cronstedtite,[21] and possibly this condition may be found in the other gelatinizing minerals, rich in ferric iron, namely, volchonskoite, some nontronites (for example, the type nontronite), thuringite, and lepidomelane.

The entrance of an ion-like ferric iron, which is appreciably larger than silicon, into the tetrahedral position of a silicate structure calls for a brief examination of the geometrical restrictions that must be complied with. This ion must have a coordination number of four, i.e., it must be of such a size, neither too small nor too large, so that it can hold four oxygen ions around itself in a stable tetrahedral arrangement. The coordination number of a cation with respect to any anion is determined by the geometrical quantity ρ, known as the radius ratio and defined as $\rho = R^+/R^-$, where R^+ and R^- are the radii of the cation and anion respectively.

The radius ratio for ferric iron with respect to oxygen, when calculated according to the method given by Pauling[22] starting with his value of 0.60Å for the empirical radius of ferric iron, is 0.45. This places ferric iron between quadrivalent germanium and divalent magnesium with respect to its coordinating number (see Pauling's table 48–52), and therefore, just within the range, delimited by the values of the radius ratio, in which tetrahedral coordination is possible.

The calculation shows that ferric iron is a borderline ion among those that can assume a tetrahedral coordination, and suggests that minerals containing this ion in such a coordination would be rare. At present ferric iron in a tetrahedral coordination is known among natural minerals only in cronstedtite and in small amounts in iron-bearing orthoclase.[23]

Glauconite is an example of a mineral of the disilicate class, rich in ferric iron, with the ferric iron in octahedral positions outside the silicon-oxygen sheets.[24] Those samples of glauconite that are decomposed by acid separate silica.[25] Experiments by Hutton and Seelye[26] show that 80–90 per cent of the silica is insoluble and remains on the filter.

The gel-forming nature of zeophyllite, gyrolite, okenite, aphrosiderite, griffithite, ganophyllite, and nepouite, cannot be explained on the basis

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[21] Hendricks, S. B., *Am. Mineral.*, **24,** 529 (1939).

[22] Pauling, L., *Nature of the Chemical Bond.* 2nd ed. pp. 345–350 and 380–382. Cornell Press (**1940**).

[23] Faust, G. T., *Am. Mineral.*, **21,** 735 (1936).

[24] Hendricks, S. B., and Ross, C. S., *Am. Mineral.*, **26,** 683 (1941).

[25] Smulikowski, K., *Arch. Min. Tow. Nauk. Warzaw,* **12,** 145–180 (1936). Turrentine, J. W., et al., *Ind. Eng. Chem.*, **17,** 1177–1181 (1925).

[26] Hutton, C. O., and Seelye, F. T., *Am. Mineral.*, **26,** 595–604 (1941).

that these minerals are made up of continuous sheet structures. It seems unlikely that nepouite, a mineral with the structure of antigorite,[27] should dissolve completely in HCl as Glasser[28] reports.

Apophyllite, listed among the miscellaneous non-aluminum disilicates by Berman, is made up of what Bragg calls the tetragonal type of silicon-oxygen sheet, in contrast to the hexagonal type of silicon-oxygen sheet shown in Fig. 2. The silicon-oxygen tetrahedra form rings of four and eight linked groups instead of rings of six linked groups.[29] The mineral is decomposed by hydrochloric with separation of silica. Skeletonized apophyllite, with composition similar to that of opal, has recently been described by Bailey.[30]

Silica type. Figure 1.

The fundamental silicon-oxygen framework possessed by minerals of this category is a three dimensional structure which results from the fullest sharing of oxygen among adjacent silicon atoms. This three-dimensional framework seems more fragile when compared with the sheet structure of the previous section, in that an appreciable substitution of the silicon atoms by aluminum renders it vulnerable toward profound attack by acid with consequent gelatinization. The presence of aluminum in a ratio of two or more aluminum to three silicon results in a structure that can gelatinize. The frameworks of many of the minerals of this class have large channels that allow base-exchange reactions and movements of water. These open channels make such minerals peculiarly susceptible to acid attack.

Among the feldspars, only celsian and anorthite are commonly reported to gelatinize, and these have an aluminum to silicon ratio of 1:1. The plagioclase feldspars are progressively more decomposed by acid as the composition changes from albite, which is unattacked, to anorthite, which gelatinizes. Bytownite, as well as anorthite, is said by Iddings[31] to gelatinize. The aluminum to silicon ratio of the least calcic bytownite is around 3:4. However, the exact relation between composition and gelatinization is obscured here because the representatives of such a large part of the plagioclase series are resistant to acid.

The fourteen minerals of the nepheline, cancrinite, and sodalite groups have an aluminum to silicon ratio of 1:1, and they all gelatinize.

The aluminum to silicon ratio in the scapolite series varies from 1:3 to 1:1, and these minerals, like the plagioclase feldspars, are progressively more decomposed by acid as the aluminum to silicon ratio becomes

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[27] Caillere, S., *Bull. soc. franc. mineral.*, **59,** 293–294 (1936).

[28] Glasser, E., *Ibid.*, **30,** 17(1907).

[29] Taylor, W. H., and Náray-Szabó, St., *Zeits. Krist.*, **77,** 146–158 (1931).

[30] Bailey, E. H., *Am. Mineral.*, **26,** 565–567 (1941).

[31] Iddings, J. P., *Rock Minerals*, 2nd ed., p. 206. New York (**1911**).

larger. However, the data on the behavior of these minerals toward acid is not very satisfactory. There are conflicting reports on whether meionite, the high-aluminum end member, gelatinizes or separates silica.[32]

The zeolites are an excellent group of minerals for studying the relation between composition and gelatinization in three-dimensional structures, because such a large number of them succumb to attack by acid, with or without gelatinization. Rinne[33] has made detailed microscopic observations on the behavior of cleavage pieces or oriented sections of some of the zeolites subjected to the action of acids.

Among the zeolites, a general rule is apparent that those species having an aluminum to silicon ratio of 2:3, or higher, will yield gelatinous silica. The sole exception, which gelatinizes with a lower aluminum to silicon ratio, is laumontite (13:27).

Epidesmine (11:29) is said by Larsen and Berman to gelatinize, but this is believed to be in error. In Hintze's *Handbuch*,[34] this species is said to dissolve in hydrochloric acid with the separation of sandy, slimy silica. Furthermore, Pabst[35] has recently shown the identity of epidesmine, stellerite, and stilbite, and all authorities agree that the last two minerals decompose without gelatinization. Erionite is erroneously reported[36] to be easily soluble, although in the original description[37] it is said to be "soluble in HCl with extreme difficulty. Silica separates as fine sand with no gelatinization."

Two exceptions to the general rule in the other direction, namely, minerals with a ratio of 2:3 or higher that succumb to acid attack but do not gelatinize, are wellsite (18:22) and arduinite (2:3). There are eleven zeolites that gelatinize and eleven zeolites that separate silica which securely establish the boundary ratio of two aluminum to three silicon.

Minerals unclassified by Berman

Among the gelatinizing minerals unclassified by Berman, allophane is of special interest, because it is one of a very few minerals that have been demonstrated by *x*-ray and dehydration studies[38] to be truly amorphous. An unorganized amorphous state would seem especially favorable for gelatinization. Such materials as the siliceous glasses[39] are amorphous

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[32] Dana's *System of Mineralogy*, 6th ed., p. 468 (**1920**).

[33] Rinne, F., *Centralbl. Mineral. Geol. Palaeont.*, 594–601 (**1902**).

[34] Hintze, C., *Handbuch d. Mineralogie*, Ergänzungsband, Lief. **1**, 157 (1936).

[35] Pabst, A., *Mineral. Mag.*, **25**, 271 (1939).

[36] 1st appendix to 6th ed. Dana's *System of Mineralogy*.

[37] Eakle, A. S., *Am. Jour. Sci.*, **6**, 67 (1898).

[38] Ross, C. S., and Kerr, P. F., *U. S. Geol. Survey, Prof. Paper* **185-G**, 144–148 (1934).

[39] Zachariasen, W. H., *Jour. Am. Chem. Soc.*, **54**, 3841 (1932).
Warren, B. E., and Loring, A. D., *Jour. Am. Ceram. Soc.*, **18**, 269 (1935).

but contain extensive, though irregular silicon-oxygen networks, and substances of this nature which might be vulnerable to acid attack would not be expected to gelatinize.

The report that greenalite is soluble in acids is not in harmony with the fact that it gives *x*-ray powder pattern of serpentine.[40] Very likely, the word "soluble" is used loosely to mean that the mineral is decomposed by acid. When the time comes for the minerals of this section to be classified, it is apparent that their gel-forming nature must be considered.

GELATINIZATION AFTER IGNITION

A number of minerals that do not gelatinize in their natural state will do so after being ignited. Examples of these are serpentine, zoisite, epidote, and the garnets. During ignition a new phase is formed which possesses the quality of gelatinizing. With serpentine it has been long known[41] that the new phase is olivine and this identification was recently checked[42] through *x*-ray powder photographs of the calcined product.

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[40] Gruner, J. W., *Am. Mineral.*, **21**, 449 (1936).

[41] Clarke, F. W., and Schneider, E. A., *Am. Jour. Sci.*, **40**, 303 (1890).

[42] Caillere, S., *Bull. soc. franc. mineral.*, **59**, 261 (1936).