

SYNTHESIS OF GRUNERITE AND OTHER PHASES
IN THE SYSTEM $\text{SiO}_2\text{-NaOH-Fe-H}_2\text{O}^1$

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ABSTRACT

Grunerite has been synthesized in the system $\text{SiO}_2\text{-NaOH-Fe-H}_2\text{O}$ under dynamic conditions at about 400°C and a total pressure of about 1.6 Kb. The grunerite was most abundant near the bases of the vessels (temperature range $400\text{--}430^\circ\text{C}$) but also occurred in the upper part of the vessels (temperature range $360\text{--}410^\circ\text{C}$). In the uppermost part of the vessels grunerite is supplanted by micaceous phases and an unusual fibrous glass. The micaceous phases most closely resemble Na-nontronite or Na-vermiculite, but also have some properties like stilpnomelane. The role of sodium ions in the formation of grunerite and the micaceous phases was demonstrated by similar experiments using KOH as a solvent which produced no amphibole and only the mica, ferriannite.

INTRODUCTION

During the course of experiments designed to grow quartz in iron liners under varying conditions of temperature, pressure, and solvent chemistry, several unusual phases were obtained when 0.1 N NaOH was used near the critical temperature of water. Based on X-ray and optical studies these phases include: grunerite $\text{Fe}^{2+}_7(\text{Si}_8\text{O}_{22})(\text{OH})_2$, micaceous phases with spacings of about 12.5 Å and 15 Å, and a fibrous "glass". Additional phases present were quartz, acmite [$\text{NaFe}^{3+}\text{Si}_2\text{O}_6$], magnetite, and possibly riebeckite [$\text{Na}_2\text{Fe}^{2+}_3\text{Fe}^{3+}_2(\text{Si}_8\text{O}_{22})(\text{OH})_2$].

Grunerite was mentioned by Flaschen and Osborne (1957) as an intermediate phase in the hydrothermal decomposition of minnesotaite but was destroyed in runs of more than a few days duration. Winchell and Winchell (1964) report data for grunerite, but reference to the original paper by Bowen and Schairer (1935) indicates that the only synthetic compounds were a series of fluoramphiboles and that the optical data for grunerite were obtained from a natural (Rockport, Massachusetts) specimen. Deer *et al.* (1963) indicate that data concerning the stability of grunerite are lacking, and so far as the present authors are aware there are no more recent articles related to synthesis of this phase.

The system studied here contained neither aluminum nor magnesium, so that any micaceous phases which develop would be presumably most closely related to the more iron-rich natural phases such as nontronite, $(\text{Na,Ca,Mg})_x(\text{Fe}^{3+},\text{Al}, \text{Fe}^{2+},\text{Mg})_{4-6}(\text{Al,Si})_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$; vermiculite,

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$(\text{Mg,Ca,Na})_x(\text{Mg,Fe}^{2+},\text{Al,Fe}^{3+})_6(\text{Al,Si})_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$; and stilpnomelane, $(\text{K,Na,Ca})_x(\text{Fe}^{3+},\text{Fe}^{2+},\text{Mg,Al,Mn})_{x-6-8}\text{Si}_8\text{O}_{20}(\text{OH})_4 \cdot n(\text{O,OH,H}_2\text{O})$. Since NaOH was used as the solvent here, the phases formed should also more closely resemble the members of these phases which contain sodium in the interlayer site.

While nontronite has been successfully synthesized (as early as 1935 by Ewell and Insley), synthetic stilpnomelane containing iron does not appear to have been reported. Koizumi and Roy (1959) report that they obtained a "regular mixed-layer" phase with a basal spacing of 11.9 Å, in the temperature range 350–800°C at 1 Kb and suggested that this

TABLE 1. SUMMARY OF EXPERIMENTAL CONDITIONS

| | K-117 | K-158 | K-160 |
|---|---|------------|------------|
| Solvent | 0.1 N NaOH | 0.1 N NaOH | 0.1 N KOH |
| Nutrient | All used 9-g quartz chips in iron wire basket | | |
| Base temperature (°C) (nutrient region) | 425 ± 5°C | 410 ± 10°C | 400 ± 10°C |
| Seeds | All used pieces of quartz oscillator plate | | |
| Upper temperature (°C) (seed region) | 395 ± 15°C | 365 ± 5°C | 365 ± 5°C |
| Baffle | All used approximately 90% closure | | |
| Pressure (Kb) | ~1.55 | ~1.55 | ~1.62 |
| Duration | 82 days | 92 days | 75 days |

phase may be a magnesian stilpnomelane rather than a regular mixed-layer of chlorite and mica.

Finally, the hydrothermal development of an amorphous phase in a fibrous form seems quite unusual.

EXPERIMENTAL CONDITIONS

The experiments described here were performed in carbon-steel lined autoclaves (Kopp *et al.*, 1963). It should be emphasized that these vessels are deliberately placed in furnaces with temperature gradients (dynamic conditions) in contrast to many hydrothermal phase investigations in which isothermal conditions are maintained. The temperature gradient helps to establish convective overturn and a solubility gradient within the vessel, which aids the growth of the phases that develop. Self-nucleated crystals up to a few millimeters are often observed, and when seeds are used larger crystals may be grown as in the case of quartz.

The experimental details of three relevant experiments are given in Table 1. Experiment numbers K-117 and K-158 used 0.1 N NaOH as a solvent while K-160 used 0.1 N KOH for comparative purposes. The low concentration of NaOH used in the first two experiments appears to

be very important to the development of the observed phases since at higher concentrations (≥ 0.5 N) the reaction between the liner, solvent, and silica produces a protective coating of acmite which reduces further liner attack.

The effect of time was not studied, but might be important. Most reported experiments in quartz synthesis appear to be of only a few weeks duration, while these experiments lasted about three months.

In each experiment the steel liner was the source of iron for the synthesized phases. Studies by Eugster and Wones (1962) have made it possible to predetermine the oxygen fugacity of a hydrothermal system through the use of suitable buffers. While the buffering technique was not used in these experiments, the nature of the final products suggests that the oxygen fugacities within these vessels exceeded those determined by the iron-magnetite buffer and were less than those determined by the magnetite-hematite buffer. The presence of quartz and magnetite in the final products further suggests that the oxygen fugacities exceeded those defined by the magnetite + quartz fayalite buffer.

DESCRIPTION OF PHASES PRODUCED

The following phases were identified in the products of K-117 and K-158: grunerite, acmite, possibly riebeckite, micaceous phases, and an amorphous, fibrous phase. Quartz and magnetite were additional phases but will not be discussed further. Only quartz, ferriannite, and magnetite were produced in K-160, which used 0.1 N KOH as solvent. The significance of the absence of other phases in K-160 will be discussed later.

Grunerite, Acmite, and Riebeckite. Grunerite is the iron-rich end member of the series anthophyllite-cummingtonite-grunerite (Boyd, 1959). Flaschen and Osborne (1957) reported grunerite as an intermediate product in the breakdown of minnesotaite to fayalite and quartz at temperatures in excess of 480°C with the optimum at 700°C and 1.2 Kb. However, in runs of more than a few days duration the replacement by fayalite and quartz was complete. Employing the bulk composition $\text{Na}_2\text{O} \cdot 5\text{FeO}_x \cdot 8\text{SiO}_2 + \text{excess H}_2\text{O}$, Ernst (1962) synthesized riebeckite and riebeckite-arfvedsonite solid solutions under a variety of experimental conditions but did not obtain any grunerite.

The grunerite obtained in K-117 and K-158 occurs as fibrous intergrowths, the individuals of which are only a few microns wide but up to 1 mm or more long. Phase identification was based on both the X-ray diffraction pattern and those optical properties which could be determined from material of this habit (see Table 2). The distinction of this phase from riebeckite was based on the differences in pleochroism and

TABLE 2. IDENTIFICATION OF SYNTHETIC GRUNERITE

| Grunerite, Synthetic ^a | | Grunerite, Natural ^b | | Riebeckite, Natural ^c | |
|--|----------------------------------|--|----------------------------------|---------------------------------------|----------------------------------|
| <i>d</i> (Å) | <i>I</i> / <i>I</i> ₀ | <i>d</i> (Å) | <i>I</i> / <i>I</i> ₀ | <i>d</i> (Å) | <i>I</i> / <i>I</i> ₀ |
| 9.17 | 10 | 9.26 | 40 | 9.3 | 30 |
| 8.33 | 100 | 8.38 | 80 | 8.42 | 100 |
| — | — | 4.87 | 30 | 4.90 | 30 |
| 4.63 | 30 | 4.65 | 50 | 4.52 | 50 |
| 4.18 | 20 | 4.17 | 50 | — | — |
| 3.90 | 25 | 3.89 | 50 | 3.88 | 30 |
| — | — | — | — | 3.67 | 20 |
| 3.47 | 40 | 3.48 | 50 | 3.43 | 60 |
| 3.29 | 40 | 3.28 | 50 | 3.24 | 30 |
| 3.08 | 75 | 3.08 | 100 | 3.09 | 80 |
| — | — | 3.01 | 20 | 2.97 | 30 |
| 2.78 | 75 | 2.77 | 100 | 2.79 | 20 |
| 2.65 | 50 | 2.64 | 80 | 2.719 | 100 |
| — | — | — | — | 2.602 | 40 |
| 2.52 | 50 | 2.51 | 80 | 2.530 | 60 |
| — | — | 2.42 | 20 | 2.327 | 40 |
| 2.31 | 10 | 2.31 | 30 | 2.261 | 40 |
| 2.22 | 40 broad | 2.23 | 40 | — | — |
| — | — | 2.21 | 40 | 2.173 | 50 |
| 2.11 | 10 | 2.11 | 40 | 2.132 | 10 |
| 2.05 | 10 | 2.05 | 40 | 2.077 | 20 |
| α = 1.688 ± 0.004 | | α = 1.665–1.696 ^d | | α = 1.654–1.701 ^d | |
| β = n.d. | | β = 1.675–1.709 | | β = 1.662–1.711 | |
| γ = 1.730 ± 0.01 | | γ = 1.698–1.729 | | γ = 1.668–1.717 | |
| γ/∠c low | | γ/∠c = 10–15° | | α/∠c = 3–21° | |
| Very pale brown to brownish gray pleochroism | | Very pale yellow to pale brown pleochroism | | Dark blue to yellow-green pleochroism | |
| Length slow | | Length slow | | Length fast | |

^a This study. CuK_α radiation, (λ = 1.5418 Å) Camera: 114.59-mm diam.

^b ASTM powder diffraction data file, card No. 7-394.

^c ASTM powder diffraction data file, card No. 14-230.

^d Optical data from Deer, *et al.* (1963).

sign of optical elongation, and the better overall fit of the powder diffraction data, such as for the grunerite line at about 2.65 Å.

The grunerite fibers completely encase the steel basket used to hold the nutrient quartz, the baffle plate and most of the steel wire used as a seed support. The amount of grunerite diminishes upward and is supplanted near the top of the vessel by the fibrous amorphous phase and the micaceous phases. Acmite, which is a minor phase, is most abundant

near the base of the vessels and occurs only in traces above the baffle plate. Its optical extinction, $X\Lambda_c=0-5^\circ$ suggests that there is little or no solid solution with clinoferrosilite which has an extinction angle in the range $Z\Lambda_c=37.5-44^\circ$.

The grunerite fibers grade into a distinctly pleochroic phase (deep blue-greenish blue) adjacent to the metal surfaces of the support wires, baffle, etc. This pleochroic phase appears to have the optical properties of riebeckite but x-ray powder diffraction photographs could not distinguish it from the grunerite as their diffraction patterns are quite similar and the phases occur interwoven together.

Ernst (1958) suggested that variations in the refractive indices of synthetic magnesioriebeckite were a measure of the oxidation state of the iron and that a possible mechanism for maintaining electrical neutrality would be minor solid solution of grunerite (or arfvedsonite) with the magnesioriebeckite. The gradational change in pleochroism observed near the bases of the grunerite fibers suggests that there is at least a partial solid solution series between grunerite and riebeckite in the compositional range: $\text{Na}_x\text{Fe}^{3+}_x\text{Fe}^{2+}_{7-2x}(\text{Si}_8\text{O}_{22})(\text{OH})_2$, where $x=0-2$.

The stability of grunerite under hydrothermal conditions is not known. Since the riebeckite obtained here appears to be restricted to the bases of the grunerite fibers, the most plausible explanation is that the first crystals to form were riebeckite, but as growth continued the conditions changed sufficiently to allow grunerite to become the stable phase. These changes might include the depletion of sodium ions from the hydrothermal fluid and also the change in reducing conditions that occurs during the early stages of heating. However, before conclusions concerning the stability of grunerite are drawn, more extensive isothermal experiments should be done using the iron-magnetite and magnetite+quartz-fayalite buffers. Ernst's (1962) numerous experiments included only seven with these buffers at temperatures less than 500°C and the longest of these runs was only about fourteen days.

Micaceous phases. Micaceous material occurs in the upper part of the liner in both K-117 and K-158 intergrown with quartz crystals, the fibrous glass phase, and magnetite. X-ray and optical study of the material indicates that it consists of mixed phases, which may be related to some known mineral phases. These phases include nontronite or vermiculite (which are very similar in their structures and other properties) (Walker, 1957) and stilpnomelane.

The micaceous material prepared here occurs as dark olive to almost black masses, and more isolated, lighter colored hexagonal platelets (up to 0.15 mm across). The more massive material has a greasy luster and

TABLE 3. COMPARISON OF X-RAY POWDER DIFFRACTION DATA FOR STILPNOMELANE AND SAMPLE K-117

| Stilpnomelane Crystal Falls, Minnesota ^a | | Micaceous Phase K-117 ^b | |
|---|----------------------------------|------------------------------------|----------------------------------|
| <i>d</i> (Å) | <i>I</i> / <i>I</i> ₀ | <i>d</i> (Å) | <i>I</i> / <i>I</i> ₀ |
| 12.3 | 10 ⁺ | 12.3 | 100 |
| 7.14 | 2 | — | — |
| 6.26 | 5 | — | — |
| 5.42 | 4 | — | — |
| 4.68 | 4 | 4.65 | 5 |
| 4.36 | 2 | — | — |
| 4.16 | 10 | 4.13 | 50 |
| 3.78 | 4 | 3.73 | 20 |
| 3.61 | 4 broad | — | — |
| 3.36 | 3 | — | — |
| 3.12 | 6 | 3.07 | 70 |
| 2.98 | 1 | — | — |
| 2.686 | 7 | 2.676 | 20 |
| 2.547 | 10 | 2.534 | 50 |
| 2.48 | 2 | — | — |
| 2.345 | 5 | 2.33 | 20 |
| 2.192 | 3 | 2.175 | 5 |

Plus several additional lines

^a Eggleton and Bailey, 1966, FeK_α Radiation, ($\lambda=1.9373$ Å), Camera: 114.59-mm diam.

^b This study. CuK_α Radiation, ($\lambda=1.5418$ Å), Camera: 114.59-mm diam.

wavy surfaces similar to stilpnomelane or vermiculite. The platelets have concave surfaces and in some cases grow into rosette-shaped polycrystals.

Results of X-ray analysis. Samples of the micaceous phase from K-117 were investigated by the powder camera method using nickle-filtered copper radiation ($\lambda=1.5418$ Å). The results are summarized in Table 3 and suggest a close relationship to the mineral stilpnomelane.

In other respects, the micaceous material does not behave like natural stilpnomelane. It undergoes partial expansion with glycol (to about 16.4 Å) and is not thermally stable above 400°C. While the available data are not conclusive, there are suggestions that there may be a close chemical and structural relationship between stilpnomelane and sodium nontronite or vermiculite. At the very least, caution should be applied when identifying stilpnomelane from X-ray diffraction patterns using the basal spacing of about 12.5 Å, since sodium nontronite and vermiculite have very similar spacings.

Fibrous glass. In the upper part of both K-117 and K-158, fibrous grunerite gradually gives way to a fibrous phase which appears to be a glass. Glassy or amorphous phases have been noted previously in hydrothermal systems, but they generally are massive, globular, or have no regular shape. The phase described here occurs in intersecting, rod-like intergrowths, often intersecting with, or branching from, other rods. They are typically about 1–2 μ in diameter and may be 100 μ or more in length. As expected, the fibers are optically isotropic, with $\alpha=1.468 \pm 0.002$. Attempts to obtain x-ray powder patterns with exposures of up to 48 hr produced no sharp diffraction lines.

Why this phase occurs in fibers or rods is not known. Replacement of preexisting fibers of grunerite or riebeckite was considered, but does not seem plausible since there is no optical evidence of the glass replacing any phase.

A SIMILAR EXPERIMENT USING KOH INSTEAD OF NaOH

Since the idealized formula of grunerite does not require the presence of sodium ions, we decided to repeat these experiments using 0.1 N KOH instead of NaOH. (See Table 1, experiment K-160). Also, natural stilpnomelane seems to contain more potassium than sodium, and the effect of treating the micaceous phases produced in K-117 and K-158 with 1 N KOH had a stabilizing effect on their lattices. They would no longer expand upon glycolation after being treated with KOH.

The purpose then was to determine whether grunerite could be synthesized in an alkaline solvent in the absence of sodium ions and also to determine if more stable micaceous phases with basal spacings near 12.5 Å might be produced. The only micaceous phase formed in this experiment with the K-Fe-mica, ferriannite, and neither grunerite nor any other amphibole was produced. The ferriannite was identified on the basis of its x-ray diffraction pattern which is virtually identical with data presented by Wones (1963).

In other experiments at higher concentrations of KOH and under various conditions of temperature and pressure, ferriannite is also the stable micaceous phase.

CONCLUSIONS

Grunerite and micaceous phases have been synthesized in the system NaOH-SiO₂-Fe-H₂O near the critical temperature of water using 0.1 N NaOH. Experimental evidence indicates that the presence of sodium ions in relatively low concentration may be important to the formation of both phases. If higher concentrations are used, acmite forms on the metal surfaces reducing the availability of iron in solution and restricting

the development of other phases. If KOH is used instead of NaOH, the K-Fe-mica ferriannite is produced, even at low concentrations.

Whether or not sodium ions are important to the stabilization of the grunerite structure or whether grunerite develops epitaxially on riebeckite must await further experimental work. However, it is well known that the small sodium ion is easily incorporated into the amphibole structure and this could serve to balance any charge deficiencies caused by variations in the $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio during growth. A gradational change in the pleochroic character of the fibers near their bases suggests that there is at least a partial solid solution between grunerite and riebeckite.

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