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HYDROTHERMAL SYSTEM SiO_2-RbOH-H_2O-Fe UNDER DYNAMIC CONDITIONS[1]

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ABSTRACT

Rubidium iron micas, feldspars, and a "zeolite" have been synthesized under hydrothermal conditions in the system SiO_2-RbOH-H_2O-Fe studied in the temperature range 300-500°C and the pressure range 1-2 Kb. A boundary curve appears to separate the field of micas plus "zeolite" from the field of "zeolite" alone, when the only source of iron is the liner of the vessel. The addition of Fe_2O_3 to the system raises the temperature of the boundary curve by as much as 60°C. The position of the boundary curve is determined by oxygen fugacity, availability of iron, growth temperature, and pressure.

A green mica is formed under low temperature reducing conditions, while a more normal, black mica is produced over a wide range of conditions below the boundary curve. The "zeolite" phase is favored by high temperatures and more oxidizing conditions. The feldspar phases (primarily the "sanidine" form, but with minor "microcline"), are produced only at the highest temperatures studied and if Fe_2O_3 has been added to the system. Feldspar crystals up to 2 mm were obtained in a four day period.

INTRODUCTION

Although the literature is replete with data concerning the natural and synthetic silicates and aluminosilicates of sodium and potassium (and to a lesser degree, those of lithium, rubidium, and cesium), comparatively little information has been published for the iron analogs of these materials. During the course of experiments designed to grow quartz from less commonly used solvents such at RbOH and CsOH (Kopp and Clark, 1968), several rubidium iron silicate phases were synthesized, some of which are analogs of natural aluminosilicates. This paper presents data for the system SiO_2-RbOH-H_2O-Fe under dynamic hydrothermal conditions.

EXPERIMENTAL

The vessels and techniques used in these experiments have been previously described (Kopp and Harris, 1967). Several grams of quartz (chips) are placed in the base of the vessel and one or more seed crystals suspended in the upper part of the vessel. The vessels were operated with temperature gradient rather than isothermal conditions and the low carbon steel liner provided the iron necessary for the development of the iron-bearing phases. The solvent used was 0.5 N RbOH. Although no attempt was made to control the oxygen fugacity, it, and the ratio of available Fe^{+2} and Fe^{+3}, is determined by the reaction between the aqueous solvent and the iron liner under the experimental conditions. The reaction products suggested that the oxygen fugacities (Eugster and Wones, 1962) in the vessels exceeded those determined by the magnetite + quartz - fayalite buffer and in most cases were also less than those determined by the magnetite - hematite buffer. In some experiments Fe_2O_3 powder (Baker and Adamson, Reagent Grade) included with the nutrient quartz affected the amount of available iron and also the oxygen fugacity.

Because of design limitations the system was studied only at temperatures less than 500°C and pressures below 2 Kb. Operating the vessels below about 300°C and pressures below about 0.75 Kb was not convenient, as long periods are required to approach equilibrium in the system; and also because of the effects of retrograde solubility (Kennedy, 1959). Retrograde solubility occurs at relatively low pressures, above the critical temperature of water. Under such conditions SiO_2 (and perhaps other substances) is more soluble at lower temperatures and therefore dissolves in the cooler region and crystallizes in the hotter region of a vessel.

APPARENT PHASE RELATIONS IN THE SYSTEM SiO_2-RbOH-H_2O-Fe

In spite of the complexities of studying a multicomponent system under dynamic conditions, when the major rubidium iron silicate phases observed here are plotted with respect to temperature and pressure only, a boundary appears to separate the field of rubidium iron micas plus a rubidium iron "zeolite" from the field of the rubidium iron "zeolite" alone. The position of the boundary is shown in Fig. 1. In all experiments in which the liner was the only source of iron, the major rubidium iron silicate reaction products were the mica and "zeolite" phases.

The structural character of the pale yellow, pseudoisometric "zeolite" obtained in these experiments is not certain. For purposes of discussion we will refer to this rubidium iron silicate as a "zeolite", although refinement of the structure may suggest a closer relationship to those minerals classified as feldspathoids.

The addition of Fe_2O_3 powder to the nutrient raised the upper limit of temperature stability of the mica by as much as 60°C, and at temperatures near 500°C rubidium iron feldspars appeared in the hottest part (nutrient region) of the vessels (see Fig. 1). The stability range of the feldspars is not known since they

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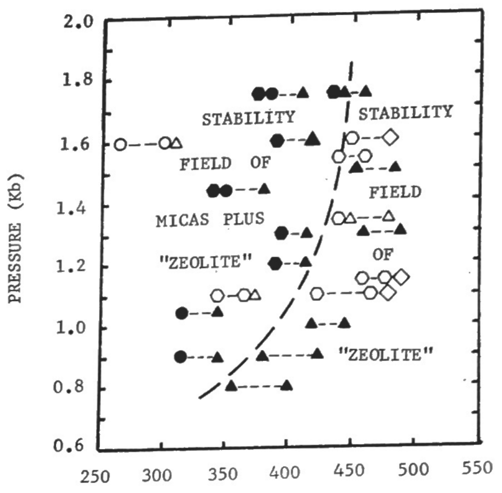

Fig. 1. Boundary Curve Separating Fields of Micas + "Zeolite" from "Zeolite" Alone for System RbOH-SiO_2-H_2O-Fe. Note effect of added Fe_2O_3

Symbols used: circle = green mica
hexagon = black mica
triangle = "zeolite"
diamond = feldspar
Open symbols indicate Fe_2O_3 added to nutrient

were observed only in experiments close to the upper operating limit of the vessels. Experiments that included Fe_2O_3 with the nutrient are more difficult to evaluate because of the obvious instability of a system which contains both Fe and Fe_2O_3 in the presence of an aqueous solvent at elevated temperature and pressure.

A major difference is obvious when the data in Fig. 1 are compared with those of Wones (1963) for the stability of ferriannite, potassium iron feldspar, and other phases. The potassium-iron-silica system does not contain "zeolite" or feldspathoidal phases in the presence of water. This may be explained by reference to studies made in the system $KAlSi_3O_8$-SiO_2. Under dry conditions, orthoclase ($KAlSi_3O_8$) melts incongruently to form leucite ($KAlSi_2O_6$), but under water pressure the stability field of leucite shrinks and presumably disappears at pressures greater than about 2 Kb (Bowen and Tuttle, 1950). Larger alkali ions such as Rb^{+1} and Cs^{+1} can form stable aluminosilicates and hydrated aluminosilicates over a wider range of temperature and pressure (Barrer and McCallum, 1953).

DESCRIPTIONS OF THE RUBIDIUM IRON SILICATE PHASES

The dominant phases produced in these experiments were micas, the "zeolite", and feldspars. In addition, quartz and magnetite were present. Fayalite was not observed; nor was hematite generally, except where it was formed from excess Fe_2O_3 powder added to the initial mixture or in a few experiments where it was present in minute amounts associated with the "zeolite" phase.

Rubidium Iron Micas

The black micaceous phase was well crystallized and formed crystals as large as 1 mm in diameter and 1 mm thick, pseudohexagonal in habit, and with characteristic excellent {001} cleavage. Some of the crystals appear to be twinned with the basal pinacoid as composition plane. X-ray powder diffraction data and optical data are presented in Table 1. These compare with data for ferriannite, $KFe_3{}^{+2}Fe^{+3}Si_3O_{10}(OH)_2$, (Wones, 1963). The probable formula for the black mica is $Rb\ (Fe^{+3}, Fe^{+2})_{2-3}\ (Fe^{+3}Si_3)O_{10}(OH)_2$.

The green mica was less well crystallized and generally occurred in platelets <0.5 mm wide and <0.01 mm thick. Its probable formula is $RbFe_3{}^{+2}(Fe^{+3}Si_3)O_{10}(OH)_2$. The green mica alone was observed to form at temperatures below 350°C although in two experiments (K-163 and K-166) near 350°C both green and black micas occurred together. The occurrence of the green mica may be explained by considering the oxygen fugacity resulting from the reaction between the iron liner and water. At low temperatures the oxygen fugacity is low, resulting in a higher Fe^{+2}:Fe^{+3} ratio. Mica formed under such conditions would tend to be richer in ferrous iron and appear green, while at higher temperatures and amount of available Fe^{+3} will increase and the darker mica will form. To compare the x-ray diffraction patterns of the green and the black micas a sample oriented by elutriation onto a glass slide was examined. The results (Table 1) confirm the existence of two distinct mica phases. Both visual and microscopic examination suggest that there is little or no solid solution between them, although the pleochroic character of the black mica is variable. Wones (1963) observed that the indices of refraction and pleochroism of ferriannite varied with oxygen fugacity, but did not mention the presence of a discrete second mica phase.

Rubidium Iron "Zeolite"

Colorless to pale yellow crystals of a rubidium iron "zeolite" up to 0.5 mm in diameter were obtained in the temperature range 350-490°C at pressures from about 1-2 Kb. This phase is orthorhombic even though crystals have a pseudoisometric, "octahedral" habit. Spectrographic analysis confirms iron, silicon, and rubidium as major constituents but the exact chemical composition is not yet known. X-ray and optical data are presented in Table 2. The x-ray powder diffraction data do not correspond with data given for reported natural phases or for synthetic rubidium aluminosilicates as presented by Barrer and McCallum (1953). Based on their studies, we may expect additional rubidium iron silicates to be synthesized as the conditions of temperature, pressure, and composition are extended beyond those of this study.

At low pressures (<1 Kb) the "zeolite" phase was sparse, poorly crystallized and contaminated by numerous inclusions of the mica phase and possibly other

Table 1. X-ray and Optical Data for Micaceous Phases

Black Rb-Fe Mica[a]			Green Rb-Fe Mica[b]
d(A)	(I/I_o)	(hkℓ)	d(A)
10.40	100	001	10.277 broad
5.145	40	002	-
4.250	10	021	-
3.986	40	111	-
3.736	50	$11\bar{2}$	-
3.440	80	003/022	3.389
3.196	50	112	-
2.978	40	$11\bar{3}$	-
2.771	30	023	-
2.644	80	200	-
2.578	60	004	2.543
2.468	50	201	-
2.206	60	202	-
2.059	20	005	2.037
a_o = 5.32±0.02A			n_α = n.d.
b_o = 9.38±0.02A			$n_\beta \sim n_\gamma$ = 1.64±0.01
c_o = 10.468±0.01A			a = n.d.
β = 100°11'±5'			γ = green
n_α = 1.68±0.01			2V ~ 10°
$n_\beta \sim n_\gamma$ = 1.72±0.01			Sign (–)
α = red brown			
γ = greenish brown			

[a] This study. CuK radiation (λ= 1.5418A).

[b] This study. CuK radiation (λ= 1.5418A). Oriented sample. Sample contained both phases. Spacings attributed to the black mica phase have been deleted. Complete x-ray powder diffraction data submitted to ASTM Powder Data File.

unidentified phases. In several experiments the "zeolite" phase was associated with traces of fine-grained Fe^{+3} oxides or hydrous oxides, but it is not known whether this formed during the run or during the cooling period.

Rubidium Iron Feldspars

Feldspar crystals (probable composition $RbFeSi_3O_8$) were obtained in three experiments that contained Fe_2O_3 powder and which were operated near 500°C. An attempt to produce feldspar at comparable temperature conditions without adding Fe_2O_3 to the nutrient (K-173) produced only the "zeolite" phase, suggesting that a relatively high oxygen fugacity is required to keep most of the iron in the +3 state.

The pale yellow crystals obtained (to 2 mm on an edge) are bounded by simple prismatic and pinacoidal forms. Many of the crystals were inhomogeneous and contained numerous inclusions of hematite and possibly other unidentified material. X-ray and optical data for some of the better crystals are presented in Table 3 and suggest that this feldspar closely resembles the potassium iron sanidine of Wones and Appleman (1963). The changes in lattice dimensions that occur because rubidium was substituted for potassium is greatest along the *a*-axis and amounts to O.2A. The cell dimensions for several natural and synthetic feldspars are compared in Table 4. Natural Na-K feldspars that crystallize at high temperatures tend to exsolve (perthitic intergrowth) upon slow cooling into K-rich and Na-rich areas. Here, the difference in lattice dimension along the *a*-axis amounts to approximately O.4A. The comparable change in lattice dimension between rubidium iron and potassium iron feldspars is about half that of the Na-K feldspars, or about 0.2A. Because of its larger size, we might expect that rubidium in an Na-K feldspar would be more likely to exsolve than potassium and hence be concentrated in the K-rich portions of such perthitic crystals. It is even possible that second exsolution will occur within the K-rich areas to form perthite-like intergrowths between K-rich and Rb-rich regions. These intergrowths should have a common *a*-axis.

Table 2. Lattice Parameters and Optical Properties of Rb-Fe "Zeolite"[a]

a_o = 13.17±0.02A	n_α = 1.548±0.002
b_o = 13.38±0.02A	n_β = 1.548±0.002
c_o = 13.67±0.02A	n_γ = 1.552±0.003
Orthorhombic	Sign (+)
Probable space group Pcab	2V ~ 60°
	Dispersion r > v moderate

[a] Complete x-ray powder diffraction data submitted to ASTM Powder Data File.

Table 3. Lattice Parameters and Optical Properties of Rb-Fe Feldspars[a]

a_o = 8.88±0.02A	n_α = 1.594±0.002
b_o = 13.04±0.01A	n_β = 1.600±0.002
c_o = 7.32±0.02A	n_γ = 1.616±0.003
β = 116°15'±11'	
	Sign (+)
	2V ~ 45°

[a] Complete x-ray powder diffraction data submitted to ASTM Powder Data File.

Table 4. Comparison of Lattice Parameters for Several Natural and Synthetic Feldspars[a]

	a_o (A)	b_o (A)	c_o (A)	β
High-Albite	8.15	12.88	7.11	116°18'
Sanidine	8.56	13.03	7.17	115°59'
K-Fe-Sanidine	8.69	13.12	7.32	116°06'
Rb-Fe-Sanidine[b]	8.88	13.04	7.32	116°15'

[a] Modified from Deer, Howie, and Zussman, 1963.

[b] This study.

Optical examination of crystal fragments between crossed Nicols reveals small patchy areas with "grid-iron" twinning, suggesting that at least a part of this phase may have the triclinic microcline (low-temperature) structure. Wones and Appleman (1963) also observed a microcline phase in their studies of potassium iron feldspar.

Acmite

In a few experiments traces of a pyroxene phase were observed and thought to be another RbFe silicate phase. However, x-ray diffracton and optical data suggested that this was acmite, $NaFeSi_2O_6$. Electron microprobe analysis confirmed that these crystals are composed of sodium, iron, and silicon, and that rubidium is absent. Analysis of the RbOH solvent used in these experiments revealed the presence of about 60μg/ml of sodium, sufficient to form traces of acmite.

INTERPRETATION OF RESULTS

Several factors determine the distribution of phases shown in Fig. 1. First, the fugacity of oxygen is essentially fixed by the reaction between the iron liner and the aqueous solvent for a given set of experimental conditions and is reflected in the phase or phases formed. To the left (low-temperature side of the boundary curve) both the mica and "zeolite" phases form, but in each experiment the "zeolite" forms in the higher temperature region (base) of the vessel. Considering either the $Fe_3O_4 + SiO_2 — Fe_2SiO_4$ buffer or the Fe_3O_4 — Fe buffer, the oxygen fugacity increases, and hence the conditions will be more oxidizing, at higher temperatures. Since the "zeolite" phase requires Fe^{+3} for its development (taking the place of $A1^{+3}$ in tetrahedral coordination with oxygen), its stability is favored by more oxidizing conditions and therefore by higher temperatures. To the right of the boundary (high-temperature side) the micas, which need both Fe^{+2} and Fe^{+3} to form, are no longer stable in the presence of the iron liner alone.

A second factor involves the availability of iron. In those experiments in which the iron was derived from the liner only, the rate of development of the phases was governed to a large degree by the rate at which iron was made available by the corrosion of the liner. However, when iron was added to the system as finely divided Fe_2O_3, its ready availability seems to have outweighed the effects of solvent reaction with the liner, and the boundary curve appears to be shifted to higher temperatures. Semi-quantitative analysis of the "zeolite" phase suggests a Rb:Fe atomic ratio of about 1:1, while the rubidium iron mica is expected to have a Rb:Fe ratio of about 1:4. The availability of iron in those experiments to which Fe_2O_3 was added seems to favor the development of the more iron-rich mica phases.

A third factor concerns the development of more hydrous phases at lower temperatures and higher pressures, consistent with observations in both natural and artificial systems, hence the development of the more hydrous micas to the low-temperature side of the boundary curve. The development of (anhydrous) rubidium iron feldspar at temperatures near 500°C results, at least in part, from increasing temperature, although the added Fe_2O_3 powder helps to maintain the high Fe^{+3}:Fe^{+2} ratio that favors the development of Rb-Fe feldspar.

GEOLOGICAL IMPLICATIONS AND CONCLUSIONS

So far as is known, rubidium does not form independent minerals. Its ionic size is close to that of potassium, and its crustal abundance is low (about 120 ppm, Mason, 1958), so it is dispersed in such potassium minerals as the micas and feldspars. The micaceous phases and feldspars formed in these experiments do not differ sufficiently from analogous potassium-based compounds to suggest that separate rubidium phases of these types might form in nature. However, the "zeolite" phase does not resemble any known phases. It is suggested that the most probable natural rubidium aluminosiliciate phases would be zeolites or feldspathoids.

As stated previously, the lattice parameters of rubidium iron and potassium iron feldspars differ by about O.2A along the *a*-axis, and it may be that exsolution takes place within natural rubidium-bearing potassium feldspars. These intergrowths would probably be microscopic or submicroscopic in size, but should be detectable by electron microprobe analysis.

Finally, the dark, rubidium iron micas obtained in these experiments are very well crystallized, and provide another member of the growing family of micaceous ferrisilicates and aluminosilicates. Detailed structural analyses of these phases may provide a more thorough understanding of the interrelationship between the inter-silicate ions and the tetrahedrally and octahedrally coordinated ions in the mica structure.

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