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ACMITE-VANADIUM ACMITE SOLID SOLUTION IN THE PRESENCE OF H₂O AT HIGH PRESSURES

by

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(with 2 text-figures and 2 tables)

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Abstract

Vanadium acmite ($\text{NaV}^{3+}\text{Si}_2\text{O}_6$) was synthesized in presence of H_2O at high pressure. The refractive indices of synthetic vanadium acmite are $\alpha=1.736$ (3), $\gamma=1.785$ (5) and the cell parameters are $a=9.640$ (1) Å, $b=8.748$ (2) Å, $c=5.297$ (1) Å, $\beta=106.89$ (1)° and $V=427.4$ (1) Å³. This pyroxene is stable at least up to 30 kb at 800°C with H_2O under reducing environment, and it melts incongruently to occur opaque crystal and liquid. Acmite₇₅-vanadium acmite₂₅, acmite₅₀-vanadium acmite₅₀ and acmite₂₅-vanadium acmite₇₅ compositions also crystallizes easily at 500 bars and 600°C with H_2O . The cell parameters of synthetic acmite-vanadium acmite series change linearly with molar compositions. This systematic changes in cell parameters suggest that a continuous solid solution series exists between $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ and $\text{NaV}^{3+}\text{Si}_2\text{O}_6$. Melting of pyroxene of composition acmite₅₀-vanadium acmite₅₀ is relatively insensitive to PH_2O in the studied pressure range of 5 – 30 kb.

Introduction

Acmite ($\text{NaFe}^{3+}\text{Si}_2\text{O}_6$) is the principal component of the clinopyroxenes in alkali rocks. The acmitic pyroxenes incorporate various pyroxene molecules. The chief molecules in the acmitic pyroxenes are acmite, diopside and hedenbergite and there may be complete solid solution series between the end-members. In some cases, acmite may also incorporate jadeite molecule, vanadium acmite molecule or johannsenite molecule in solid solution.

Diopsidic acmite containing vanadium and vanadiferous acmite have been described by Larsen and Hunt (1913). Chemical analyses of these acmites from Libby, Montana show that they contain 8.59% and 11.75% of $\text{NaV}^{3+}\text{Si}_2\text{O}_6$. Watanabe et al. (1973) reported the occurrence of vanadium-bearing aegirine from Tanohata manganese mine, Iwate Prefecture in Japan, which contains about 6wt% V_2O_3 . Recently, Watanabe (personal communication) found a

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pyroxene of composition, approximately equivalent to $(\text{NaV}^{3+}\text{Si}_2\text{O}_6)_{50}$ $(\text{NaFe}^{3+}\text{Si}_2\text{O}_6)_{50}$ in the Tanohata manganese mine. This mineral is associated with rhodonite, quartz, feldspars and $(\text{Ba, Sr})\text{VSi}_2\text{O}_7$.

Present study on acmite-vanadium acmite solid solution and the discovery of natural pyroxene of this composition series indicate that there is no solubility gap between the vanadium acmite and acmite.

Experimental results

The experiments below 1 kb pressures were made in cold seal pressure vessels made of stellite 25, whereas experiments at higher pressures were carried out with a single stage piston cylinder apparatus. In the join $\text{NaFe}^{3+}\text{Si}_2\text{O}_6 - \text{NaV}^{3+}\text{Si}_2\text{O}_6$, the end-members and three other compositions within the join were prepared by mixing reagent grade sodium disilicate, vanadium sesquioxide, hematite and quartz in appropriate proportions. Run durations of the hydrothermal experiments ranged between 30 to 45 days and whereas these at higher pressures were carried out for 5 to 8 hours. Post run phase identifications were made by x-ray powder diffraction patterns and optical microscopy. All x-ray powder diffraction studies were made with a powder diffractometer equipped with a crystal monochromator, using Cu radiation at 35 KV and 20 mA at room temperature. Reflections used for the determination of the unit-cell dimensions of the pyroxenes were obtained at a scanning speed of $1/4^\circ$ per minute, using silicon as an external standard.

Synthetic vanadium acmite occurs as long prisms from approximately $2 \times 10-15\mu$ in size with a low extinction angle. Fine-grained crystals have pale

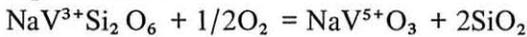
Table 1 Physical properties of synthetic vanadium acmite and acmite.

Vanadium acmite	Acmite
Refractive indices	
$\alpha = 1.736 \pm 0.003$	$\alpha = 1.776 (\pm 0.003-0.005)$
$\gamma = 1.785 \pm 0.005$	$\beta = 1.816$
$\gamma - \alpha = 0.049$	$\gamma = 1.836$
	(Washington and Merwin, 1927)
Cell parameters	
$a = 9.640 \pm 0.001 \text{ \AA}$	$a = 9.658 \pm 0.005 \text{ \AA}$
$b = 8.748 \pm 0.002 \text{ \AA}$	$b = 8.796 \pm 0.005 \text{ \AA}$
$c = 5.297 \pm 0.001 \text{ \AA}$	$c = 5.294 \pm 0.005 \text{ \AA}$
$\beta = 106.89 \pm 0.01^\circ$	$\beta = 107.42 \pm 0.05^\circ$
$V = 427.4 \pm 0.1 \text{ \AA}^3$	$V = 429.1 \pm 0.5 \text{ \AA}^3$
	(Nolan and Edgar, 1963)

greenish color. Large crystals exhibit pleochroism $X' =$ greenish yellow, and $Z' =$ blueish green. The refractive indices of synthetic vanadium acmite are slightly lower than those of acmite as shown in Table 1, which also includes the cell parameters of synthetic vanadium acmite. The ionic radius of octahedrally co-ordinated V^{3+} (0.640Å) is slightly smaller than that of octahedrally co-ordinated Fe^{3+} (0.645Å) (Shannon and Prewitt, 1969), it is therefore natural that the unit-cell volume of $NaV^{3+}Si_2O_6$ is slightly smaller than that of $NaFe^{3+}Si_2O_6$. The calculated density of vanadium acmite is 3.515 gr/cm³.

In the run products opaque crystals of two different shapes were encountered. The square crystals are probably magnetite solid solution ($Fe_3O_4 - FeV_2O_4$ series), whereas those occurring as hexagonal plates may be hematite solid solution ($Fe_2O_3 - V_2O_3$ series).

Vanadium acmite is stable at least up to 30 kb at 800°C with H_2O . This pyroxene as well as acmite has an extremely wide field of stability from low pressure to high pressure. However, it is not stable at the vicinity of oxygen fugacity in air and decomposes to $NaV^{5+}O_3$ and SiO_2 . Following reaction thus may take place in air:



$NaV^{5+}O_3$ is very similar to vanadium acmite under petrographic microscope. It occurs in prismatic crystal, light green in color with high refractive indices (>1.730), high birefringence, and almost parallel to straight extinction. When the oxides mixtures of the $NaV^{3+}Si_2O_6$ composition charged in Pt envelope was heated in the sealed pyrex glass in vacuum (10^{-3} Torr) at 550 – 600°C for 16 days, pyroxene, SiO_2 and a small amount of $NaVO_3$ and opaque crystal were detected by means of optical microscope and X-ray diffraction method. This may suggest that vanadium acmite is stable at 1 atm, under suitable fO_2 condition. In all high pressure experiments carried out without the buffers, reducing conditions were obtained. These facts indicate that the stability of

Table 2 Cell parameters of clinopyroxene solid solutions between $NaFeSi_2O_6$ and $NaVSi_2O_6$

Composition* (wt %)	Temp. (°C)	Pres. (kb)	Time (day)	Cell parameters				V (Å ³)
				a (Å)	b (Å)	c (Å)	β (°)	
Ac 100 Va 0	750	1000	5	9.658 (5)	8.795 (5)	5.294 (5)	107.42 (5)	429.1 (5)**
75 25	600	500	30	9.652 (4)	8.787 (4)	5.295 (2)	107.30 (4)	428.8 (4)
50 50	600	500	45	9.648 (2)	8.771 (2)	5.297 (1)	107.71 (2)	428.3 (2)
25 75	600	500	45	9.639 (2)	8.761 (2)	5.296 (1)	107.02 (2)	427.6 (1)
0 100	600	500	45	9.640 (1)	8.748 (2)	5.297 (1)	106.89 (1)	427.4 (1)

(*): Ac = $NaFeSi_2O_6$, Va = $NaVSi_2O_6$

(**): Nolan and Edgar (1963)

vanadium acmite is controlled by the fO_2 conditions.

At 500 bars and 600°C in the presence of H_2O , vanadium acmite crystallizes easily. Acmite₇₅-vanadium acmite₂₅, acmite₅₀-vanadium acmite₅₀ and acmite₂₅-vanadium acmite₇₅ compositions are also stable phases under this condition. The variation in the cell parameters of synthetic acmite-vanadium acmite series are summarized in Fig. 1 and Table 2, which seems to show that the cell parameters of these pyroxenes change linearly with molar compositions. This systematic change in the cell parameters suggests that there are continuous solid solution series between $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ and $\text{NaV}^{3+}\text{Si}_2\text{O}_6$.

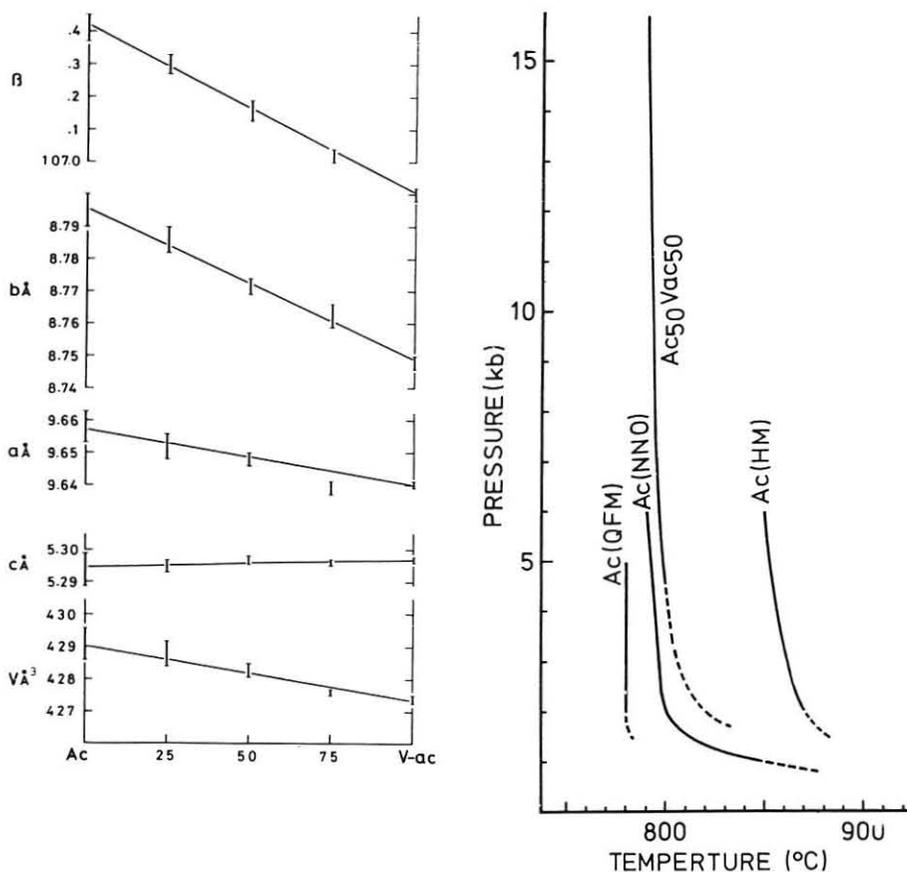


Fig. 1 Cell parameters of clinopyroxene solid solutions between $\text{NaFeSi}_2\text{O}_6$ and NaVSi_2O_6

Fig. 2 Melting curve of the pyroxene of the composition $(\text{NaFeSi}_2\text{O}_6)_{50}-(\text{NaVSi}_2\text{O}_6)_{50}$ in the presence of water. Melting curves of acmite with different partial pressures of oxygen are also shown (after Bailey, 1969): HM = hematite-magnetite buffer, NNO = nickel-nickel oxide buffer, and QFM = quartz-fayalite-magnetite buffer

In the pressure range between 5 to 25 kb P_{H_2O} , acmite₅₀-vanadium acmite₅₀ solid solution is stable up to about 790°C. This pyroxene decomposes to pyroxene + two opaque crystals + liquid at 800°C, 10 kb for 6 hours and pyroxene disappear at 950°C, 5 kb for 6 hours. These results show that vanadium acmite melts incongruently. The incongruent melting curve for this pyroxene appear to be almost straight line within the limits of experimental error. This curve in the low pressure side has a gentle slope and is slightly concave towards the temperature axis. The extrapolation of our curve is in excellent agreement with the low pressure data for acmite under conditions controlled by the nickel-nickel oxide buffer in presence of H₂O (Bailey, 1969) (Fig. 2).

Discussion

Acmite occurs in nature under widely variable conditions, and it appears to be stable under hydrous and anhydrous conditions (Bailey, 1969; Gilbert, 1969). However, vanadium pyroxene has not been found in nature, and even vanadiferous acmite is not a common mineral. It is expected that vanadium in vanadiferous acmite may occur in the trivalent state substituting Fe³⁺ because of their similar ionic radii. But, according to Leutwein (1941), the trivalent vanadium is a comparatively strong reducing agent, which, if present, would reduce ferric iron to the ferrous state. Therefore, the isomorphous substitution of V³⁺ for Fe³⁺ is not very probable. However, a few minerals which may contain both Fe³⁺ and V³⁺ have been found in nature, in addition to Na(Fe³⁺, V³⁺)Si₂O₆ (Larsen and Hunt, 1913; Watanabe et al., 1973). Radtke (1962) reported coulsonite (Fe²⁺V³⁺O₄) which contained minor amounts of Fe³⁺. Long et al. (1963) also described karelianite (V₂O₃) containing 4.1% Fe₂O₃. Recently, Nakai et al (1976) suggested that vanadium occurs as V³⁺ in the octahedral site of the crystal, from their studies of photo electron spectroscopy on vanadium-bearing aegirines from Tanohata manganese mine (V₂O₃ = 8.18 wt%) and from Libby, Montana. These reports indicate that V³⁺ is able to coexist with Fe³⁺ in the same compound in nature. In our experiments, the single-phase pyroxene was synthesized from oxides mixture in stoichiometric composition containing Fe₂O₃ and V₂O₃ under slightly reducing condition with excess H₂O. Moreover, cell parameters of synthetic pyroxenes change linearly against the variations of the bulk compositions, between NaFeSi₂O₆ and NaVSi₂O₆. These facts seem to indicate that the vanadium in synthetic pyroxene, Na(Fe, V)Si₂O₆, occurs as V³⁺ and occupies the octahedral site of the pyroxene structure.

Vanadiferous acmites from Libby, Montana occur in quartz veins, which

were probably formed under deep-seated conditions at a high temperature (some resemblance to pegmatite)(Larsen and Hunt, 1913). Vanadium-bearing acmite from Tanohata mine occurs in pegmatitic quartz vein which cuts the metamorphosed bedded manganese deposit (Watanabe et al., 1973). Vanadiferous acmite was synthesized easily even at relatively low temperature and low pressure under only slightly reducing condition with excess H_2O , and has very wide pressure stability range from 10 kb to over 30 kb. Melting of a acmite is relatively insensitive to total pressure in the 2 to 5 kb range, however it is very sensitive to the oxidation conditions and the melting temperature decreases with reducing the partial pressure of oxygen (Bailey, 1969). According to the present experimental results, vanadium bearing acmite has very similar melting relation to that of acmite. Therefore, under P_{O_2} conditions lower than those of our experiments, it may melt incongruently temperatures below $790^\circ C$. However, vanadiferous acmite in nature may be formed under slightly higher P_{O_2} conditions than that provided by the wustite-magnetite buffer, because acmite is unstable at P_{O_2} controlled by the wustite-magnetite buffer in presence of water (Bailey, 1969).

The present experimental results show that vanadium acmite as well as acmite has a very wide stability field in pressure and temperature, and that there is a complete solid solutions series between acmite and vanadium acmite. In nature, vanadiferous acmite containing almost 50 mol per cent vanadium acmite molecule was found, but our experimental data suggest that more V_2O_3 -rich pyroxenes may be found in future. Its appearance in nature seems to be effectively controlled by temperature and oxygen fugacity, rather than the total pressure.

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