

Equilibria and origin of minerals in the system $\text{Al}_2\text{O}_3\text{--AlPO}_4\text{--H}_2\text{O}$

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Abstract

Using standard hydrothermal techniques, the phase relations of three Al-phosphate minerals—berlinite, AlPO_4 ; augelite, $\text{Al}_2\text{PO}_4(\text{OH})_3$; and trolleite, $\text{Al}_4(\text{PO}_4)_3(\text{OH})_3$ —were determined in the temperature and pressure range of 400° to 600°C and 500 to 3000 bars. The univariant line, defining the upper stability limit of trolleite (trolleite = augelite + berlinite), can be expressed by $T(^{\circ}\text{C}) = 0.0373P(\text{bars}) + 350.7$. The univariant curve defining the upper stability of augelite (augelite = berlinite + corundum + vapor) is expressed by $\log P(\text{bars}) = -14,938/T(^{\circ}\text{K}) + 22.48$.

These curves intersect at an invariant point near 520°C and 4500 bars. The addition of diaspore leads to another invariant point at approximately 550°C and 12 kilobars. The complete P - T diagram indicates that the stability field of trolleite is greatly extended by pressure, whereas the stability of augelite abruptly terminates near 520°C, regardless of the pressure.

Calculations, based on the breakdown of augelite, indicate that excess quartz reduces the stability of augelite by about 35°. From the calculated free energy of augelite ($\Delta G = -671.5 \pm 1.5$ kcal at 25°C) it is concluded that Al-phosphate minerals in the presence of phosphoric acid are far more stable than any Al-silicate. This means that if Al-silicate minerals have formed by hydrolysis of micas and feldspars and if the hydrolyzing fluid contains any of an H_3PO_4 component, Al-phosphate minerals will also form.

Introduction

Al-phosphate minerals, most notably lazulite, occur with Al-silicate-quartz masses in several localities in the world, for example Horrsjöberg and Västana, Sweden; Graves Mountain, Georgia; and White Mountains, California. Three Al-phosphate minerals—berlinite, AlPO_4 ; augelite, $\text{Al}_2\text{PO}_4(\text{OH})_3$; and trolleite, $\text{Al}_4(\text{PO}_4)_3(\text{OH})_3$ —were first found with hematite, kyanite, pyrophyllite, and quartz at Västana; however, no study of the minerals *in situ* has ever been made (Geijer, 1963). Augelite and trolleite occur in well-exposed outcrops at the Mono County Andalusite Mine, White Mountains, California (Gross and Parwell, 1968). The replacement textures with quartz, andalusite, and muscovite indicate these minerals have a metasomatic origin.

Wise (1975) suggested that the assemblage quartz+Al-silicate+Al-phosphate+rutile of this

mine and others in the western U.S. forms by high temperature hydrolysis of meta-volcanic, sericitic schists. This is an extension of hydrolysis processes discussed by Hemley and Jones (1964), Eugster (1970), Gresens (1971), and Wintsch (1975). If the H^+ ions in the hydrolyzing fluids are accompanied by Cl^- anions only, the muscovite and feldspars are converted to Al-silicates (pyrophyllite, andalusite, or kyanite). However, if other anions are present in the fluid, new phases appear. For example, fluoride leads to the crystallization of topaz; sulfate, to alunite; borate, to tourmaline or dumortierite; and phosphate, to lazulite or other Al-phosphates.

In order to evaluate the hypothesized phosphate reactions, sub-solidus phase relations in the system $\text{Al}_2\text{O}_3\text{--AlPO}_4\text{--H}_2\text{O}$ were studied. This paper presents the results of that study, which shows that the stability fields of augelite and trolleite place fairly narrow limits on the P - T range in which the phosphate-bearing assemblage of the White Mountain deposit was formed. Extrapolation of the data allows the conclusion that Al-phosphates in the presence of

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phosphoric acid are far more stable than any Al-silicate.

The system $\text{Al}_2\text{O}_3\text{-AlPO}_4\text{-H}_2\text{O}$

Previous work

The phases that appear in the system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at temperatures above 300°C are shown in Figure 1. Diaspore-corundum equilibria along the $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ join have been recently studied by Haas (1972). Berlinite was found to be isostructural with quartz by Huttenlocher (1935), and the transitions to polymorphs analogous to the silica polymorphs were determined by Gruner (1945) and Beck (1949). Augelite does not appear to have been previously synthesized, but Sclar *et al.* (1963) reported the synthesis and properties of trolleite.

Experimental procedure

Berlinite, augelite, and trolleite were all synthesized in sealed gold tubes at water pressures of $\frac{1}{2}$ to 3 kilobars in standard, externally heated, cold-seal pressure vessels. Temperatures were regulated to within $\pm 3^\circ$, and pressures to within ± 10 bars. Individual runs completely crystallized, and yielded approximately 30 mg of fine-grained crystalline aggregates, which were identified by X-ray diffraction and optical methods.

Starting materials were mixes of $\text{Al}(\text{OH})_3$ or Al_2O_3 with AlPO_4 . The AlPO_4 was prepared by dissolving reagent-grade Al wire in diluted (1:1) phosphoric acid, which produces a precipitate of $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$.

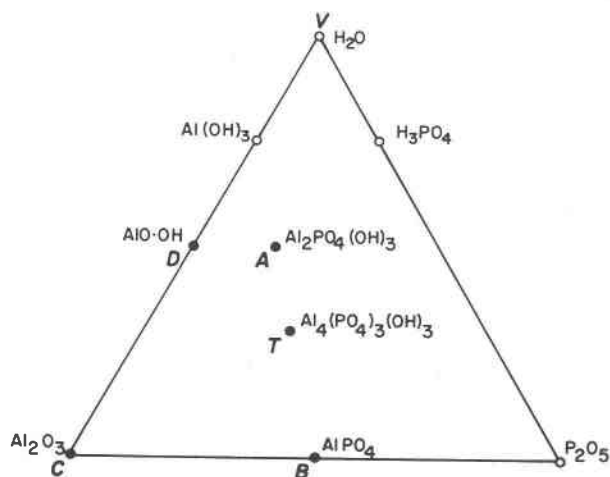


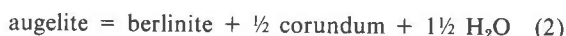
FIG. 1. Phases in the system $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ above 300°C . The experimental phases, labelled with letters, are A = augelite, B = berlinite, C = corundum, D = diaspore, T = trolleite, and V = vapor, composed mostly of water.

The precipitate heated at 600°C for 12 hours yielded berlinite. Reagent-grade $\text{Al}(\text{OH})_3$ was used in some runs, as was alpha- Al_2O_3 , prepared by heating $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ at 1000°C for 20 hours. A charge was approximately 30 mg of mix or various synthetic phases with 10 to 15 mg H_2O .

The physical properties of the synthetic phases are presented in the appendix.

Stability of augelite and trolleite

Two univariant curves for the reactions that limit the stability of augelite and trolleite are:



Runs defining the $P\text{-}T$ positions of these curves are listed in Table 1, and plotted on Figure 2.

Augelite was easily prepared, and the breakdown reaction was reversed. Reactions normally went to completion in two weeks, except when the temperature was within 5°C of the phase boundary. Trolleite generally nucleated around clusters of berlinite, preventing the reaction from going to completion. Nevertheless, the direction of the reaction was easily determined, even for runs close to phase boundaries.

Discussion of results

Since the two reactions investigated involve three components (Al_2O_3 , AlPO_4 , and H_2O) and five phases (corundum, berlinite, trolleite, augelite, and vapor), there should be two more univariant curves:

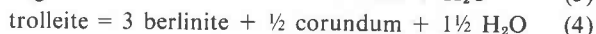
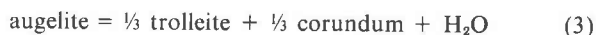


TABLE 1. Experimental data used to define univariant curves

Run Number	Starting Materials*	T(°C)	P(kb)	Run (days) Duration	Products*
118	A	482(2)	1/2	422	A
119	B + C	482(2)	1/2	422	B + C
113	A + B	375(1)	1	305	A + B + T
124	trl-1	391(1)	1	590	A + B
109	A	491(1)	1	305	A
110	B + C	491(1)	1	305	B + C
53	B + C	421(3)	2	498	T + B
32	trl-1	429(2)	2	459	B + A
73	B + C	504(3)	2	483	B + C
50	A	506(1)	2	139	A
65	A	509(5)	2	496	B + C
106	trl-1	462(1)	3	332	T(+ B)
74	trl-1	465(3)	3	287	B + A
83	B + C	505(2)	3	140	A(+ B)
89	A	520(2)	3	304	B + C

*Mineral abbreviations: A = augelite, B = berlinite, C = corundum, T = trolleite, and trl-1 = berlinite + $\text{Al}(\text{OH})_3$.

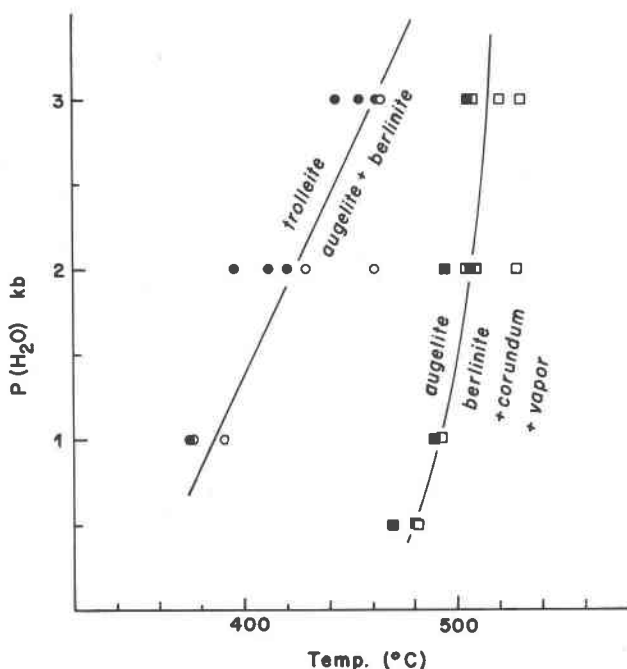


FIG. 2. P - T plot of the experimental data, defining the stability limits of trolleite and augelite. Closed circles indicate trolleite is stable; open circles, augelite + berlinite are stable. Closed squares indicate augelite is stable, open squares indicate berlinite + corundum + water vapor (augelite bulk composition) are stable.

The experimentally determined curves can be projected to the invariant point. Reaction (1) involves no vapor phase, and therefore appears as a nearly straight line in terms of P and T . The equation for this line is $T(^{\circ}C) = 0.0373P$ (bars) + 350.7. A plot of reaction (2) in terms of $\log P$ and $1/T$ ($^{\circ}K$) yields the straight line, $\log P$ (bars) = $-14,938/T(^{\circ}K) + 22.48$. Projection of the two lines gives an intersection near $520^{\circ}C$ and 4500 bars.

For reactions (1) and (2), ΔH was calculated from the Clapeyron equation, $dP/dT = \Delta H/T\Delta V$. The slope for reaction (1) was assumed to be linear to the invariant point, whereas the slope for the other reaction was calculated by differentiating the $\log P - 1/T$ expression. Values for ΔV are from $25^{\circ}C$, densities of the solid phases and specific volumes of water from Burnham *et al.* (1969). The values obtained, for $520^{\circ}C$, are $\Delta H^{\circ}(1) = 11.7$ kcal and $\Delta H^{\circ}(2) = 83.0$ kcal.

Calculation of ΔH for reactions (3) and (4) from

$$\Delta H(3) = \frac{2}{3} \Delta H(2) - \frac{1}{3} \Delta H(1) = 51.4 \text{ kcal}$$

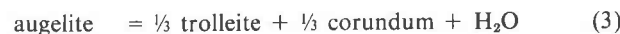
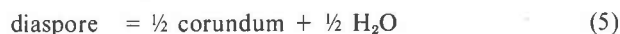
and

$$\Delta H(4) = \Delta H(1) + \Delta H(2) = 94.7 \text{ kcal}$$

allowed the calculation of curve slopes (Fig. 3). Both

curves are consistent with a Schreinemakers analysis of the univariant curves around the invariant point. The complete diagram (right portion of Fig. 3) shows that trolleite is stabilized with high pressure, which supports the observations of Sclar *et al.* (1963). The stability of augelite, however, is abruptly terminated near $525^{\circ}C$ regardless of the pressure.

Below about $400^{\circ}C$ diasporite will appear in phase assemblages. This additional phase requires an additional invariant point, at which diasporite, trolleite, augelite, corundum, and vapor are in equilibrium. The univariant curves emanating from this point are:



Since the P - T curve for reaction 5 has been determined by Haas (1972) and the curve for reaction (3) is reasonably fixed by the discussion above, the inter-

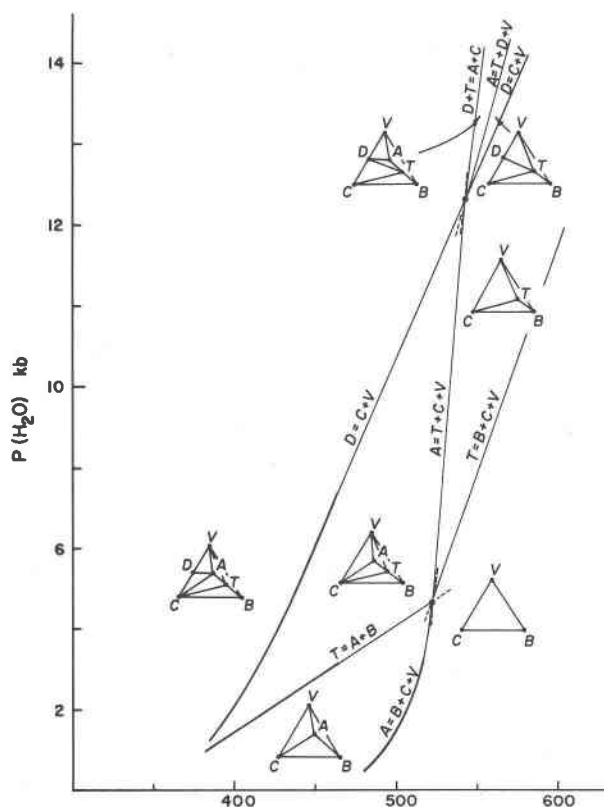


FIG. 3. P - T diagram illustrating the two invariant points and univariant curves in the system Al_2O_3 - $AlPO_4$ - H_2O . Mineral symbols are the same as in Fig. 1. The heavier curves are experimentally determined ($D = C + V$ is from Haas, 1972).

section of the two curves will determine the invariant point (Fig. 3). This intersection occurs at such a high pressure as to be geologically unimportant.

All aluminum phosphate minerals are far more commonly associated with quartz and Al-silicate than with corundum or diaspore. Therefore, an important reaction is expected to be:



Although this reaction was not investigated experimentally, the approximate location of this univariant curve can be calculated. Using the method of Fisher and Zen (1971), the free energy of formation of augelite at standard temperature and pressure was found to be $\Delta G = 671.5$ kcal (estimated error ± 1.5 kcal). The entropy of augelite used in the calculation was estimated to be equal to $S_{\text{berlinite}}^{\circ} + S_{\text{gibbsite}}^{\circ} = 38.0$ e.u. (entropy units).

Reversing the calculation for reaction (8), the equilibrium temperature at 1000 bars was calculated to be 460°C . Thus quartz lowers the stability of augelite by 35° .

Combining the curves for reactions (8) and (1) with the stability of pyrophyllite (Haas and Holdaway, 1973) and andalusite-kyanite inversion (Holdaway, 1971) produces a diagram with the stability fields of the Al-phosphates in the presence of excess quartz (Fig. 4).

Lazulite and scorzalite

A common Al-phosphate mineral in pegmatites as well as in the quartz+Al-silicate deposits is a member of the lazulite $\text{MgAl}_2(\text{PO}_4)_2(\text{OH})_2$ -scorzalite $\text{FeAl}_2(\text{PO}_4)_2(\text{OH})_2$ solid-solution series. The end members (see appendix for description) and intermediate compositions were synthesized from mixes of AlPO_4 and the desired proportions of MgO and Fe metal. Although the details of the stability limits and high-temperature products have not been fully worked out, two significant points have emerged from experimental and petrographic studies. The thermal breakdown of lazulite is near 635°C and scorzalite 515°C at 2 kb with the Ni-NiO buffer. Therefore, any member of the series is stable within the temperature range of trolleite-augelite assemblages. No Mg-bearing silicate, such as biotite, has been found in equilibrium with an Al-phosphate mineral.

Geologic applications

Augelite and trolleite in the White Mountains of California are commonly associated with andalusite and quartz. If these phases grew in equilibrium, then

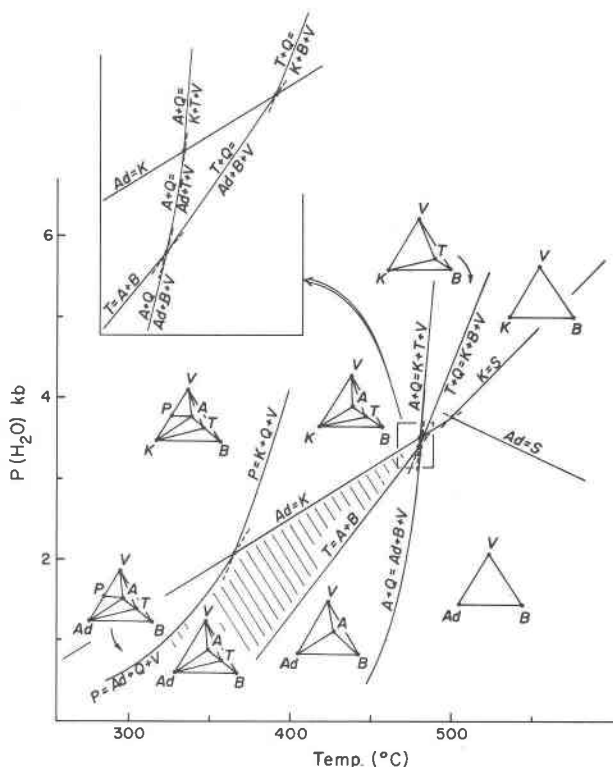
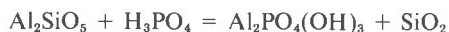


FIG. 4. P - T diagram illustrating the invariant points and univariant curves in the system Al_2O_3 - SiO_2 - AlPO_4 - H_2O . SiO_2 is considered in excess and is an indifferent phase. Mineral symbols are Ad = andalusite, K = kyanite, S = sillimanite, P = pyrophyllite, and A, B, T, and V as in Fig. 1. The Ad = K, K = S, Ad = S curves are from Holdaway (1971); the D = Ad(K) + Q + V curve is from Haas and Holdaway (1973). Trolleite and augelite coexist with quartz and andalusite in the White Mountains and probably formed in the P - T range indicated in the shaded area. The general system (Al_2O_3 , SiO_2 , P_2O_5 , and H_2O) with nine phases present (P, A, Ad, K, S, T, Q, B, and V) will have 84 invariant points. Of these 37 are degenerate, 40 are metastable, and 7 are stable. Five of the stable invariant points appear on this diagram; one of those not shown occurs at high pressures at the intersection of the $P = K + Q + V$ and $A + Q = K + T + V$ reaction curves and the other lies on the Ad = K line at low temperatures and involves the reaction $P + T = A + \text{Ad}$.

the assemblage formed within a narrow range of pressure and temperature (Fig. 4). Quartz and lazulite act as indifferent phases, having no effect on this temperature range.

The puzzling origins of this unusual assemblage have led to such suggested parageneses as metamorphism of phosphate beds in peraluminous sediments and pneumatolitic alteration of sediments. However, if the quartz+andalusite formed by hydrolysis of sericitic schists, a phosphoric acid component of the hydrolyzing fluid could enter into reactions such as



For this reaction $\Delta G = -27.4$ kcal, and appears to become more negative with increases in temperature. The high value of the equilibrium constant ($K = 1/a_{H_3PO_4} = 10^{20}$) means that the $a_{H_3PO_4}$ equilibrium with augelite and andalusite will be very small. Therefore, fluids containing H_3PO_4 will easily convert Al-silicate minerals to Al-phosphate minerals, the extent to conversion depending only on the volume of phosphate introduced.

Appendix

Description of synthetic phases

Berlinite

Crystals with average dimensions of 0.02 to 0.08 mm grow readily from $AlPO_4 \cdot 2H_2O$ precipitates. Crystals grown at temperatures of 300° to 400°C are irregular to rounded prismatic, while those grown above 600°C are sharp bipyramids. Refractive indices for crystals grown at 600°C are $\omega = 1.526(1)$ and $\epsilon = 1.532(1)$. Refined cell dimensions are $a = 4.939(1)$, $c = 10.932(5)$, and calculated density = 2.630.

Augelite

Crystals grown at 490°C developed euhedral forms up to 0.1 mm in length. Refractive indices are $\alpha = 1.574(1)$, $\beta = 1.576(1)$, and $\gamma = 1.586(2)$ with $+2V \approx 55^\circ$.

Refined cell dimensions are: $a = 13.09(1)$, $b = 7.986(3)$, $c = 5.066(3)$, $\beta = 112^\circ 20(3)'$. Calculated density = 2.711.

Trolleite

Synthetic trolleite grown at 390°C is exceedingly fine-grained ($\sim 1 \mu m$) with an average refractive index near 1.640. Refined cell dimensions are: $a = 18.857(5)$, $b = 7.110(4)$, $c = 7.178(4)$, $\beta = 100^\circ 29(2)'$. Calculated density = 3.115.

Lazulite

Crystals grown at 607°C and 2 kbar are only 5 μm in diameter, and are colorless. The average refractive index is 1.610. Refined cell dimensions are: $a = 7.146(3)$, $b = 7.257(3)$, $c = 7.231(3)$, and $\beta = 120^\circ 28(3)'$. Calculated density = 3.105.

Scorzalite

Synthetic scorzalite is deep blue; crystals are irregular in shape and up to 10 μm in size. Refractive

indices are: $\alpha = 1.640(3)$, colorless; $\gamma = 1.674(2)$ azure-blue. Refined cell dimensions are $a = 7.160(3)$, $b = 7.298(6)$, $c = 7.264(5)$, $\beta = 120^\circ 33(3)'$. Calculated density = 3.390.

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References

- BECK, W. R. (1949) Crystallographic inversions of the aluminum orthophosphate polymorphs and their relation to those of silica. *J. Am. Ceramic Soc.* **32**, 147-151.
- BURNHAM, C. W., J. R. HOLLOWAY AND N. F. DAVIS (1969) Thermodynamic properties of water to 1000°C and 10,000 bars. *Geol. Soc. Am. Spec. Pap.* **132**.
- EUGSTER, H. P. (1970) Thermal and ionic equilibria among muscovite, K-feldspar, and aluminosilicate assemblages. *Fortschritte Mineral.* **47**, 106-123.
- FISHER, J. R. AND E-AN ZEN (1971), Thermochemical calculations from hydrothermal phase equilibrium data and the free energy of H_2O . *Am. J. Sci.* **270**, 297-314.
- GEIJER, P. (1963) Genetic relationships of the paragenesis Al_2SiO_5 -lazulite-rutile. *Arkiv Mineral. Geol.* **3**, 423-464.
- GRESENS, R. L. (1971) Application of hydrolysis equilibria to the genesis of pegmatite and kyanite deposits in northern New Mexico. *Mt. Geol.* **8**, 3-16.
- GROSS, E. B. AND A. PARWELL (1968) Rutile mineralization at the White Mountain andalusite deposits, California. *Arkiv Mineral. Geol.* **4**, 493-497.
- GRUNER, J. W. (1945) Structural relationship of $AlPO_4$ and $SiSiO_4$. *Bull. Geol. Soc. Am.* **50**, 1163.
- HAAS, H. (1972) Diaspore-corundum equilibrium determined by epitaxis of diaspore on corundum. *Am. Mineral.* **57**, 1375-1385.
- AND M. J. HOLDAWAY (1973) Equilibria in the system Al_2O_3 - SiO_2 - H_2O involving the stability limits of pyrophyllite, and thermodynamic data of pyrophyllite. *Am. J. Sci.* **273**, 449-464.
- HEMLEY, J. J. AND W. R. JONES (1964) Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism. *Econ. Geol.* **59**, 538-569.
- HOLDAWAY, M. J. (1971) Stability of andalusite and the aluminum silicate phase diagram. *Am. J. Sci.* **271**, 97-131.
- HUTTENLOCHER, H. F. (1935) Kristallstruktur des Aluminiumorthophosphates, $AlPO_4$. *Z. Kristallogr.* **90**, 508-516.
- SCLAR, C. B., L. C. CARRISON, AND C. M. SCHWARTZ (1963) Synthesis and properties of trolleite (aluminian lazulite?), a high-pressure mineral from the Westana iron deposit, Kristianstad, Sweden. *Geol. Soc. Am. Spec. Pap.* **76**, 145.
- WINTSCH, R. P. (1975) Solid-fluid equilibria in the system $KAlSi_3O_8$ - $NaAlSi_3O_8$ - Al_2SiO_5 - SiO_2 - H_2O - HCl . *J. Petrol.* **16**, 57-79.
- WISE, W. S. (1975) The origin of the assemblage: quartz + Al-silicate + rutile + Al-phosphate. *Fortschritte Mineral.* **52**, 151-159.