Accessory minerals

Prof. RNDr. Milan Novák, CSc.

Al_2SiO_5 modifications and other Al-rich minerals

Thesis:

1. Introduction
2. Al_2SiO_5 modifications
3. Alteration of Al_2SiO_5
4. Related minerals
5. Other Al-rich minerals

1. Introduction

- **Minerals Al_2SiO_5 are very important accessory and locally also rock-forming minerals typical for Al-rich rocks from low- to high-grade metamorphic to various acid magmatic. Along these most common Al-rich minerals also several paragenetically and structurally related minerals occur (e.g., staurolite, boralsilite and mullite), or originated during low-T alteartions (e.g. diaspore, pyrofylite).**

Andalusite, Dolní Bory

2. Al$_2$SiO$_5$

- **Minerals Al$_2$SiO$_5$**

Sillimanite	Al^6 Al^4 O SiO$_4$	ortorombic	*Pbnm*, 2/m2/m2/m.
Andalusite	Al^6 Al^5 O SiO$_4$	ortorombic	*Pnnm*, 2/m2/m2/m
Kyanite	Al^6 Al^6 O SiO$_4$	triclinic	*C1, 1*

- **Sillimanite** *a 7.486, b 7.657, c 5.7729 Å, V 331.6 Å^3, Z 4*
- **Andalusite** *a 7.795, b 7.896, c 5.558 Å, V 342.1 Å^3, Z 4*
- **Kyanite** *a 7.112, b 7.844, c 5.574 Å, α 88.9, β 101.1, γ 105.9, V 292.9 Å^3, Z 4*

- **Chemical composition is commonly close to the ideal formula.**
  minor and trace elements:

Sillimanite	**B^{3+}, Mg, Fe^{3+}**
Andalusite	**Mn^{3+}, Fe^{3+}, Cr^{3+}**
Kyanite	**Cr^{3+}, V^{3+}, Fe^{3+}**

2. Al$_2$SiO$_5$

Crystal structures

Figure 2.3. Projection down the a axis of andalusite showing the key coordination polyhedra. (From Papike, 1987, Fig. 7d).

Figure 2.14. Projection of the sillimanite crystal structure down the a axis. (From Papike, 1987, Fig. 7b).
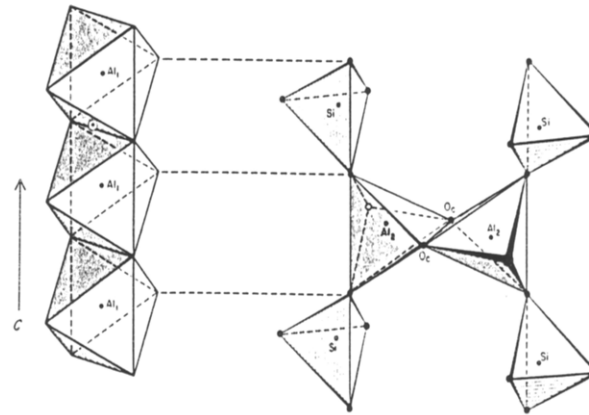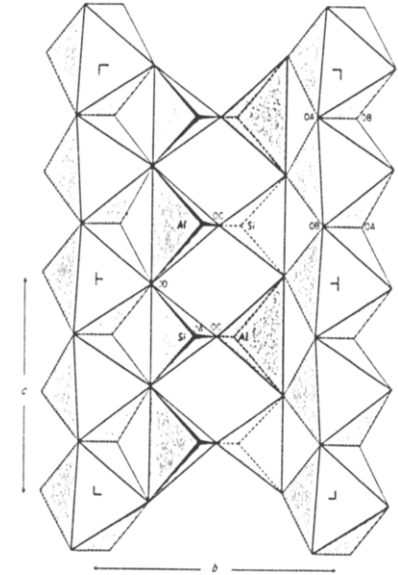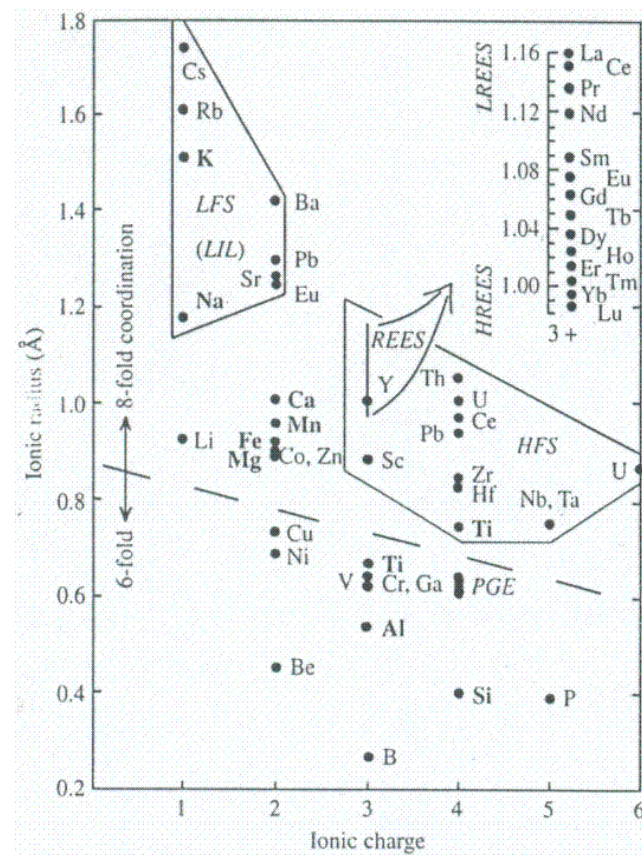
(a) Kyanite   (b) Sillimanite

(c) Andalusite   (d) Columns of Octahedra

Figure 2.1. Octahedra in the Al$_2$SiO$_5$ polymorphs. (a), (b) and (c) show the arrangement of adjacent octahedra, whereas (d) illustrates the octahedral chains parallel to c. (From Deer et al., 1982, Fig. 304; copyright Longman Group Ltd.).

2. Al$_2$SiO$_5$

- Commonly close to ideal formula except Mn^{3+} and partly in Fe^{3+} in andalusite where - kanonaite Mn^{3+6} Al^5 O SiO$_4$ is further member of this group. Entering of Al instead Si into T-site in sillimanite tends to mullite.

- Andalusite-kanonaite – Mn^{3+}

  - full miscibility.

- Sillimanite-mullite – Al

  - limited miscibility..

- Sillimanite-boralsilite – B

  - miscibility exists but not clear.

- Minor and trace elements commonly enter both Al-sites, but more into octahedral site (Mn^{3+} in Mn-andalusite), B enters T-site.

2. Al_2SiO_5

- ## Properties:

- **Sillimanite –**
  grey, white, yellowish
- **Andalusite -**
  pink, red, brown-red, grey, green pleochroic
- **Kyanite -**
  blue, grey colorless
- **Hardness 6-7, kyanite 7-5,**
- **density = 3,2-3,6 (kyanite).**

- **Variety:**
  fibrolit – fibrous sillimanite
  viridine – green Mn-andalusite
  chiastolite – andalusite se
  with sectorial zoning

Kyanit, Frymburk

2. Al_2SiO_5

- ## Tripl point Al_2SiO_5
- **All modifications have triple point and its position in PT diagrams is extremekly important for geological implications.**
- **Richardson et al. (1969)**
- **Holdaway (1971)**
- **Robie a Hemingway (1984)**
- **Holland and Powell (1985)**
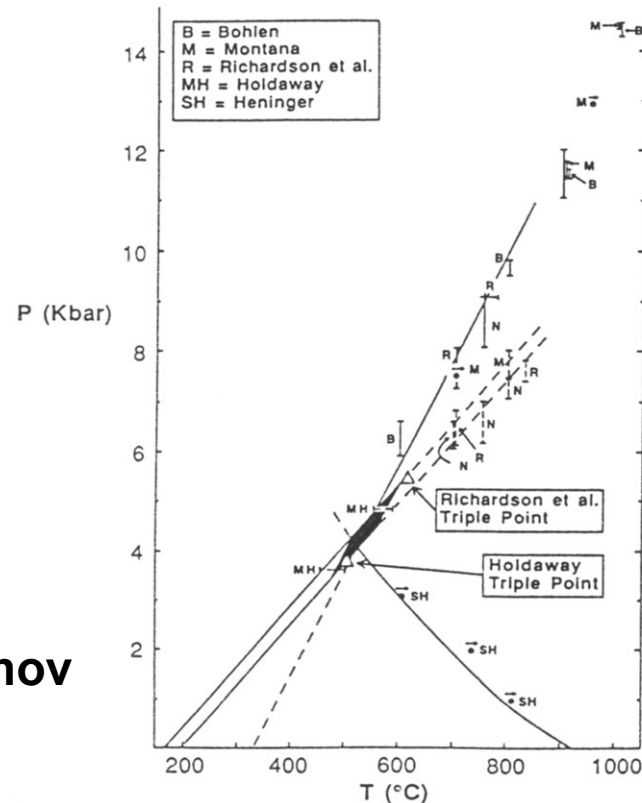- **Pattison (1989)**

Sillimanite, Něchov

Figure 3.46. Summary of experimental data providing constraints on locating the Al_2SiO_5 univariant equilibria and the triple point. The dots with arrows, and the solid brackets, refer to the following experimental studies on the kyanite $\rightleftarrows$ sillimanite reaction: B = S.R. Bohlen (Bohlen et al., ms.); M = A.L. Montana (Bohlen et al., ms.); N = Newton (1969); R = Richardson et al. (1968). The dashed brackets correspond to the following experimental studies on the kyanite $\rightleftarrows$ andalusite reaction: M = A.L. Montana; MH = Holdaway (1971); N = Newton (1966a); R = Richardson et al. (1969). The dots labeled "SH" are Heninger's (1984) determination of the reaction: andalusite → sillimanite. The kyanite-sillimanite equilibrium, and the parallel lines delimiting error envelopes encompassing the kyanite-andalusite equilibrium, are constrained by the experimental data and were calculated by J.A.D. Connolly using the VERTEX program of Connolly and Kerrick (1987). The black polygon locating the triple point is formed by the intersection of the error bands encompassing the kyanite-sillimanite and kyanite-andalusite equilibria (see text). The andalusite-sillimanite equilibrium is constrained by Heninger's (1984) 3 kbar data point.
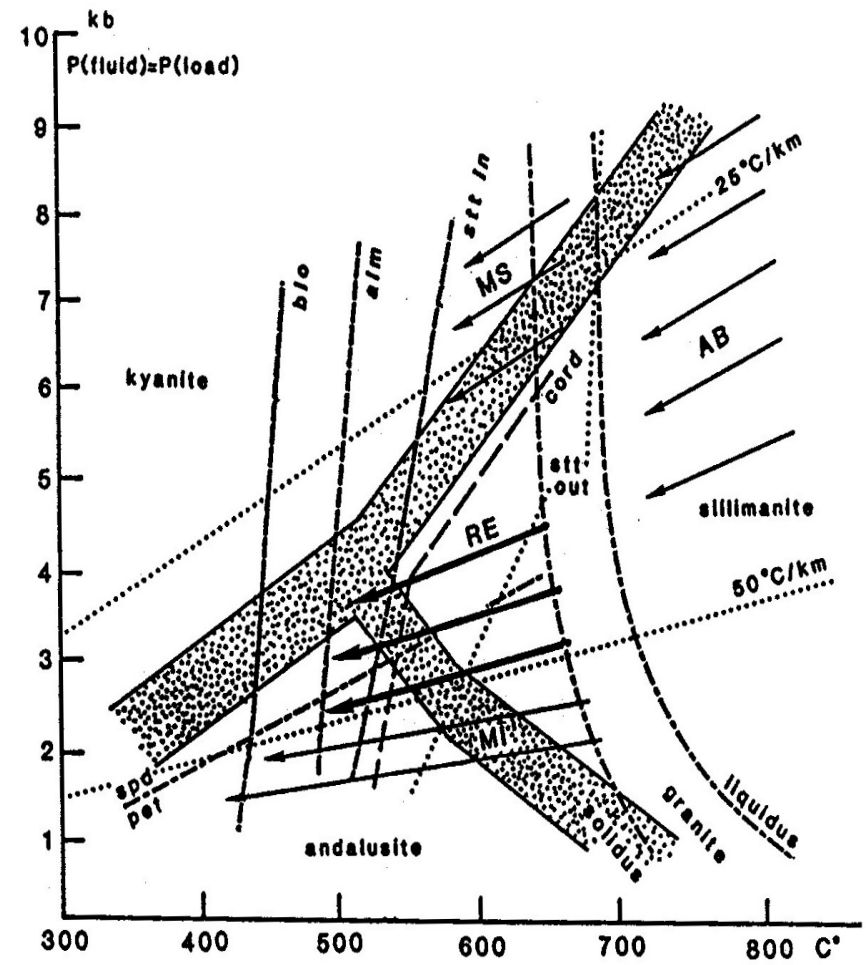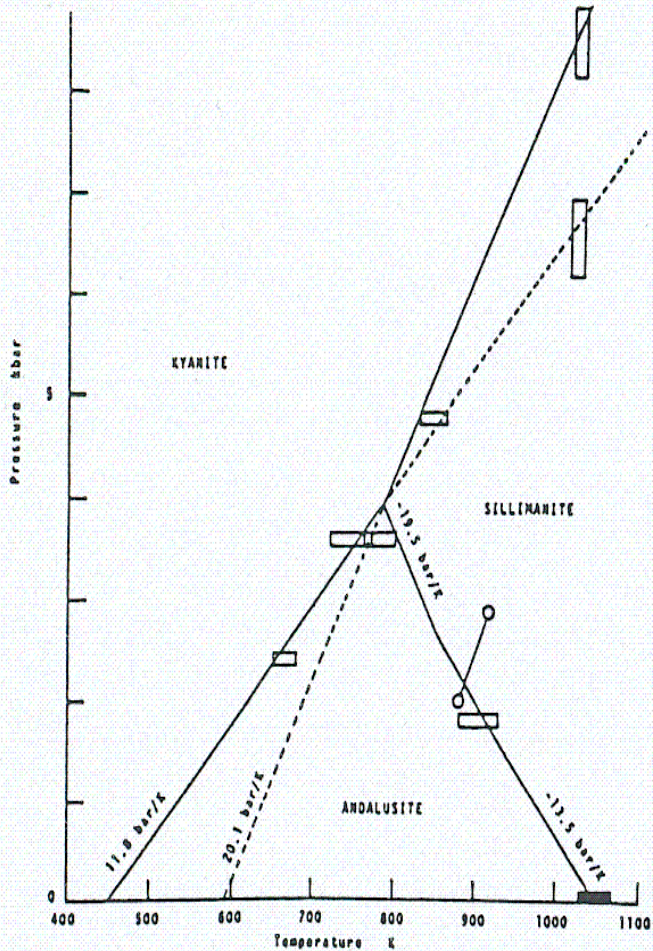
2. Al$_2$SiO$_5$

Figure 3.37. Phase equilibrium diagram showing experimental brackets for the Al$_2$SiO$_5$ equilibria (rectangles) and the univariant equilibria computed with the Clapeyron equation using entropies derived from the heat capacity measurements of Robie and Hemingway (1984). (From Robie and Hemingway, 1984, Fig. 5).
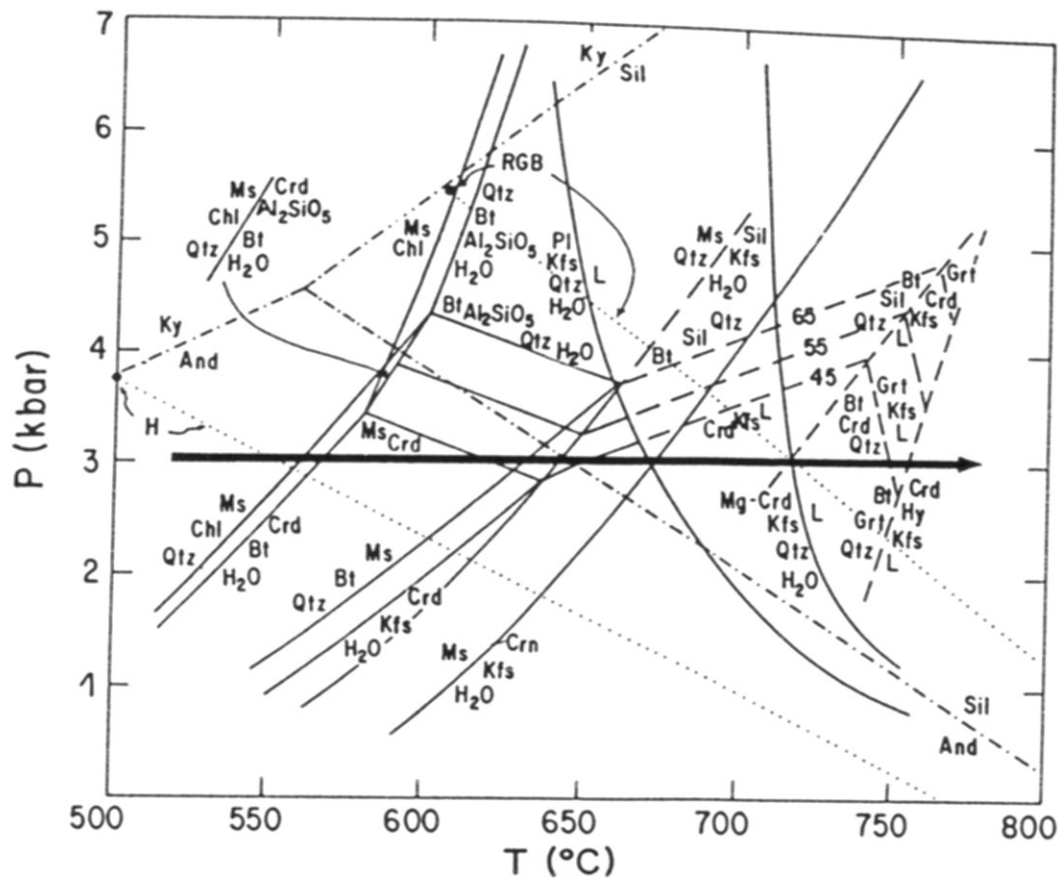
2. Al$_2$SiO$_5$

Figure 9.6. Pattison's (1989) P-T grid showing equilibria relevant to metamorphosed pelites in the Ballachulish aureole, Scotland. The numbers refer to the atomic [Mg/(Mg + Fe)] ratio in cordierite for equilibria involving this phase. The heavy line is Pattison's hypothesized isobaric prograde path in the Ballachulish aureole. The dotted line labeled "H" is Holdaway's (1971) andalusite-sillimanite equilibrium whereas the dotted line labeled "RGB" is the andalusite-sillimanite equilibrium of Richardson et al. (1969). Pattison's suggested location of the Al$_2$SiO$_5$ equilibria are shown with the dot-dash lines. (From Pattison, 1989, Fig. 5).

2. Al$_2$SiO$_5$

- **From all figures it is clear that the position of the triple point is still not strictly defined. Recently triple point of Holdaway (1971) or from Pattison (1989) is used. Chiefly the position of the univariant reaction andalusite=sillimanite is problematic.**

- **Problem of fibrolite**

  fibrous sillimanite-fibrolite is more abundatnt then prismatic sillimanite. Its stability likely overlaps field of andalusite in PT diagrams due to distinct grain-size used in experiments.

Sillimanite

Lazec u Č.Krumlova

2. Skupina Al$_2$SiO$_5$

- **Occurrences:**

  Al-rich rocks with low Na+K/Al.

- **Sillimanite – regional metamorphosed rocks of medium- to high grade, migmatites**

- **Andalusite – contakt and regional metamorphic rocks (Branná), granites, pegmatites (Dolní Bory)**

- **Kyanite – regional metamorphic rocks of medium- to high grade, (Frymburk, Kovářová, Branná), granulites**
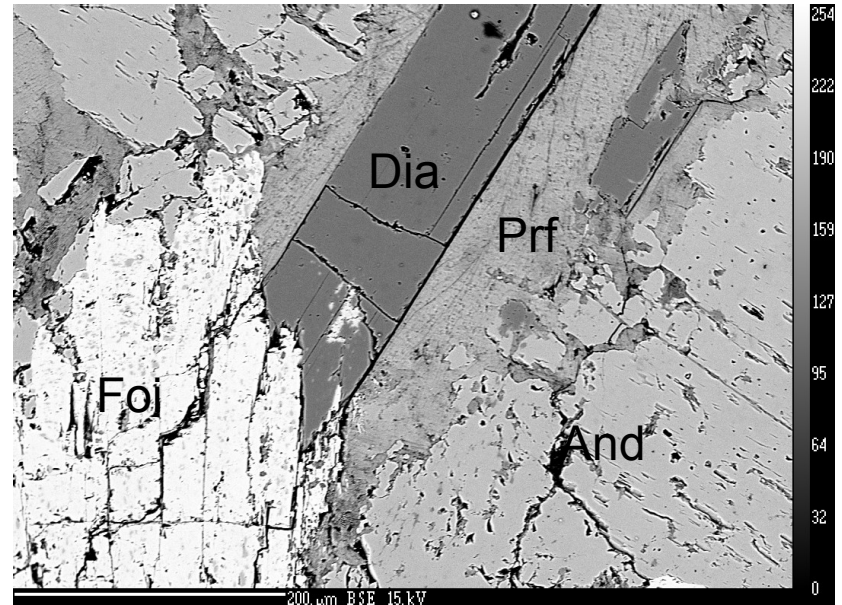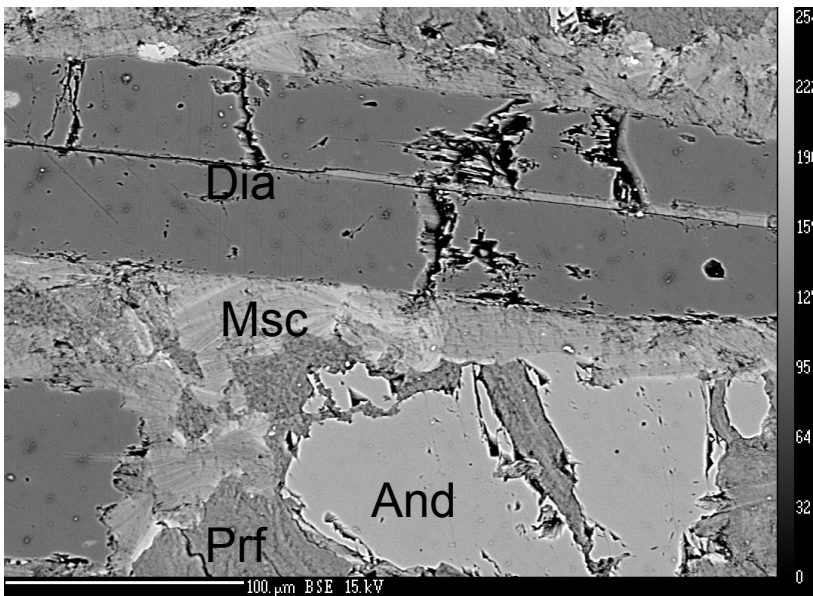

Andalusit, Dolní Bory

3. Al$_2$SiO$_5$ - alterations

Refractority of Al$_2$SiO$_5$ during hydrothermal alterations is moderate to high, highly refraktory to weathering, so they are common in clastic sediments. Produkts of alterations are:

in systems with low activity of alkalis – diaspore, pyrofylite, kaolinite

in systems with high activity of alkalis– muscovite, paragonite

Alteration of andalusite to pyrofylite and muscovite (Dolní Bory)
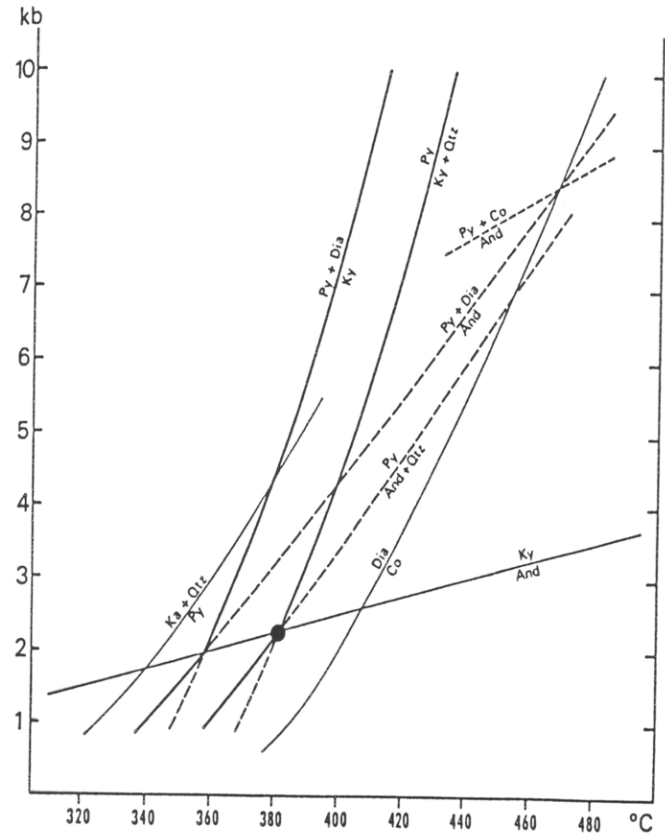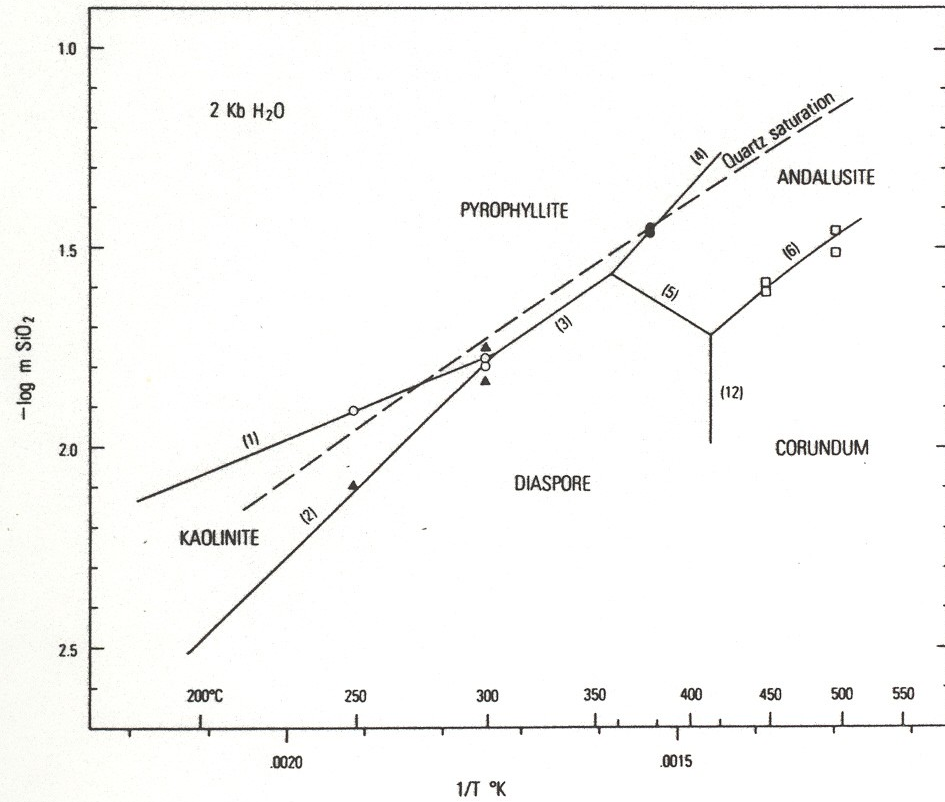
3. Al$_2$SiO$_5$ - alterations

Figure 8.11. Phase equilibrium diagram for the system Al$_2$O$_3$-SiO$_2$-H$_2$O. The invariant point formed by the intersection of the pyrophyllite = Al$_2$SiO$_5$ + quartz + water equilibrium with the kyanite = andalusite equilibrium (filled circle) marks the lowest pressure for kyanite + quartz in a system with a$_{H_2O}$ = 1.0. (From Haas and Holdaway, 1973, Fig. 3).
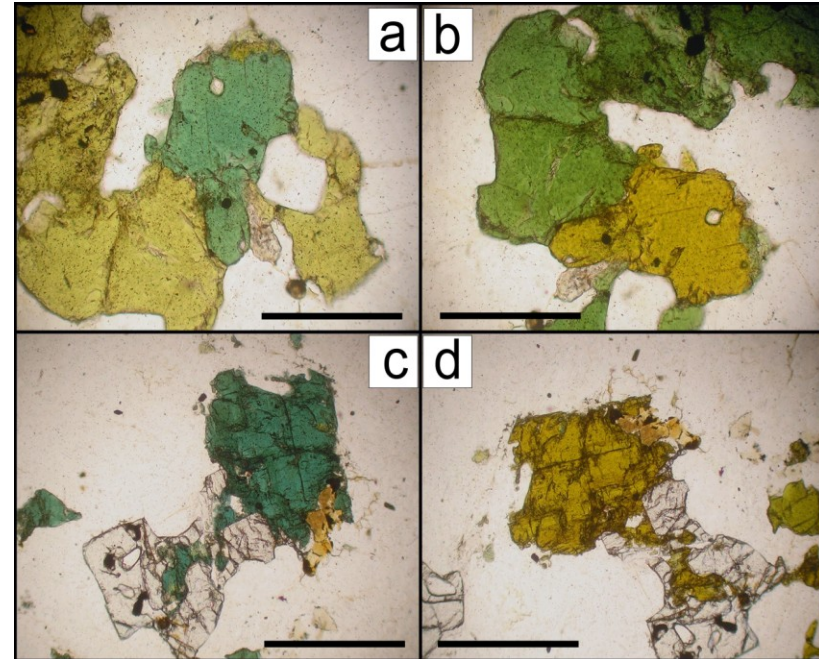
4. Related minerals

- **Kanonaite**

  Mn^{3+} Al O SiO_4

  ortrombic,

  ***Pnnm*, *2/m2/m2/m*, *a* 7.959, *b* 8.047, *c* 5.616 Å, *V* 359.6 Å3, Z 4**
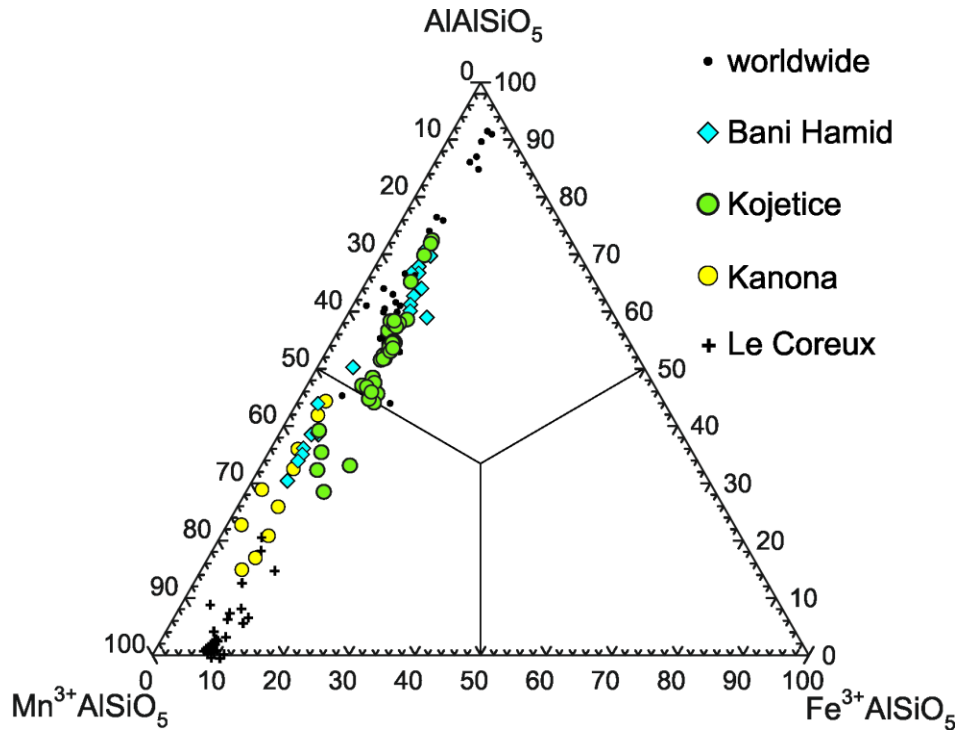
  substitution: Mn^{3+} - Al

  dark green with strong pleochroism, in Mn-rich rocks
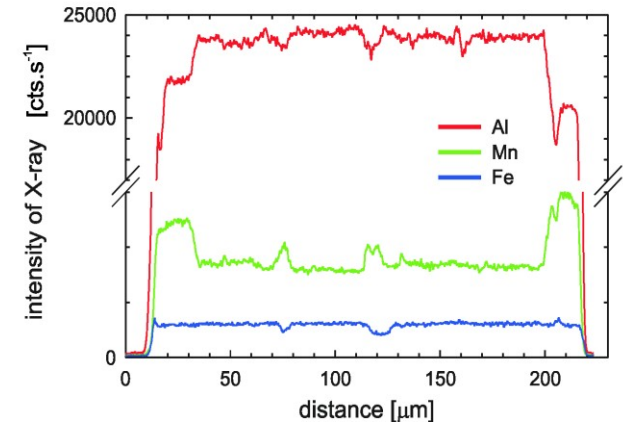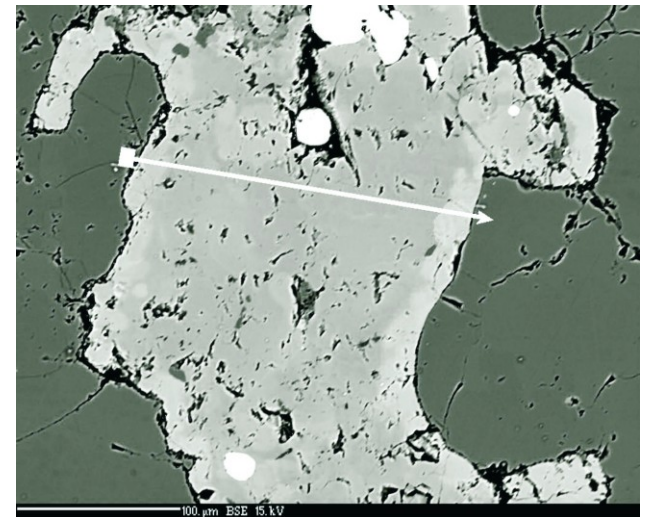

Mn-andalusite and spessartine, Kojetice

4. Related minerals

Kanonaite-Mn-andalusite, Kojetice

4. Related minerals

- **Mullite**

  $Al_{4+2x}Si_{2-2x}O_{10-x}$

  ortorombic, *Pbam*, *2/m2/m2/m*, *a* 7.5416, *b* 7.6942, *c* 2.8875 Å, *V* 167.5 Å3, Z 2,

  substitution: 2Al O - 2Si ▫

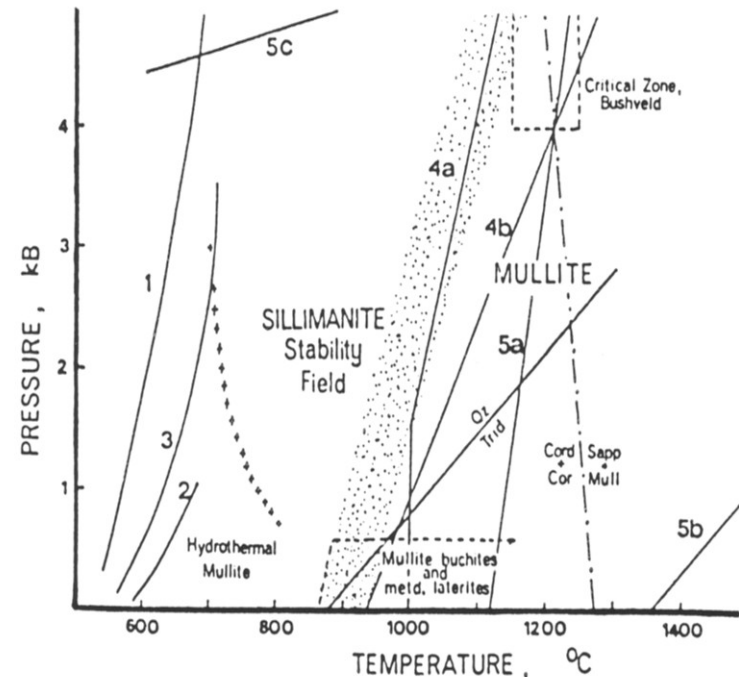- **Fine-graind fibrous in HT contact metamorphism and ceramics**

Figure 4.4. Cameron's (1976a) phase equilibrium diagram illustrating possible P-T stability fields of sillimanite and mullite. The numbered curves relevant to mullite/sillimanite stability relations are: (4) sillimanite + corundum = mullite, (5) sillimanite = mullite + "silica". The lower case letters refer to various experimental determinations of equilibria (4) and (5): (a) Holm and Kleppa (1966), (b) Weill (1966), and (c) Khitarov et al. (1963). The stippled area separates the stability fields of sillimanite and mullite. (From Cameron, 1976a, Fig. 2).
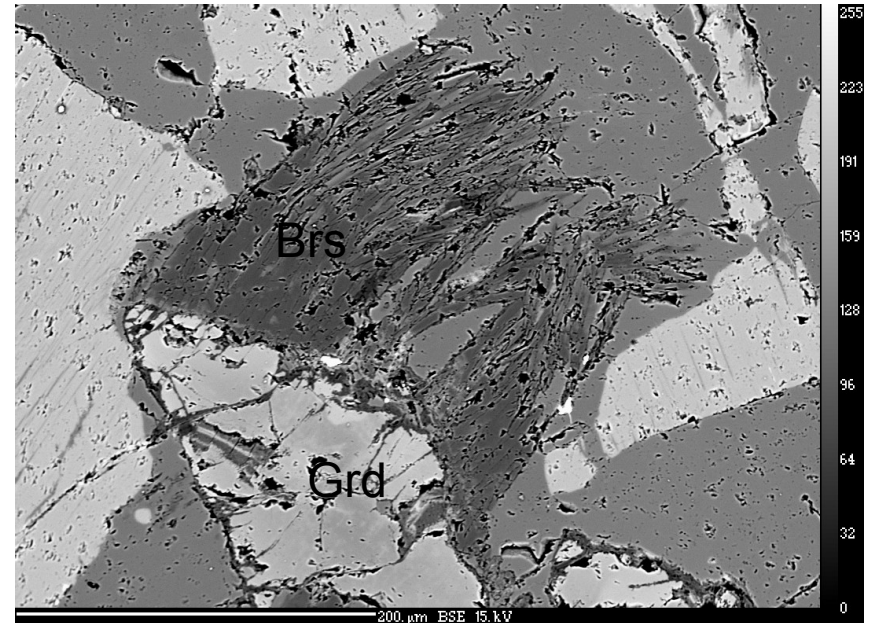
4. Related minerals

- **Boralsilite**

  $Al_{16}B_6Si_2O_{37}$

  ortorombic

  substitution: 2B ☐ - 2Si O

- **Extremely rare**

Boralsilite on grandidierite, Horní Bory

4. Related minerals

- **Staurolite**

General formula $A_4B_4C_{18}D_4T_8O_{40}X_8$
Monoclinic (pseudoortorombic)

A = Fe^{2+}, Mg, □ (□ > 2)   M(4A),M(4B)
B = Fe^{2+}, Zn, Co, Mg, Li, Al, Fe^{3+}, Mn, □ T(2)
C = Al, Fe^{3+}, Cr,V,Mg,Ti   M(1A),M(1B),M(2)
D = Al,Mg, □ (□ > 2)   M(3A), M(3B)
T = Si, Al   T(1)
X = OH,F,O   O(1A), O(1B)

End-member compositions

A	B	C	D	T	O	X
$\square_4$	$Fe^{2+}{}_4$	Al_{16}	$Al_2\square_2$	Si_8	O_{40}	$(OH)_2O_6$
$\square_2Fe^{2+}{}_2$	$\square_4$	Al_{16}	$Al_2\square_2$	Si_8	O_{40}	$(OH)_6O_2$
$\square_4$	$Fe^{2+}{}_4$	Al_{16}	$\square_4$	Si_8	O_{40}	$(OH)_8$
$\square_4$	$Fe^{2+}{}_4$	Al_{16}	$Al_2\square_2$	Si_4Al_4	O_{40}	$(OH)_6O_2$
$\square_4$	$Fe^{2+}{}_4$	$Al_{12}Mg_4$	$Al_2\square_2$	Si_8	O_{40}	$(OH)_6O_2$
$\square_4$	Li_4	Al_{16}	$Al_2\square_2$	Si_8	O_{40}	$(OH)_6O_2$

4. Related minerals

- **Properties:**
  Color: brown to black
  pleochroic
  refractory indices: a 1.736-1.747, β 1.742-1.753, γ 1.748-1.761,
  density: 3.74-3.83, hardness: 7-71/2
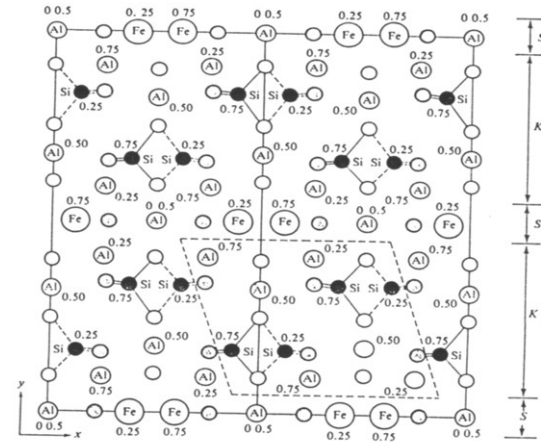
○ = Oxygen at z ∼ 0 and ∼ 0.5   ○ = Oxygen at z ∼ 0.25 and ∼ 0.75

Fig. 329.   Idealized structure of staurolite. Two cells are shown projected down z and the kyanite unit cell is also outlined. Alternate blocks of the structure are denoted K (for kyanite) and S respectively (after Náray Szabó and Sasvári, 1958).
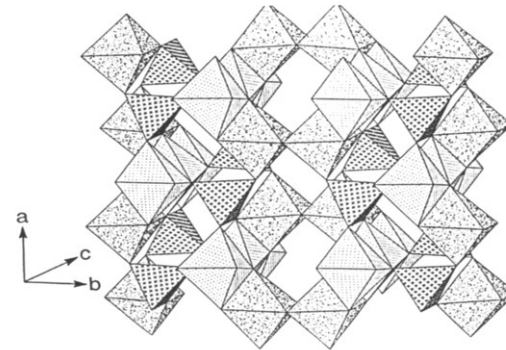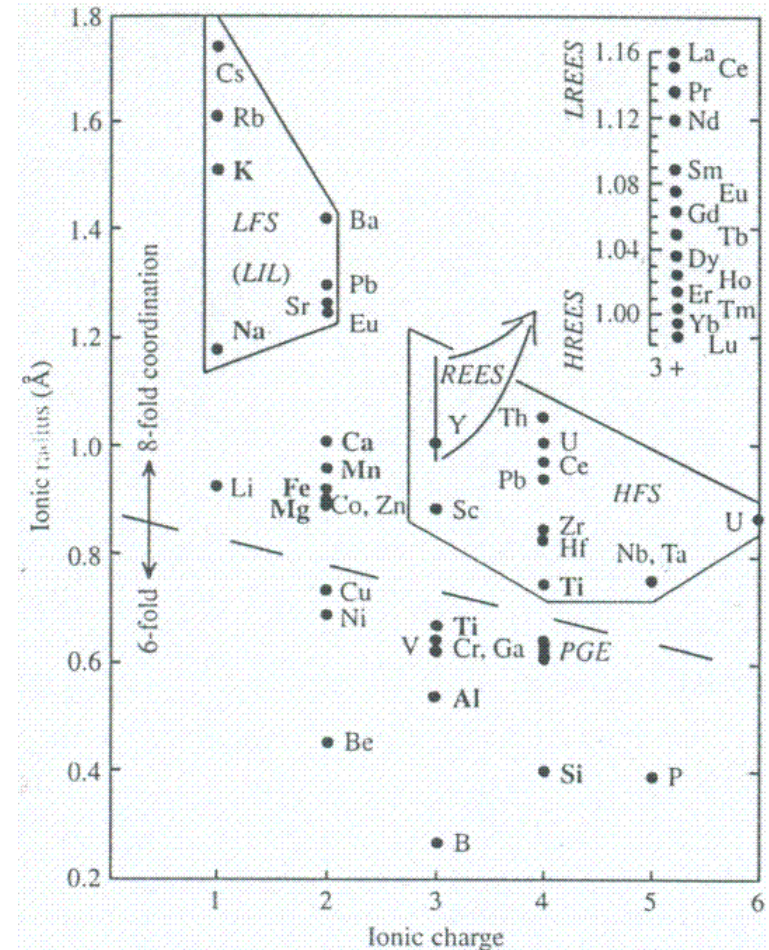
4. Related minerals

Substitutions:

TABLE 13. END MEMBERS AND IMPORTANT EXCHANGE-VECTORS IN STAUROLITE

	End member							exchange vector
Heterovalent exchanges involving hydrogen								
(1)	$\square_4$	Fe_4^{2+}	Al_{16}	$(Al_2\square_2)$	Si_8	O_{40}	$(OH)_2 O_6$	Additive component
(2)	$(\square_2 Fe_2^{2+})$	$\square_4$	Al_{16}	$(Al_2\square_2)$	Si_8	O_{40}	$(OH)_6 O_2$	$Fe\square_2(OH)_2(\square Fe_2O_2)_{-1}$
(3)	$\square_4$	Fe_4^{2+}	Al_{16}	$(\square_4)$	Si_8	O_{40}	$(OH)_5 O_3$	$\square(OH)_3(AlO_3)_{-1}$
(4)	$\square_4$	Fe_4^{2+}	Al_{16}	$(Al_2\square_2)$	(Si_4Al_4)	O_{40}	$(OH)_6 O_2$	$AlOH(SiO)_{-1}$
(5)	$\square_4$	Fe_4^{2+}	$(Al_{12}Mg_4)$	$(Al_2\square_2)$	Si_8	O_{40}	$(OH)_6 O_2$	$MgOH(AlO)_{-1}$
(6)	$\square_4$	Li_4	Al_{16}	$(Al_2\square_2)$	Si_8	O_{40}	$(OH)_6 O_2$	$LiOH(FeO)_{-1}$
Heterovalent exchanges involving ^6Al								
*(7)	$\square_4$	Al_4	Al_{16}	$(Al_{0.67}\square_{3.33})$	Si_8	O_{40}	$(OH)_2 O_6$	$Al_4\square_{1.33}(Fe_4Al_{1.33})_{-1}$
(8)	$\square_4$	Al_4	Al_{16}	$(Al_2\square_2)$	(Si_4Al_4)	O_{40}	$(OH)_2 O_6$	$AlAl(FeSi)_{-1}$
(9)	$\square_4$	Al_4	$(Al_{12}Mg_4)$	$(Al_2\square_2)$	Si_8	O_{40}	$(OH)_2 O_6$	$AlMg(FeAl)_{-1}$
Homovalent exchanges								
(1)	$\square_4$	Zn_4	Al_{16}	$(Al_2\square_2)$	Si_8	O_{40}	$(OH)_2 O_6$	$FeZn_{-1}$
(2)	$\square_4$	Co_4	Al_{16}	$(Al_2\square_2)$	Si_8	O_{40}	$(OH)_2 O_6$	$FeCo_{-1}$
(3)	$\square_4$	Mg_4	Al_{16}	$(Al_2\square_2)$	Si_8	O_{40}	$(OH)_2 O_6$	$FeMg_{-1}$
(4)	$\square_4$	Fe_4^{2+}	Fe_{16}^{3+}	$(Fe_2^{3+}\square_2)$	Si_8	O_{40}	$(OH)_2 O_6$	$AlFe_{-1}$

* note that the end member could be simplified to $\square_4Al_4Al_{16}\square_4Si_8O_{40}[(OH)_4O_4]$ at the expense of complicating the exchange vector: $Al_4\square_2(OH)_2[Fe_4^{2+}Al_2O_2]_{-1}$.

4. Related minerals

occurrences:

   Al-rich metamoprhic rocks

- Typical features of natural staurolites:

   high Fe: decrease in X_{Mg}

- Metapelites of medium-grade

   tourmaline > cordierite > chlorite > bio
   garnet

   typically minor Li: decrease in X_{Li}

- Metapelites of medium-grade

   staurolite > cordierite > biotite > muscovite > garnet,
   tourmaline, chloritoid

   commonly high Zn:

- ratio Zn/Fe in staurolite 10x to 100x highre then in
   associated minerals (garnet, biotite, chlorite).
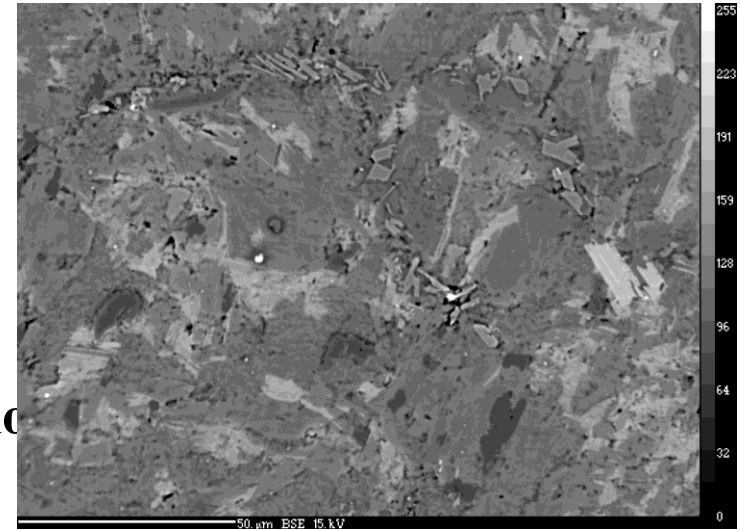
5. Additional Al-rich minerals

- ## Safiríne
  $(Mg,Fe^{2+},Fe^{3+},Al)_8 O_2 (Al,Si)_6 O_{18}$
  monoclinic, space group $P2_1/m$
- Rare accessory phase in Al-rich Si-poor metamorphic rocks

- Propeeties:
  Color: green, blue, grey
  strongly pleochroic:
  Indexy lomu: a 1.701-1.726, b 1.703-1.728, g 1.705-1.734,
  Density: 3.40-3.58 g/cm^3, hardness: 71/2

Typical substitution MgSi Al$_{-2}$

5. Additional Al-rich minerals

- ## **Corundum**

  Al_2O_3

  trigonal *R* 3 *c*

- **Color: grey, bluish, blue, red, yellow and others (ruby, sapphire)**

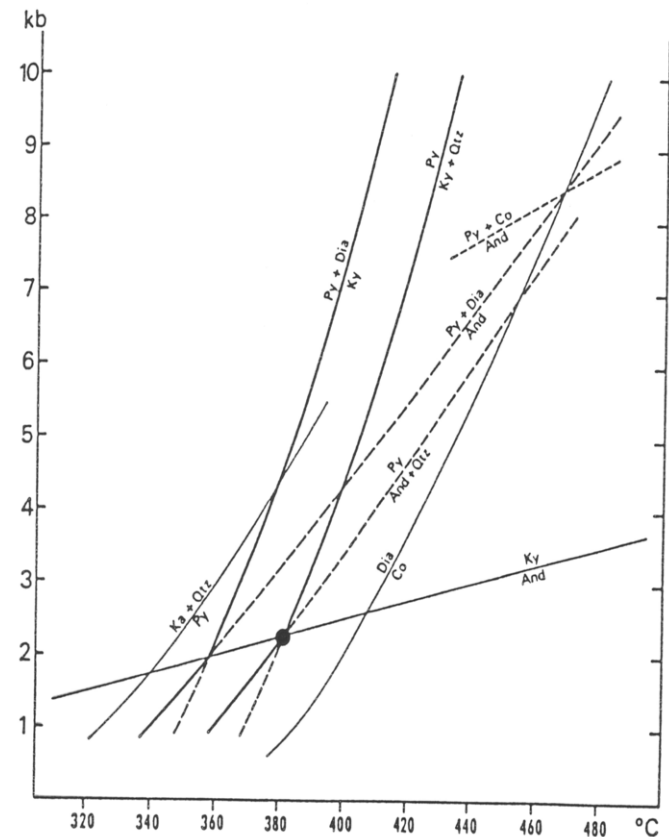**Density: 4,0-4,1   g/cm^3, hardness: 9**

Figure 8.11. Phase equilibrium diagram for the system Al_2O_3-SiO_2-H_2O. The invariant point formed by the intersection of the pyrophyllite = Al_2SiO_5 + quartz + water equilibrium with the kyanite = andalusite equilibrium (filled circle) marks the lowest pressure for kyanite + quartz in a system with a_{H_2O} = 1.0. (From Haas and Holdaway, 1973, Fig. 3).

5. Additional Al-rich minerals
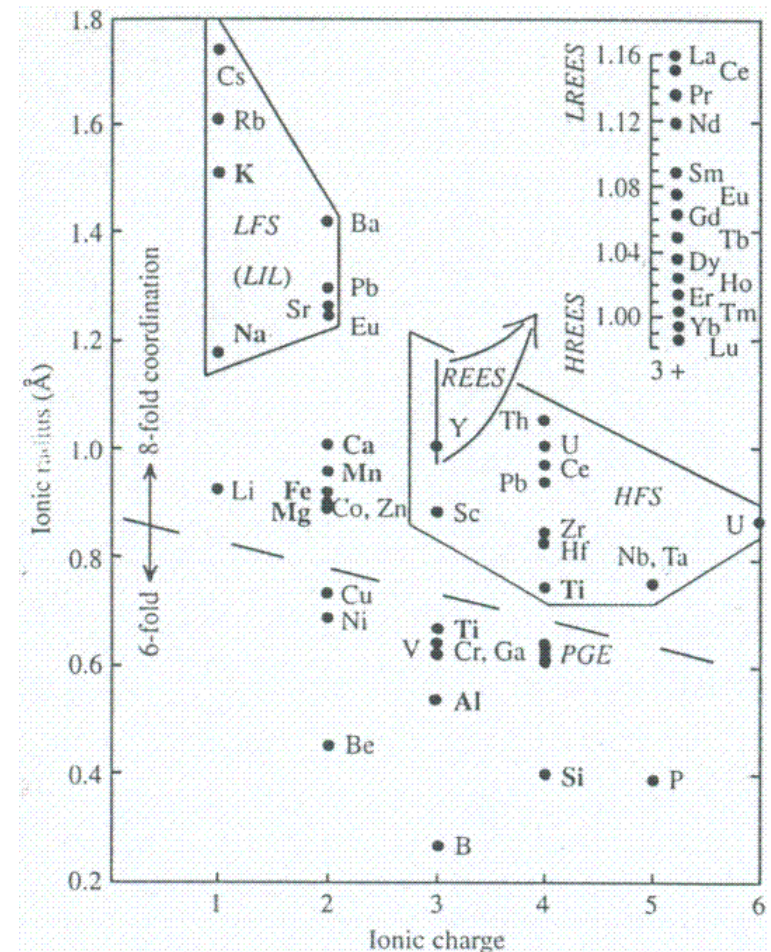

korund

5. Additional Al-rich minerals

- ## Spinels

Spinel $MgAl_2O_4$ hercynite $FeAl_2O_4$ Gahnite $ZnAl_2O_4$

- **Cubic $Fd3m$**

Color: grey, bluish, blue, red, yellow, black, green and others Density: 3,6-4,5 g/cm^3, hardness: 7-8

substitutions: $Mg-Fe^{2+}-Zn-Mn$,

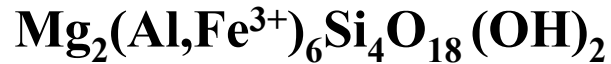**$Al-Fe^{3+}-Cr$**

5. Additional Al-rich minerals

spinel

5. Additional Al-rich minerals

- ## Yoderite
  $Mg_2(Al,Fe^{3+})_6Si_4O_{18}(OH)_2$
  monoclinic, space group $P2_1/m$, class $2/m$.

- Rare mineral known only from quartz-kyanite-talc schists (~ 10 kbar, ~ 800 º C). Yoderit je indicator of high fO$_2$ in deep part of earth crust.

- Color: dark violet to emerald green
  pleochroic
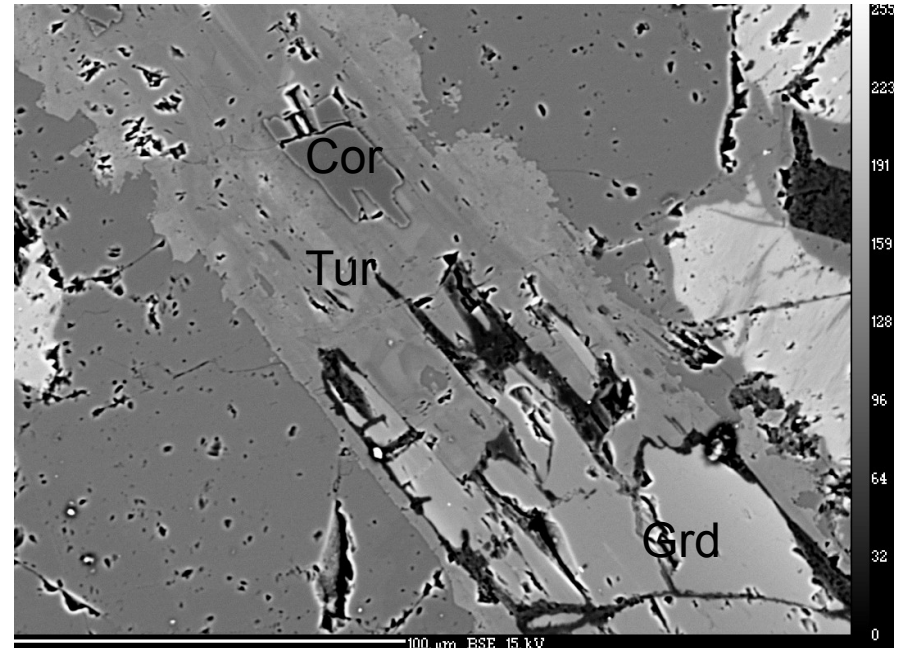 Indexy lomu: a 1.689, b 1.691, g 1.715,
  Density: 3.39 g/cm^3, hardness: 6

5. Additional Al-rich minerals

- :

- **Kornerupine**

  (Mg,Fe) (Al,Mg,Fe)$_9$ (Si,Al,B)$_3$ (O,OH,F)$_{22}$

- **Grandidierite**

  (Mg,Fe) Al$_3$O$_2$ (BO$_3$)SiO$_4$

- **Werdingite**

  (Mg,Fe)$_2$ Al$_{12}$ (Al,Fe)$_2$ Si$_4$ (B,Al)$_4$ O$_{37}$

In high-grade Al,B-rich rocks

Grandidierite replaced by tourmaline and corundum, Horní Bory

6. Conclusions

Al-rich mineráls are important for geological implications due to:

1. Al_2SiO_5 modifications are important for estimation of PT-conditions.

2. Presence of Al-rich rocks incicates:

- high Al in rock – interpretation of source sedimentary rock)

- ratio Al/Si.

- Low activity of alkalis.

3. Late alterations of Al-rich minerals indicate PTX-conditions of these proceses