

# A Unique Chloritoid — Staurolite Schist from near Squaw Peak, Phoenix, Arizona

by

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## Abstract

A local chloritoid-staurolite-biotite-garnet-quartz-muscovite schist horizon in the North Phoenix Mountains, Arizona, is interesting because of the large number of coexisting phases. It is also the only known occurrence of staurolite in this area of central Arizona. The staurolite contains 11 to 14 mole percent of the theoretical zinc end member. The staurolite grade of metamorphism presumably was not reached in this area, inasmuch as staurolite is absent from nearby rocks of otherwise similar bulk composition. The early formation of staurolite apparently was made possible by its preference for zinc and was dependent on the local availability of zinc in one schist horizon.

## Introduction

The Squaw Peak area is located within the city limits of Phoenix at the southeastern end of the Phoenix Mountains. This block-faulted mountain range is composed of steeply dipping Precambrian metavolcanic and metasedimentary rocks trending northeast. In the Squaw Peak area the metamorphic rocks can conveniently be divided into five major rock types from northwest to southeast: (1) greenschist, (2) quartzite, (3) quartz-eye schist, (4) phyllite, and (5) micaceous quartzites. The greenschists are well foliated and contain various amounts of albite, actinolite, quartz, epidote, minor carbonate, and rare biotite and garnet. The quartzite is massive, blue gray, and medium to fine grained. The quartz-eye schists, discussed in earlier papers (Thorpe and Burt, 1978a, 1978b), represent rhyolites and tuffs that apparently underwent some leaching of alkalis prior to metamorphism. The resultant rock types now include (1) metarhyolite, (2) quartz-eye muscovite schist with or without piemontite or viridine (Mn-andalusite), and (3) quartz-eye kyanite schist. Pelitic schist lenses included in the quartz-eye kyanite schists contain chloritoid, muscovite, quartz, and often chlorite. Chloritoid has been noted with kyanite in only one thin section. Phyllites are generally fine grained, gray, and composed of muscovite, quartz, and opaques. Micaceous quartzites occur south of a major northeast-trending fault, separating them from the quartz-eye schists, quartzites, and greenstones to the

north. The micaceous quartzite is an extremely variable unit over 600 m thick, composed predominantly of quartz with a few percent of muscovite that provides a weak foliation obscuring original bedding. Included within this unit are layers of biotite schist, nearly pure quartzite, and quartz-muscovite schist. Many of these layers are discontinuous and only 3 to 4 m wide; others are over 30 m wide and can be traced for over a kilometer.

## Staurolite-Chloritoid-Biotite-Garnet Occurrence

One small lens in the micaceous quartzite that is only 1.5 m wide and 10 to 15 m long in outcrop contains the assemblage staurolite-chloritoid-biotite-garnet-ilmenite-quartz-muscovite (Figs. 1 and 2). This is the only known occurrence of staurolite in the Phoenix Mountains. The low-variance assemblage provides a unique opportunity to investigate the possible local reactions among these minerals.

## Electron Microprobe Analyses

Coexisting minerals in a single sample from this locality were analyzed, courtesy of Arden Albee, using the automated electron microprobe at the California Institute of Technology. The microprobe was operated at 15 keV and a sample current of 0.05  $\mu$ A on brass. Elements were analyzed in triads and counts obtained were converted to weight percent oxides by the Bence-Albee (1968) and Albee-Ray (1970) techniques. All iron is reported as Fe<sup>+2</sup>. Structural formulas were determined on the basis of the number of oxygens in the ideal formula. Representative analyses are presented in Table 1.

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Table 1. Representative microprobe analysis of minerals from specimen 1235 of the chloritoid-staurolite schist

Garnet			Biotite <sup>c</sup>		Muscovite <sup>d</sup>	
Core <sup>a</sup>	Rim <sup>b</sup>					
<u>Oxide (Wt%)</u>			<u>Oxide (Wt%)</u>		<u>Oxide (Wt%)</u>	
SiO <sub>2</sub>	38.24	37.40	SiO <sub>2</sub>	34.55	SiO <sub>2</sub>	45.56
TiO <sub>2</sub>	0.12	0.05	TiO <sub>2</sub>	1.93	TiO <sub>2</sub>	0.38
Al <sub>2</sub> O <sub>3</sub>	21.88	22.16	Al <sub>2</sub> O <sub>3</sub>	19.80	Al <sub>2</sub> O <sub>3</sub>	35.51
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.00	MgO	6.95	MgO	0.53
MgO	0.51	1.42	CaO	0.04	CaO	0.00
CaO	4.10	1.69	MnO	0.01	MnO	0.00
MnO	9.48	1.09	FeO	22.83	FeO	2.29
FeO	28.75	39.21	Na <sub>2</sub> O	0.18	Na <sub>2</sub> O	0.56
Total	103.10	103.02	K <sub>2</sub> O	9.20	K <sub>2</sub> O	10.49
			ZnO	0.03	ZnO	0.00
			F	0.21	F	0.04
			Cl	0.01	Cl	0.01
				95.74		95.37
			Less F & Cl equivalent to Oxygen	- 0.01	Less F & Cl equivalent to Oxygen	- 0.02
			Total	95.63	Total	95.35
<u>Number of Cations Based on 12 Oxygens</u>			<u>Number Cations Based on 22 Oxygens</u>		<u>Number Cations Based on 22 Oxygens</u>	
Si	3.004	2.956	Si	5.334	Si	6.294
Al	0.000	0.044	Al	2.666	Al	1.706
Al	2.031	2.019	Al	0.932	Al	4.228
Ti	0.009	0.005	Ti	0.222	Ti	0.018
Sum	2.040	2.024	Fe	2.950	Fe	0.272
Fe	1.889	2.595	Mg	1.596	Mg	0.110
Mg	0.061	0.166	Mn	0.000	Mn	0.008
Mn	0.633	0.081	Zn	0.000	Zn	0.000
Ca	0.345	0.143	Sum	5.700	Sum	4.636
Sum	2.928	2.985	K	1.818	K	1.706
			Na	0.056	Na	0.170
			Ca	0.010	Ca	0.000
			Sum	1.884	Sum	1.876
<u>End Member Components (mole%)</u>			<u>Ratio (mole%)</u>		<u>Components (mole%)</u>	
Alm.	64.52%	86.94%	Fe <sup>+2</sup> /(Fe <sup>+2</sup> +Mg)	64.89%	Phengitic	17.53%
Pyp.	2.08%	5.56%			Paragonite	7.53%
Spes.	21.62%	2.71%				
Gro.	11.78%	4.79%				
<u>Ratio (mole%)</u>						
Fe <sup>+2</sup> /(Fe <sup>+2</sup> +Mg)	96.87%	93.99%				

a. Analysis #2-605.

b. Analysis #2-601.

c. Analysis #2-801.

d. Analysis #3-701.

*Mineralogy and Petrology*

The quartz-muscovite schist matrix is fine grained and well foliated with a few small crenulations.

The reddish-brown garnets range from 0.3 to 2 mm in diameter. They are euhedral and poikilitic with the inclusions oriented parallel to the foliation. Zoning is well developed with up to 21 mole percent spessartine and 11 mole

Table 1. *Continued*

Chloritoid <sup>e</sup>		Staurolite <sup>f</sup>	
<u>Oxide (Wt%)</u>		<u>Oxide (Wt%)</u>	
SiO <sub>2</sub>	23.91	SiO <sub>2</sub>	27.49
TiO <sub>2</sub>	0.00	TiO <sub>2</sub>	0.30
Al <sub>2</sub> O <sub>3</sub>	41.14	Al <sub>2</sub> O <sub>3</sub>	55.01
MgO	1.94	MgO	0.96
CaO	0.00	CaO	0.00
MnO	0.08	MnO	0.04
FeO	25.71	FeO	12.71
ZnO	0.09	ZnO	2.36
F	0.01	F	0.10
	<u>92.88</u>		<u>98.97</u>
Less F equivalent to Oxygen	- 0.01	Less F equivalent to Oxygen	- 0.05
Total	92.87	Total	98.92
<u>Number Cations Based on 12 Oxygens</u>		<u>Number Cations Based on 23.5 Oxygens</u>	
Si	1.979	Si	3.873
Al	0.021	Al	0.127
Al	3.987	Al	9.026
Ti	0.000	Ti	0.034
Sum	3.987	Sum	9.060
Fe	1.780	Fe	1.500
Mg	0.239	Mg	0.203
Mn	0.005	Mn	0.008
Zn	0.005	Zn	0.246
Sum	2.029	Sum	1.957
<u>Ratios (Mole%)</u>		<u>Ratios (Mole%)</u>	
Fe/(Fe+Mg+Mn+Zn)	87.73%	Fe/(Fe+Mg+Mn+Zn)	76.65%
Mg/(Fe+Mg+Mn+Zn)	11.78%	Mg/(Fe+Mg+Mn+Zn)	10.37%
Mn/(Fe+Mg+Mn+Zn)	0.25%	Mn/(Fe+Mg+Mn+Zn)	0.26%
Zn/(Fe+Mg+Mn+Zn)	0.25%	Zn/(Fe+Mg+Mn+Zn)	12.57%
Fe/(Fe+Mg)	88.16%	Fe/(Fe+Mg)	88.08%

e. Analysis #3-405

f. Analysis #2-501

percent grossular components at the core and only 3 and 4 mole percent, respectively at the rim. The Fe/(Fe+Mg) value decreases slightly from 0.969 at the core to 0.937 at the rim.

Dark-green chloritoid forms subhedral to euhedral poikilitic crystals with quartz and ilmenite inclusions oriented parallel to the foli-

ation. The size ranges from 2 to 6 mm in length and 1 to 3 mm in width. The crystals are randomly oriented within the foliation plane. A few of the grains are slightly crenulated. Garnet is often found touching chloritoid and is sometimes completely enclosed by it. Only one chloritoid was analyzed and no significant chemical variation was noticed between the core and

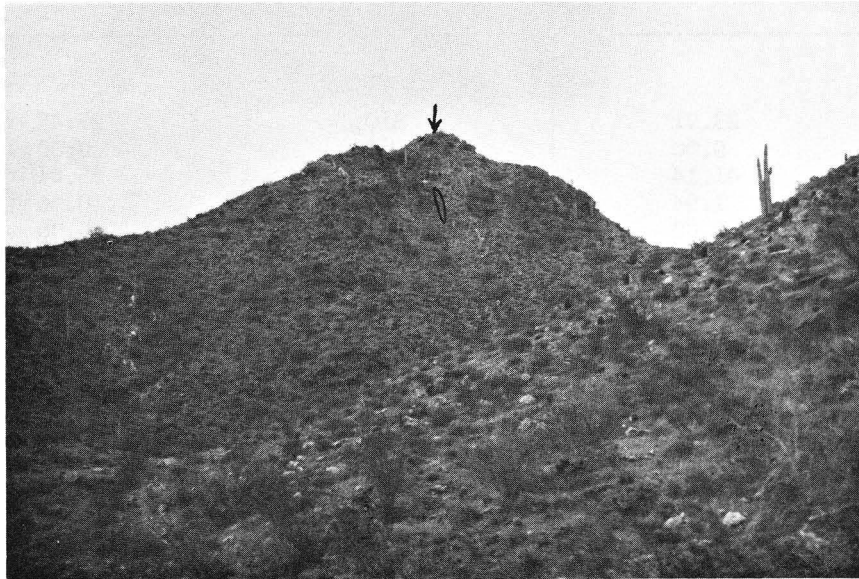


Fig. 1. Staurolite locality in Squaw Peak Park. (Arrow indicates approximate location of schist horizon.)

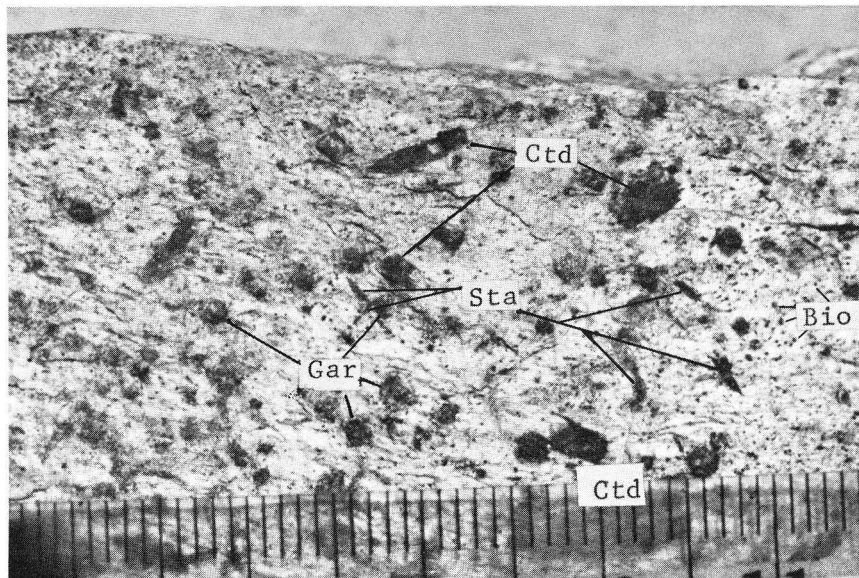


Fig. 2. Hand specimen no. 1235 of staurolite-chloritoid schist. Scale is in mm. Visible dark porphyroblast include chloritoid (large blocky crystals), staurolite (small elongated crystals), garnet (medium rounded grains) and biotite (tiny dark flakes).

the rim. Manganese and zinc are consistently low. The ratio of Fe to Fe+Mg ranges from 0.876 to 0.884.

Staurolite occurs as inconspicuous elongate crystals up to 2 mm long but only 0.5 mm wide. The poikilitic crystals are randomly oriented in the plane of foliation and are concentrated around garnets. Boundaries with garnet are very sharp. Staurolite with a very irregular boundary with chloritoid has been found in only one thin section (Fig. 3). Zinc is highly partitioned into the staurolite. The molar ratio of Zn to Fe+Mg+Zn ranges between 0.113 and 0.148. The Fe/(Fe+Mg) value varies from 0.877 to 0.895.

Biotite is evenly distributed as small (0.2 mm) flakes throughout the schist without any preferred orientation. The biotite is rather Fe rich with a Fe/(Fe+Mg) ratio of 0.626 to 0.653. Biotite is never included within garnet or chloritoid and is only partly included within staurolite.

Muscovite is abundant, well foliated, and very fine grained. The phengite component ranges between 15.5 and 18 mole percent. The paragonite component ranges between 3 and 9 mole percent.

Trace minerals present in the assemblage include schorl, apatite, and ilmenite. Chlorite is rarely present as a retrogressive alteration around garnet.

### Mineral Stabilities

With regard to the AFM diagram (Thompson, 1957) this assemblage contains an extra phase, as shown in Figure 4. This fact can be explained in two ways. One or more of the phases may contain an extra component that would remove it from the plane of the AFM diagram. Alternatively, the assemblage could indeed be univariant in terms of the AFM model system.

Garnet has been described as an "extra" phase at numerous localities, as a result of a high Mn and Ca content (Albee, 1972). Miyashiro (1973) summarized the compositional changes in composition and zoning of pyral-spite garnets with progressive metamorphism. Spessartine garnet is stable at much lower temperatures than almandine, resulting in early-formed garnet that is enriched in Mn. The spessartine content of the zoned garnets can be explained if only the outer layer of each garnet crystal is in equilibrium with the system so that, once formed, garnet is effectively removed from the system. This process results in a progressive decrease in the total Mn available to the system.

The zoning in the Squaw Peak garnets indicates that they started growing early during metamorphism. Although their rims are depleted in Mn and Ca, they still contain enough of these elements to effectively remove them from the ideal AFM system.

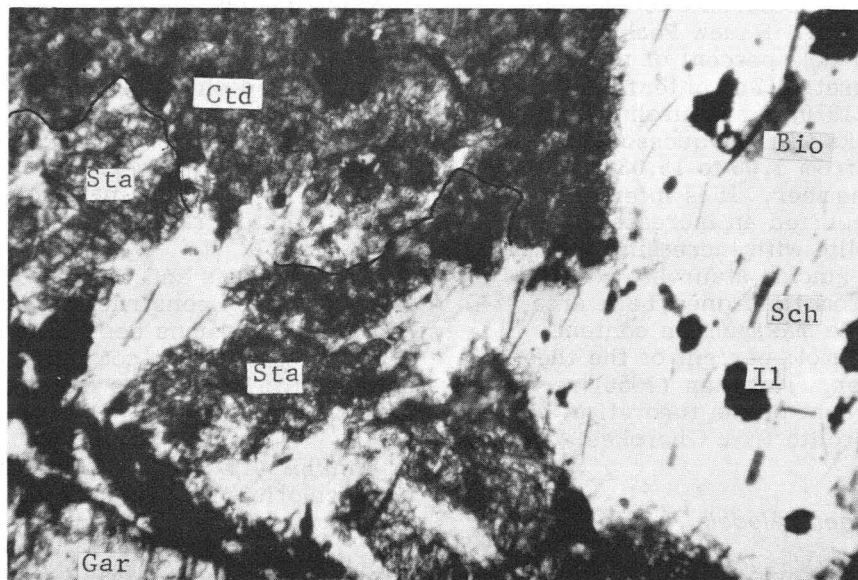


Fig. 3. Specimen no. 1235. Chloritoid in contact with staurolite. Sta = staurolite, Ctd = chloritoid, Gar = garnet, Bio = biotite, Il = ilmenite, Sch = schorl. Field of view = 3.5 mm.

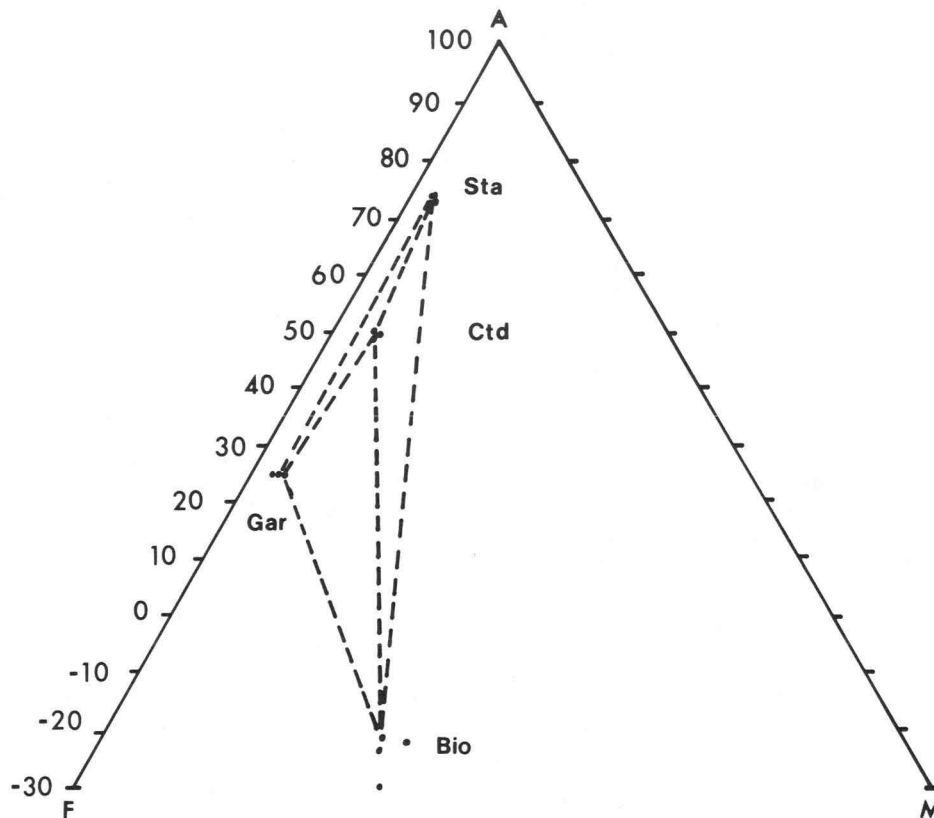


Fig. 4. APM diagram (Thompson, 1957) depicting the mineral assemblage present in the schist horizon. Quartz, muscovite, and an aqueous phase are assumed present.

Another possible "extra" phase is the Zn-rich staurolite. Zincian staurolite is rare but nevertheless well known. Squaw Peak staurolites contain 11 to 14 mole percent of the Zn end member. Comparative Zn contents are reported by Guidotti (1970) for staurolite from sillimanite-grade rocks in the Oquossoc area, Maine. They range from 1.06 to 15.03 mole percent of the Zn end member. It is interesting to note that Guidotti reported an increase in the Zn content of staurolite with increasing grade. Fox (1971) reported zincian staurolite coexisting with chloritoid from the Agnew Lake area, Ontario, Canada. The maximum Zn content corresponds to 15.74 mole percent of the theoretical Zn end member. Juurinen (1956) reported 32.8 mole percent of the theoretical Zn end member for staurolite from Cherokee County, Georgia.

#### *Petrogenetic Models*

Petrogenetic grids provide a useful representation of metamorphic assemblages and their relative stabilities. Petrogenetic grids for pelitic rocks have been constructed by Albee (1965), Ganguly (1969), Kepezhinskas and Khlestov (1977), Harte (1975), and others.

The sequence of reactions on such grids depends on the relative Fe/Mg values in staurolite and chloritoid. In an attempt to resolve this problem, Albee (1972) analyzed coexisting staurolite and chloritoid and found that staurolite usually has a slightly lower Fe-Mg ratio than coexisting chloritoid. Staurolite and chloritoid from Squaw Peak do not clarify the sequence of reactions inasmuch as they have nearly identical ratios.

Kepezhinskas and Khlestov (1977) approached the problem by constructing several grids each having two versions depending on the Fe-Mg ratio of staurolite as compared to coexisting chloritoid. Their grids differ significantly from that of Albee (1965).

Winkler (1974, p. 208) stated that the garnet + chlorite join prevents the coexistence of chloritoid + biotite. This statement is not always correct. Albee (1972) stated that the garnet + chlorite join may break at either higher or lower metamorphic grade than that of the breakdown of chloritoid and he presented two alternative reaction sequences that might occur with increasing temperature.

The presence of chloritoid plus biotite at Squaw Peak indicates that the garnet + chlorite join was broken before the breakdown of chloritoid. This breakdown must have occurred below the aluminosilicate and cordierite-absent invariant point of Albee's (1965) and Hart's (1975) grids, as shown in Figure 5.

The assemblage at Squaw Peak is represented by reaction (3) in Figure 5. The rock

probably approached its present position on the grid via reactions (1) and (2).

The correct placement of this assemblage in P-T space is still rather uncertain due to several unknowns. The first is the possible influence of other fluid components such as  $H_2$ ,  $CH_4$ , or  $CO_2$ , which might have lowered the activity of water and thus facilitated dehydration reactions producing staurolite. The exact

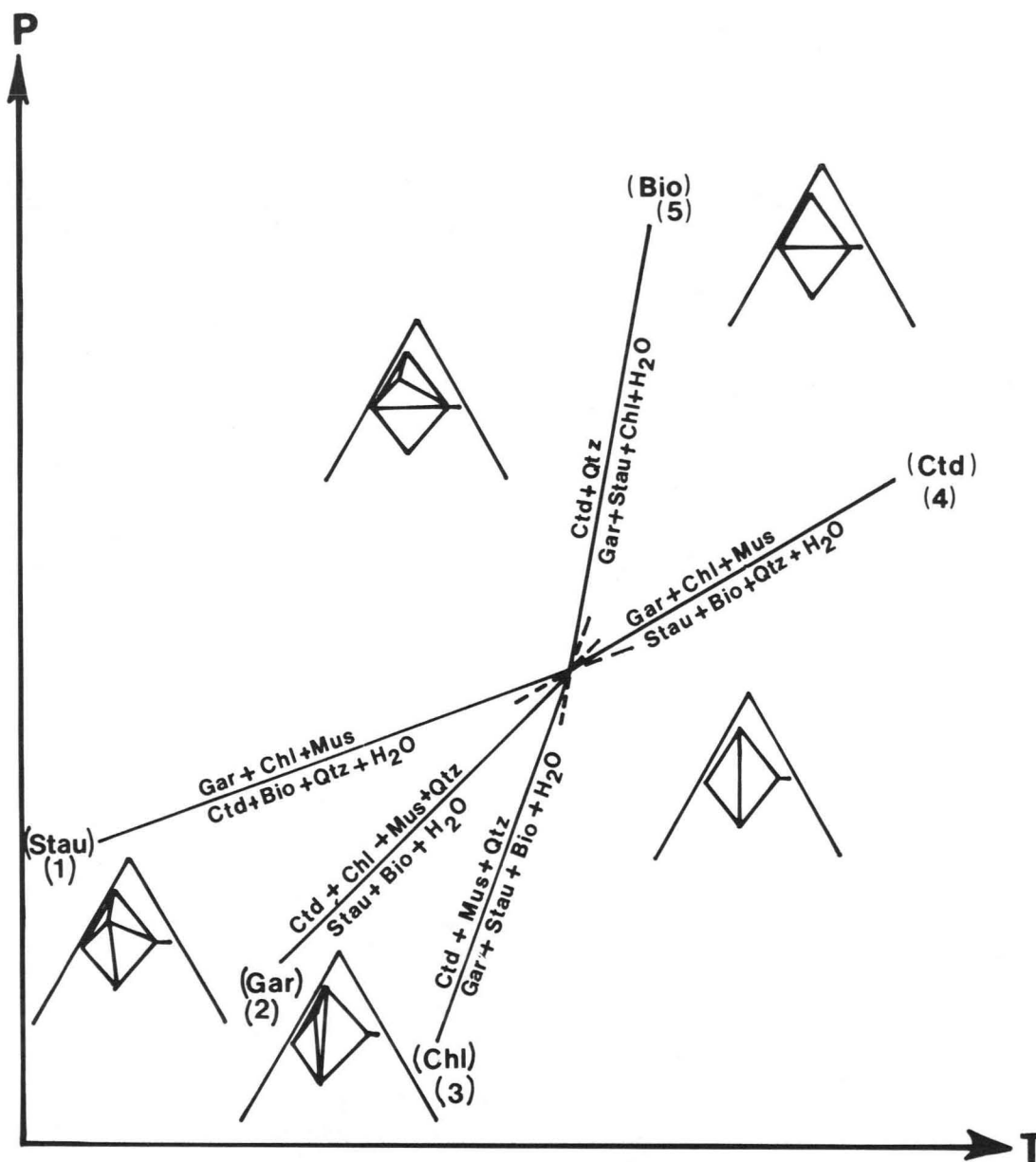


Fig. 5. Schematic arrangement of reactions around the aluminosilicate and cordierite-absent invariant point, according to Albee (1965) and Harte (1975). The assemblage discussed here is represented by reaction 3 (chlorite-absent). The quartz-absent and muscovite-absent reactions are not depicted (the latter would lie along the metastable extension of the biotite-absent curve). Abbreviations: Als = aluminosilicate, Cord = cordierite, Chl = chlorite, Mus = muscovite, Qtz = quartz. Other abbreviations as for Figure 3.

oxidation state of the rocks is another unknown, although presumably it was reduced. Experimental studies by Ganguly (1969, 1972) indicated that iron-rich staurolite, chloritoid, and garnet are unstable under relatively oxidizing conditions.

An occurrence of zincian staurolite and chloritoid reported by Fox (1971) involved more aluminous and magnesian rocks than the rocks discussed here. In the Squaw Peak rocks staurolite formed by the reaction chloritoid + andalusite  $\rightarrow$  staurolite + chlorite. Staurolite is the only zincian phase in the assemblage and, due to the wide variation in ZnO contents of the staurolite, Fox concluded that the isograd reaction would have occurred at different temperatures in each of his samples. Fox (1971, p. 215) suggested the possible existence of an "isogradic zone" enclosing an infinite number of parallel, truly univariant isograds with each isograd representing a specific staurolite zinc content."

#### Conclusions

At Squaw Peak the formation of staurolite in the unique schist horizon was probably only made possible by the presence of zinc and was thus dependent on its availability. The high zinc content of the staurolite and the absence of staurolite from nearby rocks of otherwise similar composition suggest that the grade of metamorphism never reached the P-T conditions necessary to form Zn-free staurolite by the breakdown of chloritoid.

#### Acknowledgments

We are indebted to Dr. Arden Albee for agreeing to perform the analyses of the minerals and to Henry Shaw for making the actual analyses. Dr. John Ferry is thanked for several helpful discussions.

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