

## Nearly pure iron staurolite in the Llano Uplift and its petrologic significance

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### ABSTRACT

Staurolite very close in composition to the Fe end-member is an abundant component of two lithologic layers in an unusual metasedimentary sequence in the Proterozoic Rough Ridge Formation (Packsaddle Group) along White Creek in the southeastern Llano Uplift, central Texas. The exceptional composition of this staurolite makes it an attractive candidate for use in mineralogical, experimental, and thermochemical studies.

The abundance of this nearly pure iron staurolite at White Creek contrasts with nearby evidence for early crystallization and later elimination of staurolite with a typical Fe-Mg ratio. This is consistent with the hypothesis that staurolite spanning a range of Fe-Mg ratios grew during an early moderate-*P* to high-*P* dynamothermal episode, but that only Fe-rich staurolite survived later low-*P* static metamorphism. The White Creek rocks also record incomplete reaction of staurolite + quartz to produce almandine + sillimanite. This reaction might represent the peak of prograde crystallization during early dynamothermal metamorphism near 700 °C and 7 kbar. Alternatively, the reaction might represent partial reequilibration to conditions near 550 °C at ~2.75 kbar during the later static metamorphic event; this alternative presumes that breakdown of unstable H-rich (high-*P*) staurolite yields a metastable almandine + sillimanite assemblage because conversion to a stable low-H staurolite composition is kinetically impeded. Under either interpretation, these observations imply that the southeastern Llano Uplift shared the complex polymetamorphic history documented previously for the northern and northwestern uplift.

### INTRODUCTION

Unusually Fe-rich staurolite occurs in the southeastern Llano Uplift of central Texas in a petrologic context that sheds light on the regional metamorphic history. In overview, that history is dominated by two kinematically distinct thermal events during mid-Proterozoic metamorphism. The first event produced early syndeformational metamorphism at moderate to high pressures (Wilkerson et al., 1988), but because of thorough overprinting, the principal evidence for this event is restricted to small bodies of mafic eclogite that preserve high-pressure mineral assemblages and compositions. The second event, which resulted in widespread static recrystallization and hydration at low pressures, was coincident in time with voluminous granitic intrusion and is genetically linked by isotopic and petrologic evidence to pluton emplacement (Bebout and Carlson, 1986).

Although remnants of mafic eclogites that record high pressures have been found in the northern and northwestern parts of the Llano Uplift (Wilkerson et al., 1988; Schwarze, 1990; Carlson and Johnson, 1991; Carlson, 1992), eclogitic rocks have not been found in the southeastern uplift. Instead, mafic rocks in the southeast yield only amphibolite facies assemblages that lack garnet. This fact is consistent either with an exclusively low-pressure history in the southeast or with complete reequilibration there during late static recrystallization following early

high-pressure metamorphism. Regional correspondence of structural styles suggests that the southeastern uplift shared the dynamothermal metamorphism that affected the northern and northwestern uplift, and the overprinting of early foliations by granoblastic textures records the influence of a later static thermal event. But until now, the southeastern uplift has lacked unequivocal petrologic evidence of a polythermal, polybaric metamorphic history.

In this article we document the occurrence in the southeastern Llano Uplift of rocks containing a nearly pure iron staurolite. From the staurolite's chemistry, in combination with textural observations, phase equilibria, and evidence for early crystallization and later destruction of ordinary iron-magnesium staurolite, we infer that the southeastern uplift has undergone a polymetamorphic history similar to that revealed by eclogitic remnants in the north and northwest.

### OCCURRENCE AND CHEMICAL COMPOSITION

White Creek in the southeastern Llano Uplift (Fig. 1) exposes within the Proterozoic Rough Ridge Formation (Packsaddle Group) an uncommon suite of pelitic metasedimentary rocks. Although the predominant rock types in the Packsaddle Group are felsic schists, felsic gneisses, and amphibolites, the metasedimentary package at White Creek (Universal Transverse Mercator coordinates 14RNJ487775) includes interlayered andalusite-rich

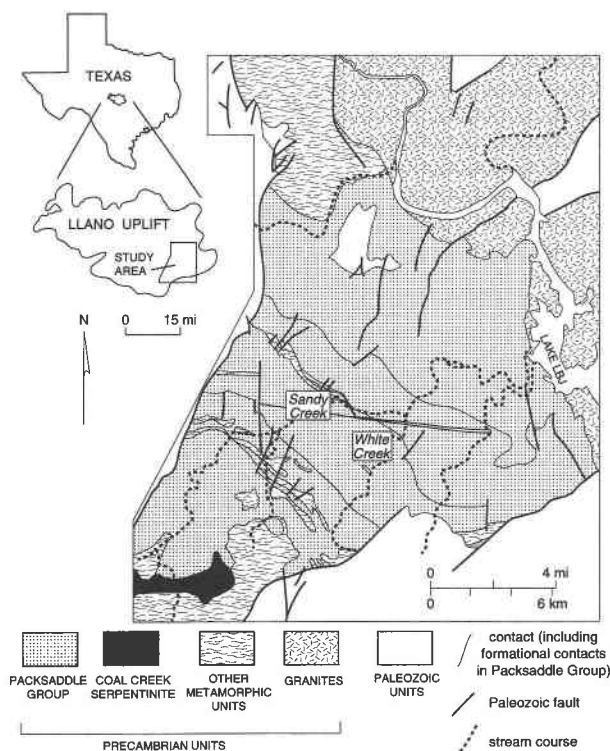


Fig. 1. Location map for staurolite occurrences in the southeastern Llano Uplift, showing highly generalized geology. Staurolite has been found only in the Rough Ridge Formation of the Packsaddle Group; nearly pure iron staurolite is abundant at White Creek, but iron magnesium staurolite occurs only as inclusions in garnet at Sandy Creek.

quartzites and muscovite schists. In this sequence, staurolite occurs abundantly in two distinct, discontinuous layers, each 25 cm thick, that are rich in Al, Si, and Fe but very poor in Na, Ca, and Mg. The mineralogy of both layers is dominated by quartz and staurolite, with subsidiary biotite, garnet, sillimanite, and ilmenite (Table 1). Trace tourmaline, apatite, zircon, and monazite are also present. Some samples of each layer contain appreciable muscovite, but others bear only traces of it. Although plagioclase and potassium feldspar were sought, they were not found.

The data in Table 2 illustrate that staurolite, garnet, and biotite at White Creek are extreme compositional variants, with atomic Fe/(Fe + Mg + Mn + Ca) of 0.99, 0.99, and 0.93, respectively; for staurolite, atomic Fe/(Fe + Mg + Mn + Zn + Li) is 0.96. Electron microprobe analysis reveals no compositional zoning within staurolite crystals and no appreciable crystal to crystal variations in composition. The staurolite compositions in Table 2 for samples WC91c and WC9117 are averages of ten analyses of randomly selected crystals from each sample. Li content was determined by secondary-ion mass spectrometry, courtesy of R. Hervig (Arizona State University). Atomic proportions were calculated as recommended by Holdaway et al. (1991): Fe<sup>3+</sup> was estimated

TABLE 1. Modes for staurolite rocks at White Creek

Sample	WC91c	WC9117	PSsg1	PSsg2	SC919C2
Quartz	45	55	45	40	45
Staurolite	25	25	20	20	15
Biotite	10	15	5	5	10
Muscovite	3	<1	10	15	20
Garnet	0	4	15	15	5
Sillimanite	15	<1	5	5	0
Ilmenite	2	1	<1	<1	4
Tourmaline	0	0	0	0	1

Note: modes are percentages estimated visually in individual thin sections. Garnet is irregularly distributed, and so its absence or high concentration in a single thin section in this table is not representative of its modal abundance at an outcrop scale (~2–5% on average). All samples also contain trace amounts of apatite and zircon, and several crystals of monazite were identified in samples WC91c and WC9117 during microprobe analysis.

as 3.5% of Fe<sub>tot</sub> (coexisting ilmenite possesses only ~0.25% hematite component), and H was estimated by subtracting the total cation charge from 96 after normalizing to fix Si + Al - 1/3Li + 2/3Ti + Fe<sup>3+</sup> at 25.55 ions pfu.

In the staurolite crystal from White Creek, components outside the system Fe-Al-Si-O-H are present only in minute amounts. On an atomic basis, the most Mg-poor sample among the 31 analyzed specimens of Holdaway et al. (1991) contains five times more Mg than is present in the White Creek samples. The specimen (from Zen, 1981) used for thermochemical measurements by Hemingway and Robie (1984) contains nine times as much Mg. Ti and Li are present in the White Creek staurolite crystal at levels just over half the average values in the tabulation of Holdaway et al. (1991); Zn and Mn are negligible. Although the estimated H contents are subject to 1σ uncertainties of about ±0.4 H pfu (Holdaway et al., 1991, p. 1917), the White Creek staurolite crystals are compositionally very close to the stoichiometric reference composition H<sub>4</sub>Fe<sub>3.85</sub>Al<sub>17.90</sub>Si<sub>7.65</sub>O<sub>48</sub> proposed by Holdaway et al. (1991). We are unaware of any staurolite more Fe-rich than those described here.

Staurolite at White Creek grew early in the sequence of deformational and metamorphic events. It displays a moderate preferred orientation of elongate crystals parallel to the rock's dominant foliation (Fig. 2), indicating that it formed during the early dynamothermal metamorphism. In many instances staurolite is included within almandine, or partially replaced by almandine, or both. Staurolite crystallization also predates the cessation of almandine growth in the only other known occurrence of staurolite in the uplift, where it appears exclusively as inclusions in garnet that grew during dynamothermal metamorphism (Carlson and Nelis, 1986).

One possible origin for the staurolite rocks at White Creek is metamorphism of intensely weathered horizons in an argillaceous sedimentary sequence. This is suggested by the close correspondence between their bulk compositions and those of some bauxites and metabauxites (cf. Table 2 of Bardossy et al., 1970) and by their intimate association with highly aluminous andalusite-rich quartz-

TABLE 2. Analyses of staurolite, garnet, and biotite from White Creek and Sandy Creek

Sample Mineral	White Creek				Sandy Creek		
	WC91c Stt	WC9117 Stt	WC9117 Grt	WC9117 Bio	GT-1 Stt	GT-1 Grt	GT-1 Bio
<b>Weight percent oxides</b>							
SiO <sub>2</sub>	26.26(18)	26.60(27)	36.14(19)	32.65(13)	26.51(6)	37.35(23)	35.13(20)
TiO <sub>2</sub>	0.30(7)	0.30(7)	0.05(1)	1.14(9)	0.47(1)	<0.01(1)	1.70(13)
Al <sub>2</sub> O <sub>3</sub>	54.03(51)	54.13(48)	20.33(9)	19.67(17)	54.01(30)	21.47(15)	17.82(15)
FeO <sub>tot</sub>	16.93(19)	16.92(16)	42.37(13)	30.87(17)	13.14(8)	25.72(17)	19.66(18)
MgO	0.13(1)	0.18(2)	0.28(1)	1.40(3)	2.05(4)	2.67(5)	11.61(14)
CaO	n.a.	n.a.	n.a.	<0.01(2)	n.a.	1.66(3)	n.a.
MnO	0.01(1)	<0.01(1)	0.32(1)	<0.01(1)	0.74(1)	11.16(10)	0.94(3)
ZnO	0.01(1)	0.01(1)	n.a.	n.a.	0.74(1)	n.a.	n.a.
Na <sub>2</sub> O	n.a.	n.a.	n.a.	0.43(1)	n.a.	n.a.	0.30(2)
K <sub>2</sub> O	n.a.	n.a.	n.a.	8.24(1)	n.a.	n.a.	8.35(4)
Li <sub>2</sub> O	0.09*(1)	0.13*(1)	n.a.	n.a.	0.20**	n.a.	n.a.
Total	97.76	98.28	99.76	94.39	97.86	100.03	95.51
<b>Atomic proportions</b>							
O	48	48	12	22	48	12	22
Si	7.41	7.47	3.00	5.31	7.48	3.00	5.19
Ti	0.06	0.06	0	0.14	0.10	0	0.11
Al	17.99	17.95	1.99	3.77	17.97	2.03	3.44
Fe <sup>3+</sup> †	0.14	0.14	0.01	0	0.11	0	0
Fe <sup>2+</sup>	3.86	3.84	2.93	4.20	2.99	1.73	2.53
Mg	0.05	0.07	0.04	0.34	0.86	0.32	2.66
Ca	0	0	0.02	0	0	0.14	0
Mn	0	0	0.02	0	0.18	0.76	0.12
Zn	0	0	0	0	0.15	0	0
Na	0	0	0	0.14	0	0	0.15
K	0	0	0	1.71	0	0	1.71
Li	0.10	0.15	0	0	0.23	0	0
H ‡	3.78	3.63	0	2	2.85	0	2

Note: numbers in parentheses are one standard error of the mean; n.a. = not analyzed. Data for staurolite in sample GT-1 are from Carlson and Nelis (1986). Electron microprobe data were acquired with wavelength-dispersive techniques (60-s analyses, 15 kV, 15 nA on brass, 10- $\mu$ m beam diameter) using natural and synthetic silicate standards and employing the correction scheme of Albee and Ray (1970).

\* Ion-probe analysis (R. Hervig, Arizona State University); average of three analyses per sample.

\*\* Not analyzed. Value of 0.20 is assumed, following the recommendation of Holdaway et al. (1991).

† Fe<sup>3+</sup> is calculated from the stoichiometry for staurolite (see text) and garnet, but all Fe in biotite is reported as Fe<sup>2+</sup>.

‡ Atomic proportions for H are calculated from the stoichiometry for staurolite (see text) but are assigned arbitrarily for garnet and biotite.

ites. The bulk chemistry and mineral textures in the Llano rocks are distinctly different from those of modally similar staurolite quartzites in New Mexico described by Schreyer and Chinner (1966), for which a metasomatic origin was proposed.

#### MINERALOGIC AND PETROLOGIC SIGNIFICANCE

Staurolite comprises ~20 modal% of the layers in which it occurs, shows minimal alteration in thin sections, and is relatively free of inclusions. Combined with its exceptional composition, these characteristics make the White Creek staurolite an excellent subject for a variety of mineralogic, crystallographic, experimental, and thermochemical investigations. (This occurrence is entirely on private property, however, and can be visited only with prior permission from the landowner.)

#### Polymetamorphic history inferred from contrasting staurolite occurrences

When contrasted with the regional scarcity of staurolite in the Llano Uplift, the Fe-rich occurrence at White Creek takes on petrologic significance. As noted above, only one other occurrence of staurolite in the uplift is known. Carlson and Nelis (1986) report its presence, exclusively as inclusions in a large garnet, in a garnet-biotite gneiss of

the Rough Ridge Formation exposed in Sandy Creek, roughly 4 km west of the White Creek locality (Fig. 1). The staurolite inclusions in garnet at Sandy Creek (Table 2, sample GT-1) have ordinary Fe-Mg ratios and typical minor-element contents. The matrix enclosing the garnets contains quartz, biotite, calcic oligoclase, and microcline but is entirely devoid of staurolite. Nearby units bear large (up to 10-cm) postkinematic poikiloblasts of iron-magnesium cordierite that overgrow all metamorphic foliations (Nelis et al., 1989).

These observations must be interpreted in light of the evidence summarized above for two kinematically distinct thermal events in the Llano Uplift. Thermobarometry on remnants of mafic eclogites in the northern and northwestern parts of the uplift (Wilkerson et al., 1988; Schwarze, 1990; Carlson and Johnson, 1991; Carlson, 1992) demonstrates that early dynamothermal metamorphism in those areas took place at pressures ranging from 6 (?) to 11 kbar and temperatures from 670 to 750 °C. Later static metamorphism took place at lower temperatures and substantially lower pressures. Calcite-dolomite thermometry, calc-silicate phase equilibria, garnet-biotite thermometry, garnet-ilmenite thermometry, garnet-cordierite thermometry, O-isotope thermometry, and the stability of muscovite + quartz and aluminum silicate

assemblages all indicate that  $T$  and  $P$  for the static event are in the range  $550 \pm 75$  °C and  $2.75 \pm 0.75$  kbar across the entire uplift (Bebout and Carlson, 1986; Schwarze, 1990; Letargo and Lamb, 1992, 1993). Gradients in peak temperatures for the late static metamorphism spanning  $\sim 125$  °C have been documented in proximity to some granitic intrusions (Letargo and Lamb, 1991).

In the context of this regional perspective, we suggest that staurolite with a range of ordinary Fe-Mg ratios (like the inclusions within garnet at Sandy Creek) may have formed during the early dynamothermal event at moderate to high pressures, but that only nearly pure iron staurolite (like that at White Creek) survived later static metamorphism at low pressure. Although phase equilibria involving staurolite and cordierite in the system Fe-Al-Si-O-H continue to defy precise experimental definition (cf. Holdaway and Mukhopadhyay, 1993b), early experimental results (e.g., Richardson, 1968) indicate in at least a qualitative way that iron staurolite + quartz should react to produce iron cordierite + aluminum silicate as pressures drop; the equilibrium boundary for Fe end-members probably passes slightly below 2 kbar at temperatures near 550 °C. Because cordierite preferentially incorporates Mg, "the low-pressure termination [of the staurolite + quartz stability field] will be significantly raised" for Mg-bearing staurolite (Richardson, 1968, p. 484). It is therefore likely that regional reequilibration at  $\sim 550$  °C and  $\sim 2.75$  kbar could eliminate staurolite with ordinary Fe-Mg ratio while preserving nearly pure iron staurolite.

Conditions of final equilibration at White Creek and Sandy Creek appear to match those found regionally. Thermometry for garnet rims and matrix biotite using Ferry and Spear's (1978) experimental calibration in conjunction with Berman's (1990) activity model for garnet yields  $\sim 530$  °C at White Creek and  $\sim 570$  °C at Sandy Creek. (Representative analyses appear in Table 2.) Assemblages suitable for quantitative barometry are absent, but aluminum silicate phase relations provide some barometric constraints at White Creek. The metasedimentary sequence there contains both andalusite and sillimanite; slightly ferruginous andalusite is spectacularly abundant in quartzites only a few meters away from staurolite rocks bearing small amounts of sillimanite. It is conceivable that both polymorphs occur in equilibrium assemblages, but, we suggest below, that sillimanite is probably metastable, either a relic from the early dynamothermal event or the product of a metastable reaction that took place at low pressure in the later static event. Thus the aluminum silicates at White Creek require pressures beneath or perhaps along the equilibrium boundary between andalusite and sillimanite; at 530 °C, the inferred maximum pressure is  $\sim 3.3$  kbar (Holdaway and Mukhopadhyay, 1993a). (The triple point of Bohlen et al., 1991, would yield pressures nearly 1 kbar higher.) Although aluminum silicates are not found at Sandy Creek, regionally uniform pressures for the late static event across the uplift are inferred from the ubiquity of Buchan-series static mineral assem-

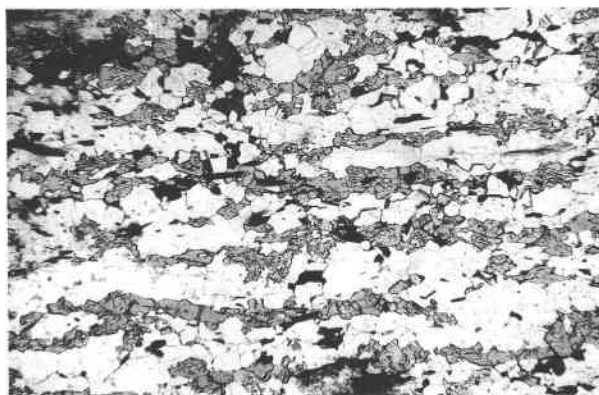


Fig. 2. Staurolite (gray) from White Creek with quartz (white), biotite (dark gray to black), and minor ilmenite (black). Moderate dimensional preferred orientation parallels dominant foliation, defined by compositional layering and aligned biotite. Sample WC9117. Photomicrograph in plane-polarized light. Long dimension of field of view is 4.1 mm.

blages and from quantitative barometry where suitable assemblages exist. Combined with the proximity of the two localities, this makes it unlikely that pressures at Sandy Creek were markedly different from those at White Creek.

Thus regional reequilibration to  $\sim 550$  °C and  $\sim 2.75$  kbar during late static metamorphism in the southeastern uplift would account for the elimination of iron-magnesium staurolite from the matrix of garnet-biotite gneisses at Sandy Creek despite the persistence of nearly pure iron staurolite at White Creek. This requires only that the magnesian bulk composition at Sandy Creek raises the minimum pressure for stability of iron magnesium staurolite above  $\sim 2.75$  kbar, a displacement of  $\sim 1$  kbar or less, relative to pure iron staurolite. The abundance of iron-magnesium cordierite in some layers at Sandy Creek suggests that conditions of final reequilibration there were indeed outside the field of stability for staurolite of ordinary Fe-Mg ratio.

#### The reaction staurolite + quartz $\rightarrow$ almandine + sillimanite

Petrographic evidence for the incomplete reaction of staurolite + quartz to produce almandine + sillimanite is unmistakable in the rocks from White Creek, but it is difficult to assess unambiguously the conditions under which this reaction occurred. Figure 3a illustrates a reaction texture in which almandine has engulfed and replaced iron staurolite as garnet crystallized along staurolite-quartz interfaces. Elsewhere in that specimen, small amounts of sillimanite have grown, after nucleating preferentially upon biotite. In other thin sections from this outcrop, sillimanite replaces staurolite directly. Development of almandine + sillimanite is limited and highly localized; most contacts between staurolite and quartz show no evidence of reaction (Fig. 2). Figure 3b documents the same reaction in a contrasting texture. In that

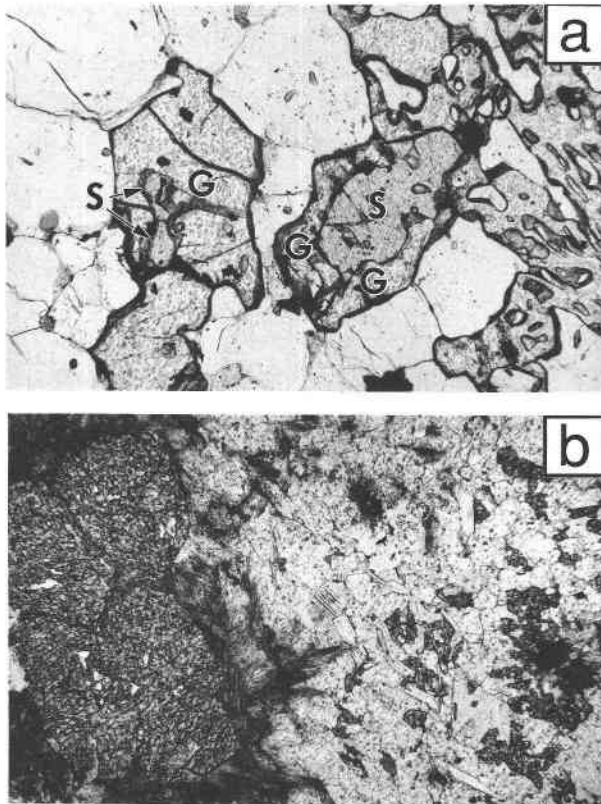


Fig. 3. (a) At right center, a basal section through a formerly euhedral staurolite crystal (S) is engulfed and embayed by almandine garnet (G) at the boundary along which staurolite and quartz were formerly in contact. Garnet crystal at left center (G) encompasses large inclusion of staurolite (S, arrows). Sample WC91c. Photomicrograph in plane-polarized light. Long dimension of field of view is 1.25 mm. (b) Cluster of euhedral garnets with staurolite inclusions (left) is surrounded by selvage of felted sillimanite needles (left center), within a quartz-rich, staurolite-free halo (center). Small crystals of staurolite (right center and right) appear only at greater distances from the almandine + sillimanite cores; these crystals are embayed and have irregular margins, whereas staurolite crystals at still greater distances (beyond this field of view) are subhedral to euhedral. Sample PSg2. Photomicrograph in plane-polarized light. Long dimension of field of view is 4.9 mm.

specimen, euhedral garnet with numerous inclusions of staurolite is surrounded by a felted selvage of sillimanite; both are encompassed within a quartz-rich, staurolite-absent halo. Although two interpretations of these textures are offered below, both alternatives support the hypothesis that the rocks at White Creek underwent moderate- to high-*P* metamorphism during the early dynamothermal event.

**Reaction at high pressures during dynamothermal metamorphism.** One interpretation is that this reaction represents a situation in which peak metamorphic conditions during the early dynamothermal event simply exceeded the high-temperature limit for staurolite + quartz

stability. This explanation is somewhat problematic, however, because the temperature and pressure required for the reaction of staurolite with quartz depends upon the H content of the staurolite, and the White Creek staurolite crystals have high estimated H contents (on average, 3.7 H pfu). The preliminary calculations of Holdaway, Mukhopadhyay, and Dutrow (presented in Holdaway and Mukhopadhyay, 1993b, their Fig. 5) indicate that the reaction between quartz and staurolite with 3.7 H pfu to produce almandine should occur at  $\sim 675^\circ\text{C}$  and 11 kbar, within the kyanite stability field (Fig. 4). Although it is possible that fibrous sillimanite formed metastably in place of kyanite in this incomplete reaction, a stable reaction to produce sillimanite would be expected only for the breakdown of staurolite with a H content of  $\sim 3.3$  H pfu or less. However, the  $1\sigma$  uncertainty in the estimates of H content from electron microprobe data is on the order of  $\pm 0.4$  H pfu (Holdaway et al., 1991, p. 1917), and so the Llano staurolite crystals might in fact contain as little as 3.3 H pfu. Furthermore, additional uncertainty must exist in the calculated locations of the contours of H content. Thus one cannot rule out the possibility that at White Creek, prograde metamorphism in the early dynamothermal event peaked in the vicinity of  $700^\circ\text{C}$  at 7 kbar, triggering the partial reaction of staurolite + quartz to almandine + sillimanite.

Reaction at high temperatures during the early dynamothermal event would be consistent with the occurrence in ultramafic tectonites of the nearby Coal Creek Serpentinite (Garrison, 1981) of a relict metamorphic assemblage of forsteritic olivine + enstatitic orthopyroxene ( $\pm$  anthophyllite, which may, however, have grown in the static event). For the magnesian end-members, this ultramafic assemblage demands minimum temperatures of  $\sim 700^\circ\text{C}$  between 2 and 7 kbar, given unit activities of  $\text{H}_2\text{O}$  (Greenwood, 1963; Day et al., 1985). The small Fe components of olivine ( $\text{Fo}_{94}$ ) and orthopyroxene ( $\text{En}_{93}$ ) in the Coal Creek body would have a negligible effect on the equilibrium conditions (Trommsdorff and Evans, 1972). Reduced activity of  $\text{H}_2\text{O}$  might decrease somewhat this estimate of minimum temperature, but high  $\text{H}_2\text{O}$  activities are indicated by foliated amphibolites that result from thorough hydration during dynamothermal metamorphism of basaltic dikes crosscutting the ultramafic body (cf. Gillis, 1989, p. 16). Peak temperatures between  $670^\circ\text{C}$  and  $750^\circ\text{C}$  for dynamothermal metamorphism in the southeastern uplift are also indicated by the extent of partial homogenization of garnet growth zoning (Schwarze, 1990; Carlson and Schwarze, 1993).

The localized persistence of almandine + sillimanite, despite reequilibration to  $530^\circ\text{C}$  of the Fe-Mg exchange between garnet rims and biotite during the late static metamorphism, must be rationalized under this interpretation as a consequence of the slower kinetics of retrograde net-transfer reactions in comparison with reactions involving only exchange equilibria. Also, if this interpretation is valid, one might expect the formation of sillimanite needles with a preferred orientation (not in un-

oriented felted masses), unless the thermal maximum was reached after deformation had waned—a reasonable possibility.

**Reaction at low pressures during static metamorphism.** A second possible interpretation arises from the likelihood that the high H contents of the White Creek staurolite crystals, ascribed to their origin at high pressures during the early dynamothermal metamorphism, would render them unstable during static metamorphism at  $\sim 2.75$  kbar. Because recrystallization to the stable staurolite composition with lower H content would require reaction to produce the exchange of  $H^+$  for  $Fe^{2+}$ , it is possible that these high-H staurolite crystals might react to a wholly metastable intermediate assemblage of almandine + sillimanite instead of producing low-H staurolite directly.

This interpretation readily explains both the unoriented fabric of the sillimanite and the fact that many of the White Creek almandine crystals are euhedral, in contrast to the highly resorbed, anhedral character of nearly all other almandine-rich garnet found in the uplift (excepting only those occurrences with high spessartine contents). It also accounts easily for the fact that garnet-biotite Fe-Mg exchange thermometry reflects equilibration at conditions matching those found throughout the uplift for the late static metamorphism. However, it requires acceptance of the disconcerting notion that a wholly metastable assemblage was produced in this rock during a metamorphic event that had sufficient duration and intensity nearly to obliterate in most other rocks in the uplift those mineral assemblages reflecting early metamorphism at high pressure. Reaction kinetics that compel production of a metastable intermediate assemblage in preference to a stable lower-H staurolite are difficult to reconcile with an event that has largely rehydrated and recrystallized eclogitic and amphibolitic masses on the scale of several hundred meters and that has completely eliminated early-formed matrix staurolite from the nearby occurrence at Sandy Creek.

### CONCLUSION

Staurolite at White Creek may represent the most Fe-rich occurrence of this mineral known. The occurrence and textural relations of stable nearly pure iron staurolite at White Creek, in conjunction with the evidence at Sandy Creek for initial crystallization and later destruction of iron-magnesium staurolite, imply that the southeastern Llano Uplift experienced a polythermal and polybaric metamorphic history similar to, and possibly identical with, that which has been more rigorously documented for the northern and northwestern parts of the uplift.

### ACKNOWLEDGMENTS

Michael Holdaway and William Lamb provided insightful and helpful formal reviews; in particular, the suggestion that almandine + sillimanite may have formed at low pressure as metastable products of the breakdown of high-H staurolite originated with Holdaway's review. We are

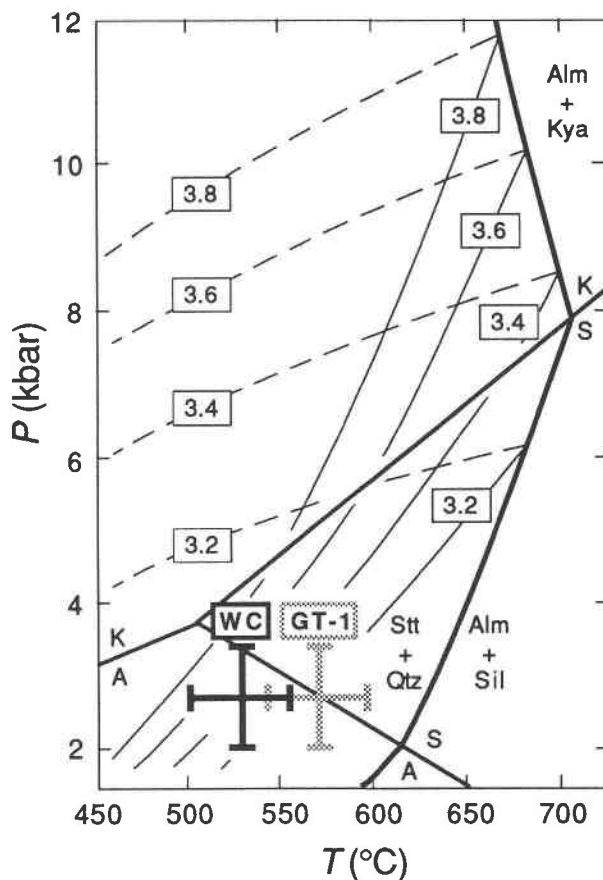


Fig. 4. Comparison between inferred conditions for static reequilibration in the southeastern Llano Uplift and  $P$ - $T$  limits of staurolite stability in the presence of quartz. Stability field for iron staurolite + quartz is that calculated by Holdaway, Mukhopadhyay, and Dutrow (Fig. 5 of Holdaway and Mukhopadhyay, 1993b) and is contoured in terms of the H content of staurolite. Numbers in boxes label contours of H atoms pfu, corresponding to iron staurolite in equilibrium with almandine (dashed contours) and with aluminum silicate (solid contours). The limit of staurolite + quartz stability is given by the locus of intersections of the contours, and is shown here by the bold curves. Stability relations for aluminum silicates are from Holdaway and Mukhopadhyay (1993a). A = andalusite, K and Kya = kyanite, S and Sil = sillimanite, Stt = staurolite, Alm = almandine, and Qtz = quartz.

Darker cross locates conditions of final reequilibration for White Creek crystals (WC) at  $530 \pm 30$  °C and  $2.75 \pm 0.75$  kbar. Lighter cross locates nearly equivalent conditions of final reequilibration for the Sandy Creek crystal (GT-1) at  $570 \pm 30$  °C and  $2.75 \pm 0.75$  kbar. The low-pressure limit of stability of iron staurolite is not shown because of the uncertainty in its precise location, but it is likely to be just below 2 kbar for  $T$  near 550 °C. Because staurolite inclusions in garnet in GT-1 contain appreciable Mg, the low-pressure limit of stability for staurolite at Sandy Creek lies at significantly higher pressures than the limit for the staurolite at White Creek, which is close in composition to the Fe end-member.

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#### REFERENCES CITED

- Albee, A.L., and Ray, L. (1970) Correction factors for electron probe microanalysis of silicates, oxides, carbonates, phosphates, and sulfates. *Analytical Chemistry*, 42, 1408-1414.
- Bardossy, G., Mesko, L., Panto, G., and Sajgo, C. (1970) Le métamorphisme de contact de la bauxite de Bédarioux et quelques aspects généraux du métamorphisme des bauxites (Contact metamorphism of the Bédarioux bauxite and some general aspects of bauxite metamorphism) (in French). *Bulletin de Société Géologique de France*, 12, 856-869.
- Bebout, G.E., and Carlson, W.D. (1986) Fluid evolution and transport during metamorphism: Evidence from the Llano Uplift, Texas. *Contributions to Mineralogy and Petrology*, 92, 518-529.
- Berman, R.G. (1990) Mixing properties of Ca-Mg-Fe-Mn garnets. *American Mineralogist*, 75, 328-344.
- Bohlen, S.R., Montana, A., and Kerrick, D.M. (1991) Precise determinations of the equilibria kyanite = sillimanite and kyanite = andalusite and a revised triple point for  $Al_2SiO_5$  polymorphs. *American Mineralogist*, 76, 677-680.
- Carlson, W.D. (1992) Polymetamorphism in the Llano Uplift. *Geological Society of America Abstracts with Programs*, South-Central Section, 24, 6.
- Carlson, W.D., and Johnson, C.D. (1991) Coronal reaction textures in garnet amphibolites of the Llano Uplift. *American Mineralogist*, 76, 756-772.
- Carlson, W.D., and Nelis, M.K. (1986) An occurrence of staurolite in the Llano Uplift, central Texas. *American Mineralogist*, 71, 682-685.
- Carlson, W.D., and Schwarze, E.T. (1993) Petrologic and tectonic significance of geographic variations in garnet growth zoning in the Llano Uplift. *Geological Society of America Abstracts with Programs*, 25, 101-102.
- Day, H.W., Chernosky, J.V., and Kumin, H.J. (1985) Equilibria in the system  $MgO-SiO_2-H_2O$ : A thermodynamic analysis. *American Mineralogist*, 70, 237-248.
- Ferry, J.M., and Spear, F.S. (1978) Experimental calibration of the partitioning of Fe and Mg between biotite and garnet. *Contributions to Mineralogy and Petrology*, 66, 113-117.
- Garrison, J.R., Jr. (1981) Coal Creek serpentinite, Llano Uplift, Texas: A fragment of an incomplete Precambrian ophiolite. *Geology*, 9, 225-230.
- Gillis, G.M. (1989) Polyphase deformation and metamorphism of the Middle Proterozoic Coal Creek Serpentinite, Gillespie County, Texas, 103 p. Master's thesis, University of Texas, Austin, Texas.
- Greenwood, H.J. (1963) The synthesis and stability of anthophyllite. *Journal of Petrology*, 4, 317-351.
- Hemingway, B.S., and Robie, R.A. (1984) Heat capacity and thermodynamic functions for gehlenite and staurolite: With comments on the Schottky anomaly in the heat capacity of staurolite. *American Mineralogist*, 69, 307-318.
- Holdaway, M.J., and Mukhopadhyay, B. (1993a) A reevaluation of the stability relations of andalusite: Thermochemical data and phase diagram for the aluminum silicates. *American Mineralogist*, 78, 298-315.
- (1993b) Geothermobarometry in pelitic schists: A rapidly evolving field. *American Mineralogist*, 78, 681-693.
- Holdaway, M.J., Mukhopadhyay, B., Dyar, M.D., Dutrow, B.L., and Rumble, D., III (1991) A new perspective on staurolite crystal chemistry: Use of stoichiometric and chemical end-members for a mole-fraction model. *American Mineralogist*, 76, 1910-1919.
- Letargo, C.M.R., and Lamb, W.M. (1991) Granite emplacement pressures and metamorphism in the Llano Uplift of central Texas. *Geological Society of America Abstracts with Programs*, 23, 446.
- (1992) Comparative thermometry on pelitic rocks and marbles of the Llano Uplift, Texas. *Geological Society of America Abstracts with Programs*, 24, 219.
- (1993) *P-T-X* conditions of calc-silicate formation: Evidence from fluid inclusions and phase equilibria, Llano Uplift, central Texas, USA. *Journal of Metamorphic Geology*, 11, 89-100.
- Nelis, M.K., Mosher, S., and Carlson, W.D. (1989) Grenville-age orogeny in the Llano Uplift of central Texas: Deformation and metamorphism of the Rough Ridge Formation. *Geological Society of America Bulletin*, 101, 876-883.
- Richardson, S.W. (1968) Staurolite stability in a part of the system Fe-Al-Si-O-H. *Journal of Petrology*, 9, 467-488.
- Schreyer, W., and Chinner, G.A. (1966) Staurolite-quartzite bands in kyanite quartzite at Big Rock, Rio Arriba County, New Mexico. *Contributions to Mineralogy and Petrology*, 12, 223-244.
- Schwarze, E.T. (1990) Polymetamorphism in the Llano Uplift: Evidence from geothermobarometry and compositional zoning in garnet, 275 p. Master's thesis, University of Texas, Austin, Texas.
- Trommsdorff, V., and Evans, B.W. (1972) Progressive metamorphism of antigorite schist in the Bergell tonalite aureole (Italy). *American Journal of Science*, 272, 423-437.
- Wilkerson, A., Carlson, W.D., and Smith, D. (1988) High-pressure metamorphism during the Llano orogeny inferred from Proterozoic eclogite remnants. *Geology*, 16, 391-394.
- Zen, E-an (1981) Metamorphic mineral assemblages of slightly calcic pelitic rocks in and around the Taconic allochthon, southwestern Massachusetts and adjacent Connecticut and New York. U.S. Geological Survey Professional Paper, 1113, 128 p.

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