

Comparison of calcite + dolomite thermometry and carbonate + silicate equilibria: Constraints on the conditions of metamorphism of the Llano uplift, central Texas, U.S.A.

CHERITH M. R. LETARGO, WILLIAM M. LAMB*

Department of Geology and Geophysics, Texas A & M University, College Station, Texas 77843, U.S.A.

JONG-SIM PARK**

Department of Geology and Geophysics, University of Wisconsin-Madison, Madison, Wisconsin 53706, U.S.A.

ABSTRACT

Temperatures based on the composition of calcite coexisting with dolomite (calcite + dolomite thermometry) range from 475 to 600 °C for 63 marbles from the Llano uplift of central Texas. The highest temperatures, ~600 °C, were obtained by carefully reintegrating calcite containing exsolved lamellae of dolomite. In some cases, these high temperatures were determined for marbles that contain an isobarically invariant assemblage consisting of calcite + dolomite + tremolite + diopside + forsterite. At a pressure of 3 kbar, these five minerals are stable at 630 °C and $X_{\text{CO}_2} = 0.62$. In contrast, relatively low calcite + dolomite temperatures of 475–480 °C were obtained for marbles containing the assemblage calcite + dolomite + tremolite + talc. This talc-bearing assemblage is stable at ≤ 475 °C, depending on fluid composition, at a pressure of 3 kbar. Additional isobarically univariant equilibria are stable at intermediate temperatures (generally between 535 and 630 °C), and these are also generally consistent with results obtained from calcite + dolomite thermometry. Agreement between the calcite + dolomite temperatures and those inferred from silicate + carbonate equilibria in the marbles indicates that the temperatures generally reflect peak conditions of metamorphism, although some resetting has occurred. The marbles having the highest calcite-dolomite temperatures, as well as those containing the high-temperature isobarically invariant assemblage, are generally found close to post-tectonic pluton contacts, indicating that some of the amphibolite-facies assemblages are related to the emplacement of the granitic intrusions. Relatively low temperatures are recorded within approximately 2 km of pluton contacts, suggesting a possible thermal aureole. However, relatively high temperatures of 550–600 °C are recorded in marbles that are not spatially related to post-tectonic granites (>2 km from pluton contacts). These temperatures may be relicts of an earlier metamorphic event, although they could be related to granites that were emplaced above or below the current erosional level.

INTRODUCTION

The determination of peak metamorphic pressure and temperature (*P-T*) conditions is important in deciphering the thermal and tectonic evolution of metamorphic terranes. A variety of geothermometers and geobarometers have been applied to constrain peak metamorphic *P-T* conditions in a number of areas (for reviews, see Essene, 1986; Spear, 1989). However, geothermometry may be rendered inaccurate by (1) a lack of experimental calibration of end-member reactions, (2) a lack of measured activity-composition relations for minerals that exhibit solid solution, and (3) reequilibration during retrograde metamorphism. If well-calibrated geothermometers are available, then problems associated with resetting can be evaluated by comparing geothermometers.

One geothermometer of particular interest to petrologists investigating metamorphic terranes that contain marbles and calc-silicates is the calcite-dolomite solvus, whose potential in providing temperature constraints was introduced by Harker and Tuttle (1955) and Graf and Goldsmith (1955). Equilibrium temperatures can be estimated from compositions of coexisting calcite + dolomite by determining the MgCO_3 content in calcite, which is fixed as a function of temperature on the calcite-dolomite miscibility gap or solvus. The calcite + dolomite thermometer has been characterized both experimentally and empirically by Goldsmith and Newton (1969), Bickle and Powell (1977), Powell et al. (1984), and Anovitz and Essene (1987). These formulations have been used to constrain metamorphic temperatures in regionally metamorphosed greenschist, amphibolite, and granulite facies terranes (e.g., Puhan, 1976; Garde, 1977; Perkins et al., 1982), as well as in contact metamorphic zones (Tracy

* To whom reprint requests should be addressed.

** Present address: 1700 Murfin Avenue, Apartment 32, Ann Arbor, Michigan 48105, U.S.A.

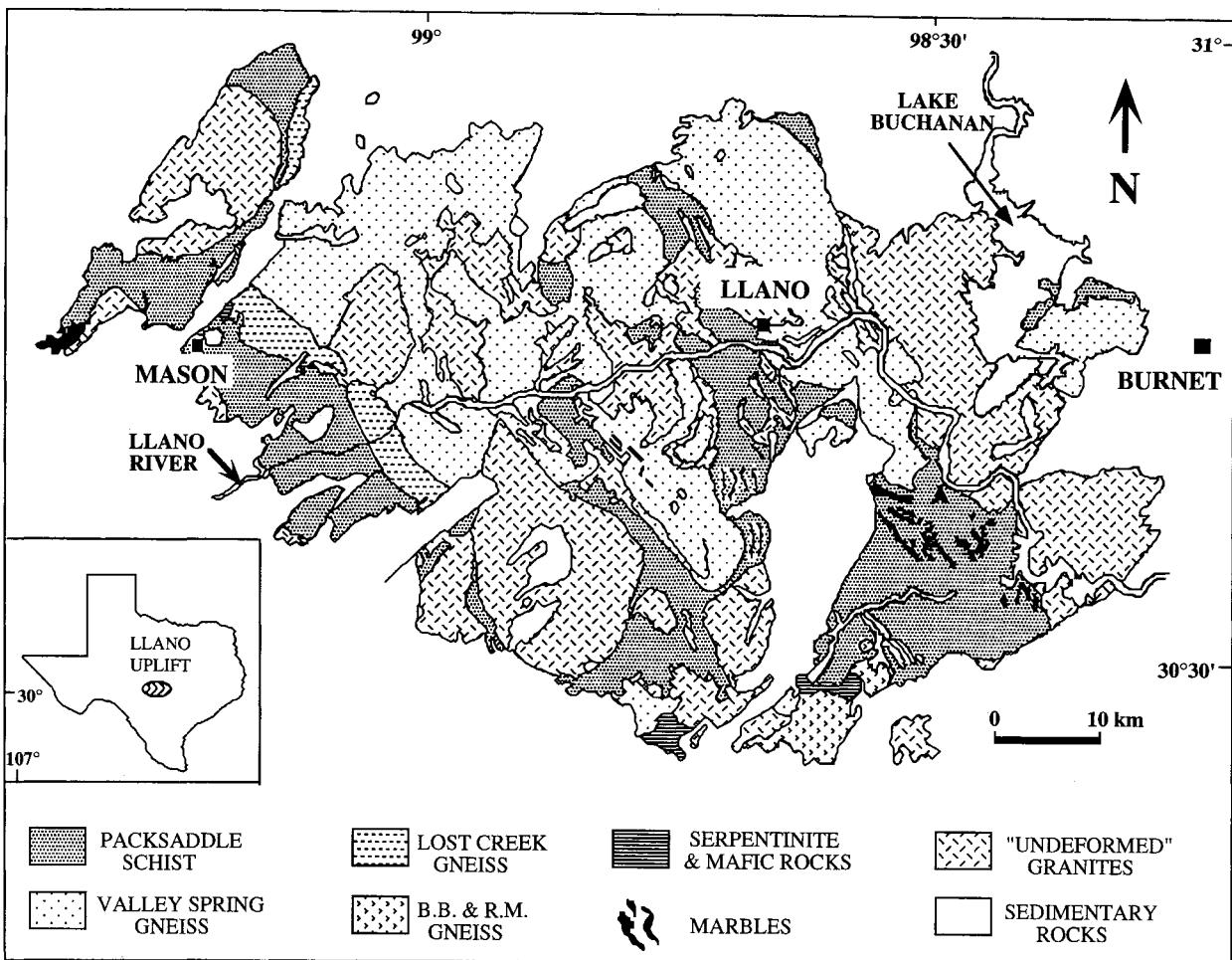


Fig. 1. Geologic map of the Llano uplift showing the metamorphic units and the relatively undeformed granite intrusives (after Barnes, 1981). Marbles are generally present as intercalated beds in Packsaddle schist and Valley Spring gneiss. In the legend, B.B. and R.M. refer to Big Branch and Red Mountain.

and Frost, 1991). Although the calcite + dolomite thermometer is precisely calibrated, this method is still generally viewed with caution because of possible resetting or reequilibration of temperatures upon cooling (Moore and Kerrick, 1976; Rice, 1977; Perkins et al., 1982).

This study applies calcite + dolomite thermometry across the Llano uplift of central Texas and compares the resulting temperatures with those inferred from silicate + carbonate equilibria. Careful reintroduction techniques were applied in an effort to determine peak metamorphic and not reequilibrated calcite compositions. The results of this study provide additional insights into the timing of the development of the amphibolite-facies assemblages that are predominant throughout much of the uplift and also provide information concerning the evolution of this segment of Grenville-aged crust in central Texas.

GEOLOGIC SETTING

The Llano uplift is composed primarily of meta-igneous and metasedimentary rocks that are intruded by rel-

atively undeformed granitic plutons (Fig. 1). The metamorphic units have been subdivided into the following formations: (1) Packsaddle schist, (2) Big Branch and Red Mountain gneiss, (3) Valley Spring gneiss, (4) Lost Creek gneiss, and (5) Coal Creek serpentinite (Paige, 1912; Mutis-Duprat, 1972; Garrison, 1979; Barnes, 1981). However, units within these formations differ in protolith age (Walker, 1992; Reese et al., 1992), and so these formation names may be useful only as guides to rock type.

The marbles examined in this study occur as intercalated beds within the Packsaddle schist and the Valley Spring gneiss. The Packsaddle group is composed primarily of hornblende, mica, and graphite schists, whereas the Valley Spring gneiss consists predominantly of quartz + feldspar gneiss, some calc-silicate rocks, and amphibolites. These metamorphic units are intruded by relatively undeformed granite plutons (Fig. 1). All these granites are shown as one unit in Figure 1, although some workers have proposed that these rocks may be subdivided into two or more mappable units. For example, Barnes (1981) classified the larger and more circular plutons as Town Mountain gran-

ite, whereas the less extensive and more irregularly shaped plutons with finer grained textures are grouped together as younger granite. Existing isotopic data (Zartman, 1965; Garrison et al., 1979) do not distinguish between the ages of the two granites, and although field evidence suggests that some of the younger granites may have been intruded later than the Town Mountain variety (Barnes, 1981), the ages of the various intrusions may overlap.

Metamorphism in the Llano region was originally perceived as a single dynamothermal event that occurred during the Grenville orogeny and produced amphibolite-facies rocks (Zartman, 1965; Muehlberger et al., 1967; Droddy, 1978; McGehee, 1979). Recent U-Pb geochronology has revealed a more complex history. U-Pb ages of 1215–1355 Ma, obtained for zircons collected from highly deformed metamorphic units, apparently reflect early igneous crystallization ages (Reese et al., 1992). A second set of younger ages, ranging from 1070 to 1116 Ma, was obtained from the post-tectonic granite plutons (Walker, 1992). These results suggest that deformation occurred between the two igneous events (1215 and 1116 Ma).

The deformation that predates the emplacement of the granitic intrusives was accompanied by an early metamorphic episode. Metamorphism also accompanied the emplacement of the granite plutons, although this does not require two orogenic events, since it is possible that the granites were intruded during the waning stages of a single tectonic cycle. There are a few isolated examples of granulite-facies (and possibly eclogite-facies) mineral assemblages that may be remnants of an early metamorphic episode (Wilkerson et al., 1988; Carlson and Johnson, 1991). *P-T* estimates for the earlier metamorphism, as inferred from garnet + pyroxene rocks from the western and northern part of the uplift, are approximately 6–11 kbar and 670–750 °C. Temperature estimates for the amphibolite-facies metamorphism are highly variable, ranging from 475 to 710 °C (Workman, 1968; Kohl, 1976; Droddy, 1978; Garrison, 1979; McGehee, 1979), although more recent work has refined these estimates by differentiating between those assemblages that may be relict higher *P-T* assemblages and those that may have formed later under more moderate conditions (Bebout and Carlson, 1986; Carlson and Nelis, 1986; Letargo and Lamb, 1993). Pressures of the amphibolite-facies metamorphism in the Llano uplift have been constrained in various locations. The presence of andalusite, which co-exists with sillimanite in some areas, constrains pressures to <4.2 kbar (Bohlen et al., 1991). Other geobarometry yields pressures of approximately 2.5–3.5 kbar for rocks from the southeastern part of the uplift (Carlson and Nelis, 1986; Schwarze, 1990; Letargo and Lamb, 1992). Furthermore, pressures of 1–2 kbar have been determined for calc-silicates whose development is related to the intrusion of some post-tectonic granites in the central part of the uplift (Letargo and Lamb, 1993). Thus, pressures of amphibolite-facies metamorphism range from ≈1 to 4 kbar, with most estimates falling in the 2–3 kbar range.

It has been argued that the amphibolite-facies assem-

blages that predominate throughout the region were stabilized during the intrusion of the granites and that this metamorphic episode was largely static (Garrison et al., 1979; Wilkerson et al., 1988; Carlson and Johnson, 1991). However, any metamorphic episode that occurred earlier than approximately 1116 Ma may not have achieved granulite-facies pressure and temperature conditions in all parts of the Llano uplift, as these high temperatures are inferred for a few scattered localities in the northern and western portions of the terrane. Thus, some amphibolite-facies mineral assemblages might be related to an early metamorphic episode that occurred prior to the intrusion of the post-tectonic granites.

MINERAL ASSEMBLAGES OF THE LLANO MARBLES

Marbles from the Llano uplift contain calcite, dolomite, and one or more of the following silicate minerals: talc, amphibole, diopside, forsterite, clinochlore, spinel, and phlogopite (Table 1). Plagioclase, potassium feldspar, graphite, magnetite, and pyrite are also present in some samples. Talc generally occurs as subhedral flakes with lengths reaching 1 mm. Most of the amphiboles analyzed are essentially tremolite, except for three samples that contain a significant tchermakitic or pargasitic component (Table 2; see also Letargo, 1993).¹ For the sake of brevity, the amphiboles are referred to here as tremolite. Tremolite is the most abundant silicate phase in most of the Llano marbles, and it generally occurs as fine to coarse fibers. These fibers may be randomly oriented, although in some samples they exhibit a preferred orientation. In some cases, tremolite may be a late phase, as evinced by fine tremolite aggregates that form rims around diopside. Diopside and forsterite are present as subhedral to anhedral grains, although in some marbles these minerals are seen as relict islands because of extensive alteration to serpentine.

ANALYTICAL PROCEDURES

Compositions of the minerals in the marbles were obtained by wavelength-dispersive spectrometry using an ARL-SEMQ electron microprobe analyzer at the University of Wisconsin-Madison and a CAMECA SX-50 at Texas A & M University. The analytical conditions employed on the ARL-SEMQ microprobe were (1) sample currents of 6 nA for carbonates, 18 nA for silicates, and 10 nA for F, (2) count times of 40 s for F and 25 s for all other elements, and (3) beam diameters of 30 µm for carbonates, 5 µm for silicates, and 10 µm for F. The analytical conditions employed on the CAMECA SX-50 were (1) a beam current of 10 nA, (2) count times of 10 s for carbonates that were reintegrated (see below), 30 s for silicates and spinels, and 40 s for F, and (3) beam diameters of 20–30 µm for carbonates and 15 µm for silicates. In every case, an accelerating potential of 15 kV

¹ For a copy of Tables 2–7, order Document AM-95-574 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 1. Minerals in Llano marbles

Sample	Cal	Dol	Qtz	Tlc	Tr	Fo	Di	Phl	Cln	Srp	Other	T_1 (°C)	T_2 (°C)
81-LL-3*	X'	X'			X							550	
81-LL-11	X'	X'			X'		X'					560	555–630
81-LL-12	X'	X'			X'	X'	X'	X	X	O	Gr	550	≈630
81-LL-14	X'	X'			X'	X'	X'	X	X	O	Spl, Ap	600	630
81-LL-19	X'	X'	X		X				X	O	Pl, Kfs	530	530
81-LL-37*	X'	X'			X				X			500	
81-LL-38*	X'	X'			X'	X'			X			500	
81-LL-39*	X'	X'			X		X		X	O	Mag, Spl	570	≈630
83-LL-1*	X'	X'			X				X			510	
83-LL-3*	X'	X'			X				X			560	
83-LL-5*	X'	X'			X				X			550	
83-LL-6*	X'	X'			X				X		Pl	560	
83-LL-17	X		X		X'		X'	X'	X				
83-LL-41*	X'	X'			X			X			Gr	510	
83-LL-43*	X'	X'			X							510	
83-LL-50*	X'	X'					X				Mag	570	
83-LL-51*	X'	X'					X					570	
83-LL-74*	X'	X'			X	X'			X		Spl	560	630
83-LL-75*	X'	X'				X					Spl, Rt	540	
83-LL-110*	X'	X'				X						560	
83-LL-111*	X'	X'							X		Mag	600	
83-LL-117*	X'	X'			X				X			500	
83-LL-126*	X'	X'			X							540	
83-LL-130*	X'	X'			X				X		Gr	540	
83-LL-131*	X'	X'			X	X						550	
83-LL-139	X'		X	X'	X'				X'				<480
83-LL-142*	X'	X'			X'	X'						580	
83-LL-143*	X'	X'			X'	X'	X'	X	X	O		600	630
83-LL-145*	X'	X'										560	
83-LL-147*	X'	X'			X				X		Gr	520	
83-LL-158*	X'	X'							X			520	
83-LL-192	X'	X'			X'	X'	X'					580	630
83-LL-193	X'	X'			X	X						550	
83-LL-198*	X'	X'			X				X			560	
83-LL-236	X'	X'			X'	X'	X'				O	510	630
83-LL-237	X'	X'			X'	X'	X'	X				530	555–630
83-LL-239*	X'	X'				X						530	
83-LL-259	X'	X'			X'		X'	X'				590	555–630
83-LL-312*	X'	X'			X'	X	X'		X			580	630
83-LL-512	X'	X'			X							550	
83-LL-514	X'	X'			X'	X'			X			520	
83-LL-516*	X'	X'			X				X			560	
83-LL-524*	X'	X'				X			X			520	
83-LL-557*	X'	X'							X			580	
83-LL-558*	X'	X'			X				X		Gr	530	
83-LL-564*	X'	X'			X						Gr	530	
83-LL-567*	X'	X'			X				X		Gr	530	
83-LL-570*	X'	X'							X			500	
88-CM-1a	X'	X'			X'			X'				520	
88-CM-2a	X'		X	X'	X'			X'			Ttn		
88-CM-4c	X'	X'		X'	X'			X'				480	<480
89-DM-1	X				X'			X	X'		Ttn		
89-LS-2	X'	X'			X	X'	X'		X	O	Gr	600	630
90-DM-11	X'	X'		X'	X'			X'				480	<480
90-DM-12	X'	X'		X'	X			X	X'		Ap	480	<480
90-DM-27	X'	X'		X'	X'	X'	X'	X'			Py, Ap	600	630
91-DM-19	X'	X'			X'	X'	X'	X		O		510	
91-DM-57	X					X'			X		Pl, Py, Ttn		
91-KL-2	X'	X'			X'	X'		X'	X	O	Spl, Gr	580	630
91-KL-3	X'	X'			X'			X'	X	O	Spl, Rt	590	
91-LS-5	X'	X'			X'		X'	X	X		Gr	580	≈630
91-LS-7	X'	X'				X		X	X	O	Gr	600	
92-CL-4	X'	X'			X						Py	560	
92-GR-5	X		X	X'		X'					Kfs		
92-LG-5	X'	X'			X'	X'	X'	X'				550	630
92-LG-8	X'	X'			X'	X'	X'	X		O		560	630
92-LN-9	X'	X'			X	X		X			Gr	550	
92-LN-15	X'	X'				X						550	
92-OX-16	X'	X'			X	X				O		550	

Note: abbreviations: Ap = apatite; Cal = calcite; Di = diopside; Dol = dolomite; Fo = forsterite; Gr = graphite; Kfs = potassium feldspar; Mag = magnetite; Phl = phlogopite; Pl = plagioclase; Py = pyrite; Qtz = quartz; Rt = rutile; Spl = spinel; Srp = serpentine; Tlc = talc; Tr = tremolite; Ttn = titanite (Kretz, 1983); Cln = clinochlore; X = mineral present; X' = with probe analysis; O = secondary mineral. For sample locations, refer to Park (1986) and Letargo (1993). T_1 (°C): from calcite-dolomite geothermometry. T_2 (°C): from carbonate-silicate equilibria.

* Data from Park (1986).

was used for all elements except for F, which was analyzed at 10 kV to avoid volatilization. Data from the ARL-SEMQ were corrected and reduced through the Bence and Albee method (Albee and Ray, 1970), whereas those from the CAMECA SX-50 were corrected using the PAP $\phi(\rho, Z)$ procedure (e.g., Pouchou and Pichoir, 1985). The accuracy of the analyses is better than $\pm 1\%$ of the amount present for the major elements and $\pm 10\%$ for minor elements (<1 wt%).

Mineral analyses were normalized on a cation basis (Tables 2–7).¹ Forsterite formulae were normalized to three cations, diopside to four, tremolite to 13 cations (M1, M2, M3 and T sites, assuming that vacancies are on the A site only), talc to seven cations, and chlorite to ten cations. For diopside, Fe^{3+} was calculated from charge-balance considerations using $\text{Fe}^{3+} = {}^{[4]}\text{Al} - {}^{[6]}\text{Al} - 2\text{Ti} + \text{Na}$; for tremolite, $\text{Fe}^{3+} = {}^{[4]}\text{Al} - {}^{[6]}\text{Al} + {}^{[6]}\text{Na} - {}^{[14]}\text{Na} - {}^{[14]}\text{K} - 2\text{Ti}$; for talc and chlorite, $\text{Fe}^{3+} = {}^{[4]}\text{Al} - {}^{[6]}\text{Al} - 2\text{Ti} + \text{K} + \text{Na}$. The carbonates were normalized to two cations. All minerals were examined for the presence of unanalyzed elements using energy-dispersive analysis with counting times of 500–1000 s.

Reintegrating the compositions of exsolved dolomite lamellae in calcite to yield pre-exsolution calcite compositions was achieved by two methods. Generally, calcite grains having a homogeneous distribution of dolomite lamellae were chosen for analysis (Fig. 2). The first method of reintegration involved microprobe traverses that covered approximately 85–90% of the surface of the grain using a broad-beam diameter (~ 20 – $30\ \mu\text{m}$). Depending on the size of the grain, the total number of points analyzed varied from 50 to 1000 points. The broad-beam technique of reintegration was used mainly for calcites with very fine dolomite lamellae (i.e., < $10\ \mu\text{m}$). For calcites with coarser blebs of dolomite (i.e., $10\ \mu\text{m}$ or greater), the compositions of both calcite host and exsolved dolomite were determined through microprobe analysis. In this case, analyses were taken from various parts of the calcite host and from different dolomite blebs to ensure that a representative average composition was obtained. In addition, the total area covered by the calcite host and dolomite lamellae were determined by converting a backscatter image into a digital image that allowed the area of each phase to be calculated. Assuming constant thickness in the third dimension, the area of each unit is recalculated as volume percent. The pre-exsolved calcite composition is obtained by recasting the volume percent into weight fraction using the average host and lamellae analyses, as well as the equations employed by Bohlen and Essene (1977).

CALCITE + DOLOMITE THERMOMETRY

Three types of textures were observed for the calcite and dolomite in the marbles of the Llano uplift: (1) fine- to medium-grained granoblastic calcites and dolomites exhibiting 120° triple-point junctions (Fig. 2a); (2) very fine (< $10\ \mu\text{m}$) optically continuous dolomite exsolution lamellae in calcite; and (3) coarse (> $10\ \mu\text{m}$) and optically



Fig. 2. (a) Photomicrograph of coexisting calcite (Cal) and dolomite (Dol) with well-developed 120° triple-point junctions classified as textural type 1. (b) Photomicrograph of a calcite grain (in extinct position) containing a homogeneous distribution of exsolved dolomite. This is classified as textural type 3 (see text). Scale bar = 0.10 mm.

distinct dolomite exsolution blebs in calcite (Fig. 2b). In some samples, dolomite occurs as anhedral masses along calcite grain boundaries and may reflect a coarse exsolution bleb that has diffused out of the calcite host. Calcites having textures classified under type 2 were reintegrated using the broad-beam technique, whereas those belonging to type 3 were reintegrated by calculating the relative volume of each phase. The compositions of the homogeneous calcites belonging to type 1 were obtained by averaging microprobe analyses taken from various parts of the grain. The calcites and dolomites generally contain only small amounts of MnO and FeO (i.e., <2 wt%). The MgO contents in the calcites range from 1.5 to 3.0 wt% (Table 3).

Calcite + dolomite thermometry was applied using the formulation of Anovitz and Essene (1987). This calibration accounts for Fe in the system, although for the carbonates analyzed, Fe-correction is minimal, since this component (along with Mn) is present in very small amounts (Tables 3 and 4). Temperature estimates were

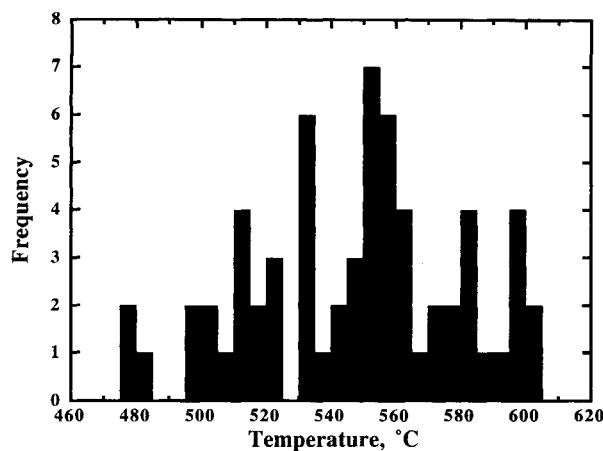


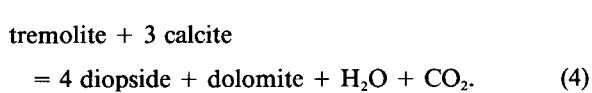
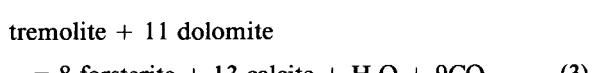
Fig. 3. Frequency distribution diagram of temperatures inferred from the composition of calcite coexisting with dolomite in 63 samples. These temperatures range from 475 to 600 °C.

obtained from 63 marbles collected from various parts of the uplift, although the majority of these estimates are from the eastern part of the terrane. The temperatures range from 475 to 600 °C (Table 1, Fig. 3). Calcites having the coarsest exsolution lamellae generally yielded the highest temperatures (575–600 °C).

SILICATE + CARBONATE EQUILIBRIA

Various mineral assemblages found within the marbles from the Llano uplift restrict the temperature and fluid composition at a given pressure. For the following discussion of silicate + carbonate equilibria, 3 kbar is employed (see previous discussion). In general, a pressure difference of ± 1 kbar will introduce uncertainties of only ± 30 °C in our temperature estimates and therefore have little effect on our conclusions.

Nine samples (81-LL-14, 83-LL-143, 83-LL-192, 83-LL-236, 83-LL-312, 89-LS-2, 90-DM-27, 92-LG-5, and 92-LG-8) contain a relatively high-temperature assemblage consisting of calcite + dolomite + tremolite + diopside + forsterite (Table 1). In the CaO-MgO-SiO₂-H₂O-CO₂ system, these minerals constitute an isobarically invariant assemblage that is defined by the following equilibria:



This isobarically invariant assemblage is located at $X_{\text{CO}_2} = 0.62$ at a temperature of 630 °C for $P = 3$ kbar (Point

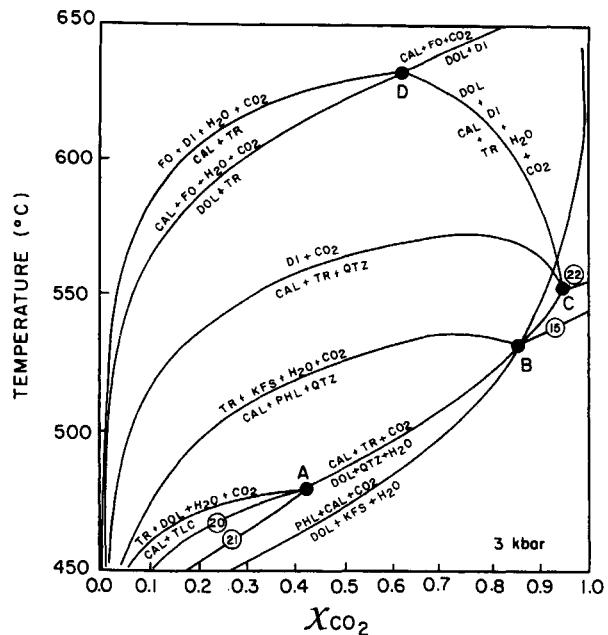


Fig. 4. T - X diagram at 3 kbar for the system K₂O-CaO-MgO-Al₂O₃-SiO₂-H₂O-CO₂. The stability of the phases were calculated using the internally consistent thermodynamic data of Berman (1988) and Ge0-Calc (Brown et al., 1988). For key to abbreviations, see Table 1. Invariant point A = calcite + dolomite + quartz + talc + tremolite; B = calcite + dolomite + quartz + tremolite + potassium feldspar + phlogopite; C = calcite + dolomite + quartz + tremolite + diopside; D = calcite + dolomite + tremolite + diopside + forsterite. Equilibrium 22 corresponds to dolomite + 2 quartz = diopside + 2 CO₂. Equilibria 15, 20, and 21 correspond to Equations 15, 20, and 21 in the text.

D, Fig. 4), calculated using the thermodynamic data base of Berman (1988) and the program Ge0-Calc (Brown et al., 1988). This position is ~ 50 °C higher than an alternate location suggested by Eggert and Kerrick (1981) from experimental results of G. K. Jacobs. However, the location of point D in T - X space for 3 kbar is in good agreement with that determined using the experimental reversals of Metz (1967, 1976), Slaughter et al. (1975), and Kase and Metz (1980), in conjunction with the computer program Thermo (Perkins et al., 1987).

Determination of T - X conditions based on the isobarically invariant assemblage produced by the intersection of Equilibria 1–4 requires an assessment of the effect of any solid solution in the minerals in the nine samples mentioned. Microprobe analyses have shown that most of the minerals in the isobarically invariant assemblage are nearly pure end-members (Tables 2–7). The sample containing minerals whose compositions deviate greatly from ideality is 92-LG-8. For this sample, activities of 0.96, 0.99, and 0.34 were calculated for forsterite, diopside, and tremolite, respectively, using ideal ionic mixing models (Kerrick and Darken, 1975; see also Wood and

Fraser, 1976). The activities determined for these phases were used in the following relation:

$$\Delta G = -RT \ln K_{eq} \quad (5)$$

where

$$K_{eq1} = \frac{a_{Di}^{11} a_{Fo}^2 a_{H_2O}^3 a_{CO_2}^5}{a_{Tr}^3 a_{Cal}^5} \quad (6)$$

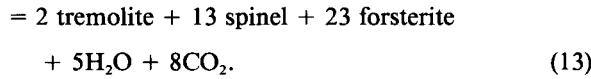
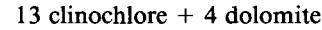
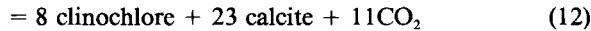
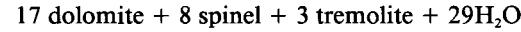
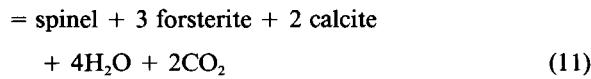
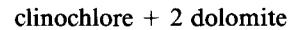
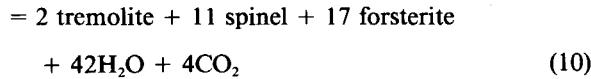
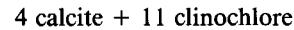
$$K_{eq2} = \frac{a_{Fo}^2 a_{Cal}^4 a_{CO_2}^2}{a_{Dol}^3 a_{Di}} \quad (7)$$

$$K_{eq3} = \frac{a_{Fo}^8 a_{Cal}^{13} a_{H_2O} a_{CO_2}}{a_{Tr} a_{Dol}^{11}} \quad (8)$$

$$K_{eq4} = \frac{a_{Di}^4 a_{Dol} a_{H_2O} a_{CO_2}}{a_{Tr} a_{Cal}^3} \quad (9)$$

to determine the change in Gibbs free energy due to solid solution starting from the end-member equilibria of Equations 1–4. In the most extreme case, the position of the isobarically invariant assemblage is shifted to the relatively higher temperatures of 650 °C and more CO₂-rich conditions ($X_{CO_2} = 0.88$) at $P = 3$ kbar.

Another relatively high-temperature assemblage that provides constraints on peak temperatures attained by some Llano marbles consists of calcite + dolomite + tremolite + forsterite + spinel + clinochlore. Samples 81-LL-14, 83-LL-74, and 91-KL-2 contain these minerals (Table 1). In the system CaO-Al₂O₃-MgO-SiO₂-H₂O-CO₂, this assemblage represents the isobarically invariant intersection of Equation 3 and the following equilibria:



The position of this isobarically invariant assemblage is constrained at $X_{CO_2} = 0.60$ at $T = 630$ °C for $P = 3$ kbar (point A, Fig. 5). Adjusting for the effects of solid solutions in tremolite, forsterite, spinel, and clinochlore in sample 81-LL-14 shifts the position of the isobarically invariant assemblage close to relatively more CO₂-rich conditions ($X_{CO_2} = 0.69$) at $T \approx 640$ °C for 3 kbar.

The phase relations depicted on Figures 4 and 5 indicate that the assemblage diopside + tremolite + clinochlore + calcite + dolomite also requires temperatures

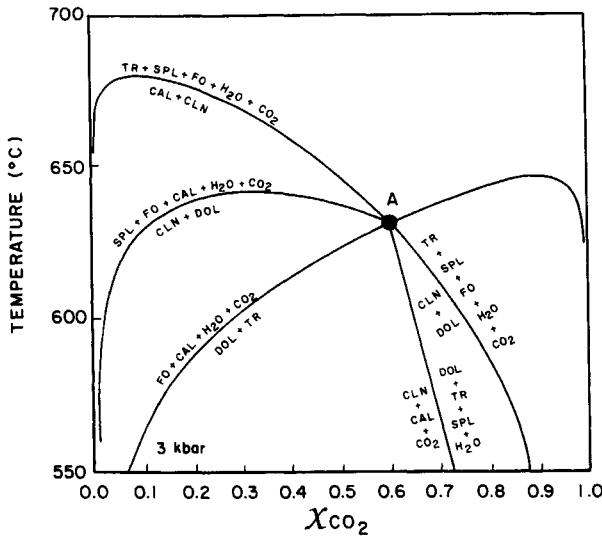
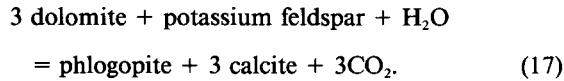
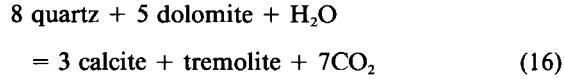
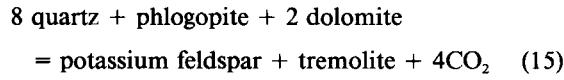
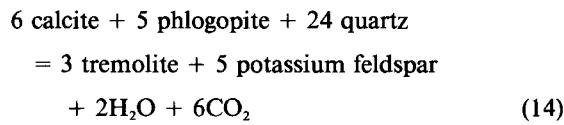


Fig. 5. *T-X* diagram at 3 kbar showing the stability of the isobarically invariant assemblage: calcite + dolomite + tremolite + forsterite + spinel + clinochlore (point A). The location of this invariant point at $T \sim 630$ °C and $X_{CO_2} = 0.60$ was calculated using Ge0-Calc (Brown et al., 1988) and the thermodynamic data base of Berman (1988).

of approximately 630 °C. Thus, samples 81-LL-12, 81-LL-39, and 91-LS-5 experienced relatively high temperatures.

Another sample that provides temperature constraints is 81-LL-19, which consists of calcite + dolomite + quartz + tremolite + phlogopite + potassium feldspar. This assemblage constitutes invariant point B (Fig. 4), which is defined by the following equilibria:



This isobarically invariant assemblage is located at $X_{CO_2} = 0.85$ at $T = 530$ °C for $P = 3$ kbar.

Other mineral assemblages contained within the Llano marbles restrict temperatures to a range of values that is generally <630 °C but greater than approximately 500 °C. For example, the assemblage consisting of calcite + dolomite + tremolite + diopside (Eq. 4) constrains temperatures to 555–630 °C and fluid compositions to $X_{CO_2} = 0.62$ –0.95 (i.e., between invariant points C and D, Fig. 4). The assemblage calcite + dolomite + tremolite +

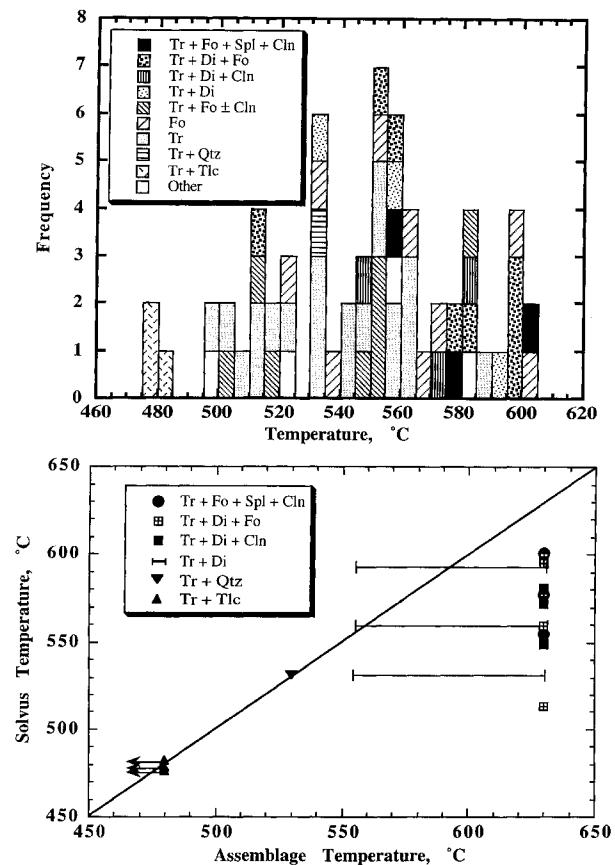
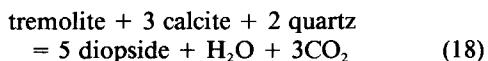


Fig. 6. (top) Histogram of calcite-dolomite temperatures similar to Fig. 3, but modified to show coexisting spinel and silicate assemblages. Note the correlation of temperatures inferred from calcite compositions as compared with temperatures inferred from spinel and silicate assemblages (see text). (bottom) Plot of calcite-dolomite temperatures vs. temperatures inferred from the most restrictive assemblages listed in top. The diagonal line indicates one to one correspondence between the two temperature determinations. A number of the silicate assemblages restrict temperatures to approximately 630 °C; however, the temperatures inferred from the compositions of calcites coexisting with dolomites in these samples are <630 °C. At lower temperatures, the agreement between the two temperature determinations is relatively good (see text).

forsterite (Eq. 3), on the other hand, is stable over a wider range of fluid compositions and restricts temperatures to 535–630 °C, unless the fluids are extremely H₂O-rich (i.e., $X_{\text{CO}_2} < 0.05$). Relatively lower temperatures can be inferred from the assemblage consisting of calcite + tremolite + quartz + diopside. This assemblage is defined by the isobarically univariant equilibrium



which restricts temperatures to approximately 490–565 °C for fluid compositions ranging from 0.05 to 0.95

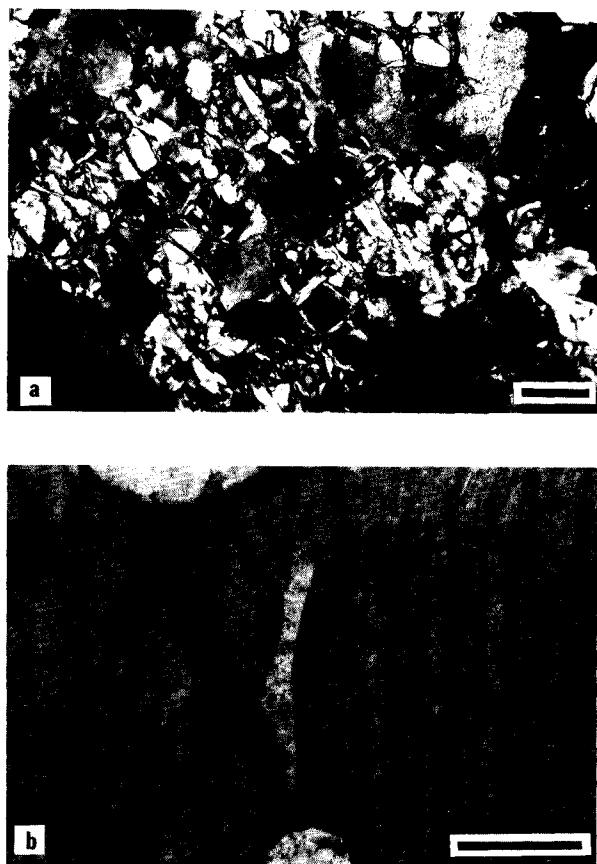
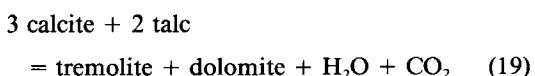


Fig. 7. (a) This sample, which contains abundant secondary serpentine (Srp) after forsterite (Fo), yielded an unusually low calcite-dolomite temperature (see text). (b) Photomicrograph showing an example of dolomite (Dol) that may have exsolved completely out of calcite (Cal), resulting in anhedral dolomite bordering calcite. Scale bar = 0.10 mm.

X_{CO_2} (Fig. 4). A mineral assemblage providing less rigid constraints of temperature, observed in 20 samples, consists of calcite, dolomite, and tremolite. At $X_{\text{CO}_2} > 0.10$, temperatures of 460–630 °C can be inferred from this assemblage (Fig. 4).

Finally, the lowest temperatures inferred from the silicate + carbonate equilibria are from those marbles that contain talc. Three samples (88-CM-4c, 90-DM-11, and 90-DM-12) contain an isobarically univariant assemblage consisting of calcite + dolomite + tremolite + talc, and one sample (83-LL-139) has calcite + quartz + tremolite + talc. These assemblages restrict temperatures to <480 °C or below invariant point A (Fig. 4), which is defined by Equation 16 and the following equilibria:



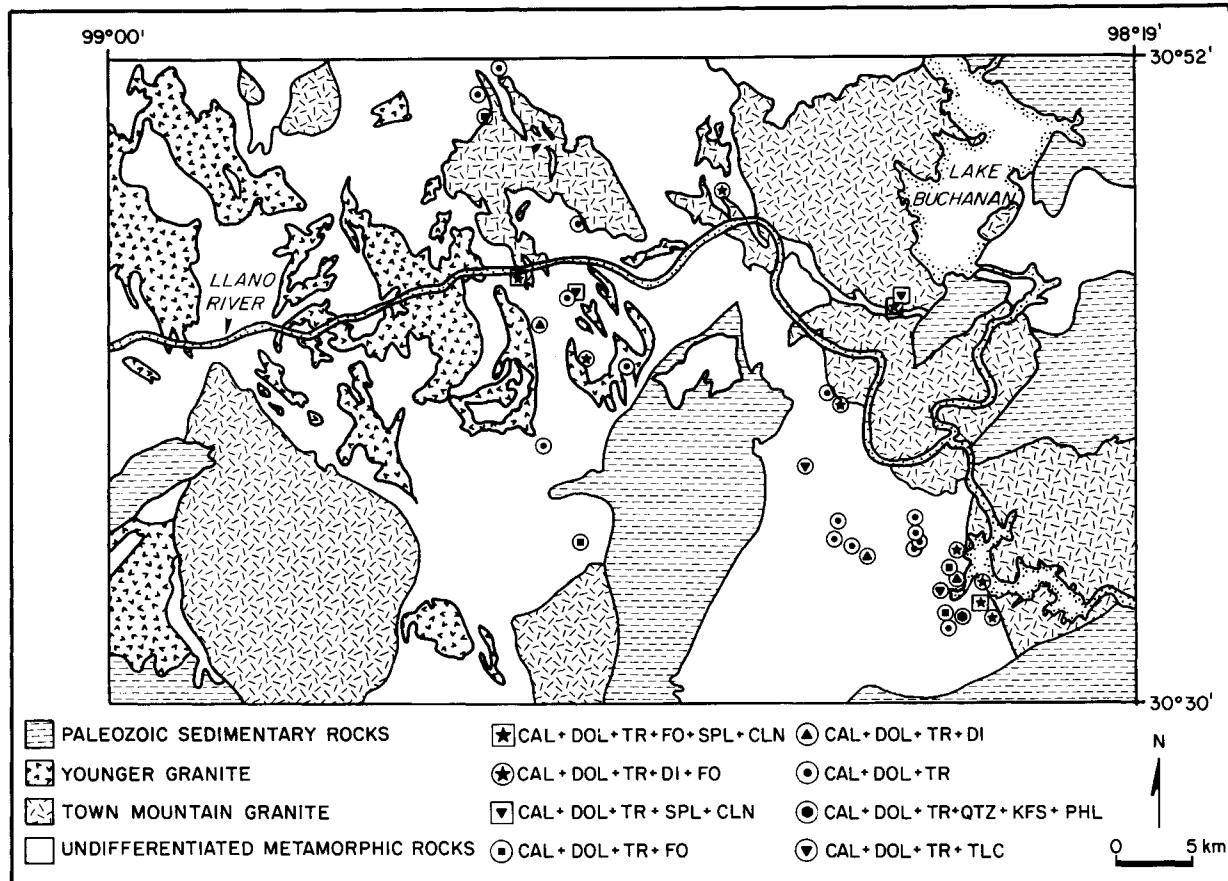
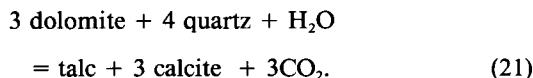
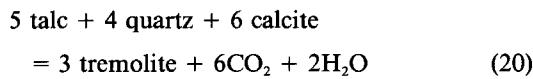


Fig. 8. Simplified geologic map of the Llano uplift showing the distribution of samples containing spinel and silicate assemblages coexisting with calcite and dolomite. Note that the high-temperature invariant assemblages consisting of calcite + dolomite + tremolite + diopside + forsterite and calcite + dolomite + tremolite + forsterite + spinel + clinochlore are found close to contacts between metamorphic rocks and the relatively undeformed granitic plutons.



CORRELATION OF SOLVUS TEMPERATURES WITH SILICATE + CARBONATE EQUILIBRIA

Temperatures obtained from the application of solvus thermometry to calcite + dolomite pairs range from 475 to 600 °C. This wide range of temperatures could result from either (1) variable resetting, or (2) real variations in peak metamorphic conditions. These two explanations are not mutually exclusive, since the effects of resetting may be superimposed on peak metamorphic temperature variations. Effects of resetting can be evaluated by comparing temperatures obtained from calcite + dolomite pairs with temperatures determined from silicate + car-

bonate equilibria. The range in temperatures obtained from calcite + dolomite thermometry is shown in a histogram (Fig. 3). A modification of this diagram shows silicate assemblages (Fig. 6 top), thereby allowing a comparison to be made between the calcite-dolomite solvus temperatures and those inferred from silicate + carbonate equilibria.

The marbles containing the mineral assemblages that correspond to equilibria given by the isobarically invariant points labeled D (calcite + dolomite + tremolite + diopside + forsterite) on Figure 4 and A (calcite + dolomite + tremolite + forsterite + clinochlore + spinel) on Figure 5 were metamorphosed to a temperature of approximately 630 °C at 3 kbar. Eleven of the samples contain one of these restrictive assemblages. These eleven samples also have temperatures determined from solvus thermometry, and seven of these temperatures lie between 575 and 600 °C, which are only slightly lower than temperatures inferred from silicate + carbonate mineral equilibria (Fig. 6 top). Four of the 11 temperatures are

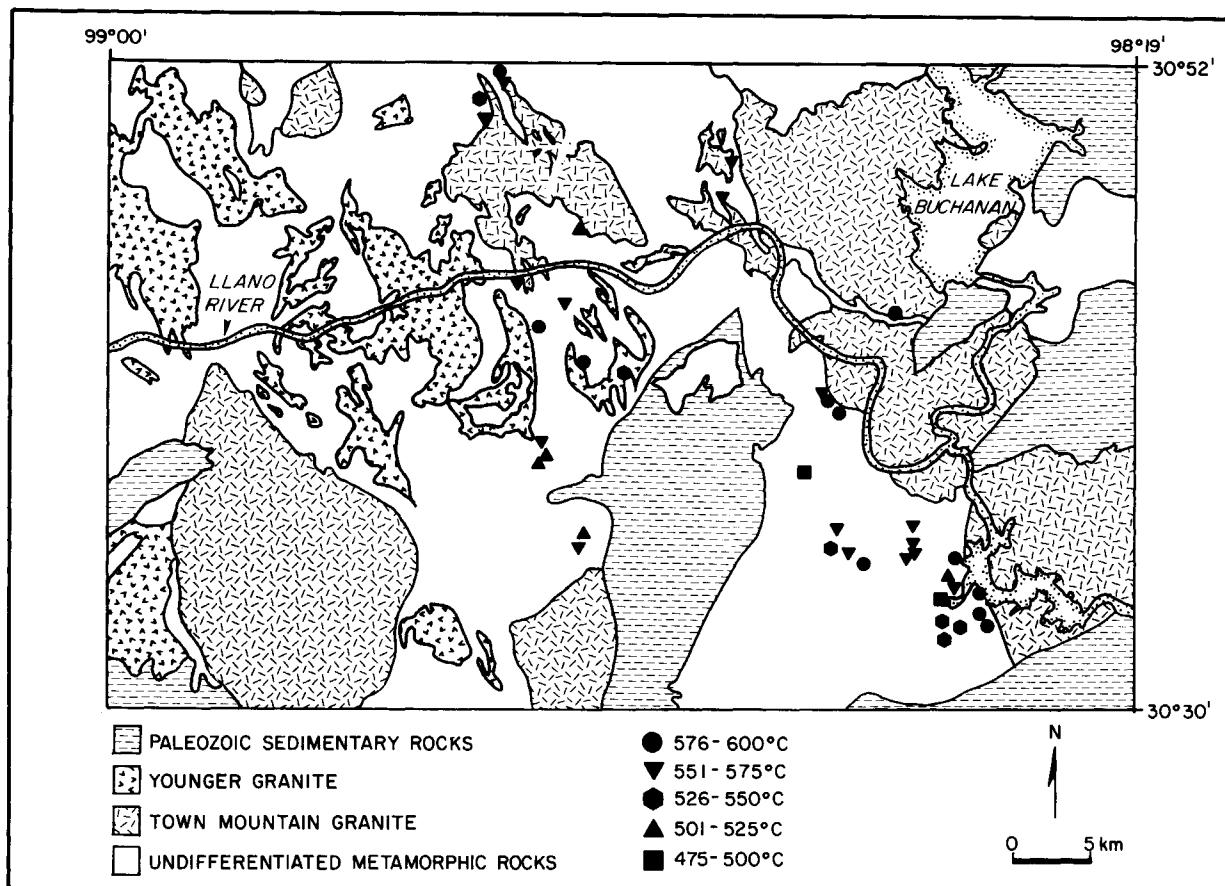


Fig. 9. Simplified geologic map of the Llano uplift showing the distribution of calcite-dolomite temperatures (see also Fig. 8). The highest temperatures are often obtained from marbles close to the granitic intrusives (see text).

lower; however, they are still ≥ 550 , and one temperature is 513 °C.

The assemblage calcite + dolomite + tremolite + diopside or forsterite is stable at intermediate temperatures of 535–630 °C, depending on fluid composition at $P = 3$ kbar (Fig. 4). Solvus thermometry on eight samples containing calcite + dolomite + tremolite + forsterite (Eq. 3) and on three samples with the assemblage calcite + dolomite + tremolite + diopside (Eq. 4) resulted in temperatures of 500–580 °C and 530–590 °C, respectively. One sample having the isobarically invariant assemblage calcite + dolomite + tremolite + quartz + potassium feldspar + phlogopite (point B, Fig. 4), which constrains T to 530 °C, $X_{\text{CO}_2} = 0.85$ for $P = 3$ kbar, yields a calcite-dolomite temperature of 531 °C (Table 1, Fig. 6 top). Twenty samples containing calcite + dolomite + tremolite correspond to intermediate temperatures ranging from 460 to 630 °C for $X_{\text{CO}_2} > 0.10$ at $P = 3$ kbar. Calcite-dolomite temperatures obtained for these samples range from 500 to 565 °C, again showing that temperatures inferred from silicate-carbonate equilibria are generally consistent with those obtained from calcite + dolomite thermometry.

The lowest temperatures are inferred for marbles having calcite + dolomite + talc + tremolite. This assemblage restricts temperatures to < 475 °C at $P = 3$ kbar (below invariant point A, Fig. 4). The calcite + dolomite temperatures of 475–480 °C obtained for the three samples having this assemblage are analytically identical to the temperatures inferred from the silicate + carbonate equilibria.

The general agreement between temperatures obtained from calcite + dolomite thermometry from those inferred from mineral equilibria indicates that many of the solvus temperatures obtained from calcite + dolomite pairs are real and reflect peak metamorphic conditions. However, some problems related to resetting are apparent. Figure 6 (bottom) is a plot of temperatures inferred from the most restrictive silicate + carbonate equilibria vs. temperatures inferred from the calcite-dolomite solvus. The agreement between these two temperatures estimates is excellent for temperatures less than approximately 550 °C. However, at higher temperatures the agreement deteriorates, as solvus temperatures are often lower than temperatures inferred from silicate + carbonate equilibria. For example, those mineral assemblages that require temperatures of approximately 630 °C all

have solvus temperatures below 610 °C (Fig. 6 bottom), although, as noted previously, a majority of these samples still yield solvus temperatures in excess of 575 °C. One notable observation associated with those samples that apparently suffered the greatest resetting of calcite compositions is the presence of abundant secondary serpentine (Fig. 7a). It is possible that late fluids associated with the formation of serpentine at the expense of forsterite or diopside may have resulted in preferential resetting of some of the calcite-dolomite temperatures. Furthermore, the presence of anhedral grains of dolomite touching calcite (Fig. 7b) may indicate that some dolomite may have exsolved completely out of the calcite host. In cases where dolomite exsolution in calcite appears to be heterogeneous, this may be indicative of incipient removal of dolomite from the calcite host along edges of the grain. Therefore, when interpreting results obtained from calcite + dolomite thermometry, it is important to consider the textural relations between calcite-dolomite pairs, particularly the homogeneity of exsolved dolomite in calcite whose composition is being reintegrated.

DISCUSSION

The temperatures obtained from calcite + dolomite thermometry, as well as those inferred from silicate + carbonate equilibria, have important implications for the possible peak metamorphic conditions attained by the marbles. Marbles containing the high-temperature invariant assemblage calcite + dolomite + tremolite + diopside + forsterite or the assemblage calcite + dolomite + tremolite + forsterite + spinel + clinochlore are generally found close to post-tectonic plutons, namely the Town Mountain and the Younger granite (Fig. 8). In contrast, samples containing calcite + dolomite + tremolite + talc are found farther away from the same contact. The closest sample having this assemblage is ~1700 m from a Town Mountain granite pluton in the southeastern part of the uplift. The same relations are seen with the calcite-dolomite temperatures. Temperatures of 575–600 °C are generally found closer to the post-tectonic pluton contacts in both the eastern and central portions of the uplift (Fig. 9).

Figures 8 and 9 suggest a correlation between relatively high temperatures and pluton contacts, and so we have plotted temperature as a function of distance to the relatively large plutons shown on Figures 8 and 9 (Fig. 10). Figure 10 top, which is a plot of solvus temperatures vs. distance to pluton contacts, does not show a strong correlation of temperature with pluton proximity. However, some of the temperature variation shown in Figure 10 top may be the result of resetting of calcite compositions. Consequently, we have plotted temperatures inferred from the most restrictive silicate + carbonate equilibria vs. distance to the granitic plutons (Fig. 10 bottom). Mineral assemblages that require temperatures of approximately 630 °C all lie within 1 km of one of the relatively undeformed granitic plutons. Thus, all the isobarically invariant assemblages that require relatively high peak meta-

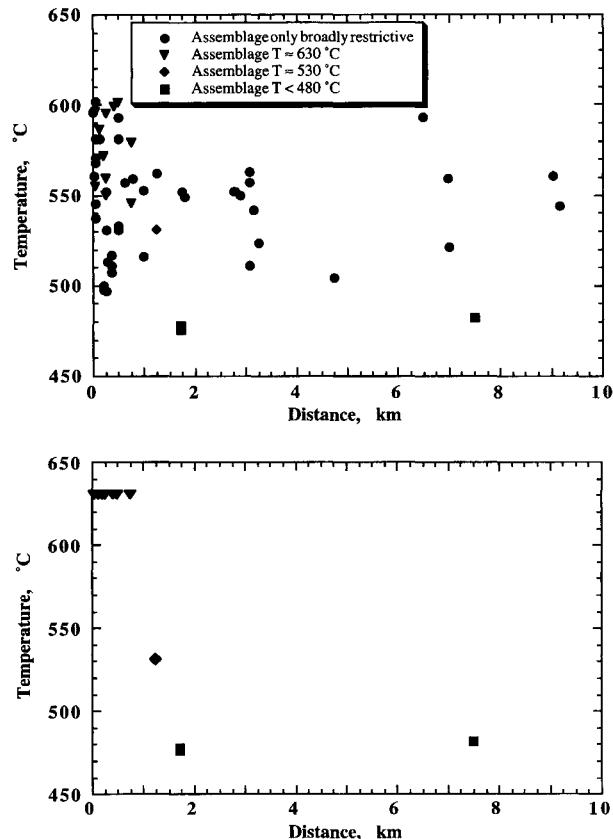


Fig. 10. (top) Temperatures inferred from the compositions of calcite coexisting with dolomite plotted as a function of distance from the relatively undeformed granitic plutons (0 km = contact). In some cases, symbols denote samples that also contain silicate or spinel assemblages that, along with calcite and dolomite, restrict metamorphic temperatures. Although many of the highest temperatures were determined for marbles that lie close to granites, there is no obvious trend, given the variability in temperature determinations. (bottom) Temperatures inferred from the most restrictive silicate or spinel-bearing assemblages plotted as a function of distance from the relatively undeformed granitic plutons. All mineral assemblages that require temperatures of approximately 630 °C lie within 1 km of a pluton contact, whereas lower temperatures are only recorded in samples further from plutons. The lowest temperatures are based on the compositions of calcites in talc-bearing samples (talc-bearing assemblages require $T < 480$ °C). Thus, the mineral assemblages suggest that a thermal aureole is present; however, calcite + dolomite thermometry shows that relatively high temperatures are also recorded in samples farther from the plutons (see text).

morphic temperatures are relatively close to pluton contacts, and this observation could be an indication that the metamorphic assemblages found throughout much of the Llano uplift were produced during the relatively static metamorphic event related to the intrusion of the post-tectonic granites. However, some exceptions exist wherein relatively high calcite + dolomite temperatures are found away from igneous intrusions (Fig. 10 top). Furthermore, temperatures ranging from 590 to 650 °C,

determined using garnet + biotite or garnet + ilmenite thermometry, were obtained from pelitic schists that are ~4–10 km away from the nearest exposed granite pluton (Letargo and Lamb, 1992; Letargo, 1993). These high temperatures may be attributed to small intrusions, or to intrusions that were emplaced above or below the current erosional level, or even to channelized fluid movements. Thus, high temperatures determined for rocks that are not close to currently exposed granite plutons could still be related to the relatively late static metamorphic event. However, the possibility that these temperatures may be related to the effects of an earlier metamorphism cannot be dismissed.

Another interesting feature of the metamorphism in the Llano region is the inferred fluid compositions. Although we recognize that there is substantial uncertainty in the location of invariant point A in Figure 4 (Eggert and Kerrick, 1981), the mineral assemblage in the talc-bearing marbles (occurring away from pluton contacts) apparently requires relatively H₂O-rich conditions, whereas the marbles containing the high-temperature invariant assemblage (occurring close to plutons) are more CO₂-rich. In contrast, some calc-silicate rocks occurring next to pluton contacts in the central uplift were infiltrated by H₂O-rich fluids (Bebout and Carlson, 1986; Letargo and Lamb, 1993). Thus, close to pluton contacts, there is evidence that in some cases, fluids buffered by mineral equilibria may be more CO₂-rich, whereas in others, fluid composition may be more H₂O-rich as a result of the infiltration of externally derived fluids.

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