Journal of Structural Geology 33 (2011) 343–361

Contents lists available at ScienceDirect

Journal of Structural Geology

journal homepage: www.elsevier.com/locate/jsg

An Alpine-style Ordovician collision complex in the Sierra de Pie de Palo, Argentina: Record of subduction of Cuyania beneath the Famatina arc

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ARTICLE INFO

Article history:
Received 12 April 2010
Received in revised form
23 September 2010
Accepted 25 October 2010
Available online 20 November 2010

Keywords:
Cuyania
Collision complex
Fold nappes
Thrusts
Subduction channel

ABSTRACT

The Caucete Group and structurally overlying Pie de Palo Complex in western Argentina are characterised by two generations of west-verging folds and thrust-related shear zones, which formed under amphibolite facies conditions. The Caucete Group is separated from the Pie de Palo Complex by the Pirquitas thrust. These structures are interpreted to have formed as a result of a progressive deformation, generated during Middle Ordovician, underthrusting of the Laurentian-derived Cuyania microcontinent beneath the active Famatina margin. Geometrical relationships are most simply explained if the Pie de Palo Complex was basement to the Caucete Group prior to Ordovician orogenesis. We propose that this basement-cover relationship was established during Cambrian rifting of the Cuyania microcontinent from Laurentia. The Pirquitas fault may have been initiated during this extension prior to its long-lived remobilization as a thrust. We cannot rule out the possibility that the Pie de Palo Complex was exotic with respect to the Caucete Group, but for this to be possible we have to introduce an extra generation of structures, for which no evidence is preserved.

The deformation was characterised by early strain localization followed by a more homogeneously distributed non-coaxial flow during F_2. Thermal softening probably dominated over fabric softening during this stage.

1. Introduction

The proto-Andean margin of west Gondwana accreted terranes from the late Neoproterozoic to the Late Paleozoic (Ramos et al., 1986, 2010; Ramos, 2004, 2008; Escayola et al., 2007). The docking of the composite Cuyania (Precordillera terrane sensu stricto plus Pie de Palo terranes, Ramos et al., 1998) or greater Precordillera terrane (Finney, 2007) with the Early Paleozoic west-facing, proto-Andean Famatina arc (Pankhurst et al., 1998) has been extensively discussed in terms of provenance, time of accretion, and regional extent. Fossil evidence (Benedetto et al., 1999), subsidence history, isolation of the carbonate platform from clastic input during the Early to Middle Ordovician (Astini, 1998; Keller et al., 1998) and paleomagnetic evidence (Rapalini and Astini, 1998; Rapalini, 2005) suggest that at least the Precordillera terrane had a Laurentian provenance during the Early Cambrian, to which it remained attached after the break-up of Rodinia, and moved as an independent microcontinent across Iapetus (Ramos et al., 1986; Astini et al., 1995; Thomas and Astini, 1996). The time of initial accretion (Ordovician; Astini, 1998; Casquet et al., 2001; Vujovich et al., 2004) or Siluro-Devonian (Rapela et al., 1998; Keller et al., 1998) and whether the colliding Famatinian arc was separated from the proto-Andean margin by a significant marginal basin or seaway (Bahlburg and Hervé, 1997; Rapela et al., 1998; Rapalini, 2005) remain contentious.

We present results of studies carried out in the western Sierra de Pie de Palo, in west-central Argentina (Fig. 1), which is located close to the boundary between the Cuyania composite terrane and remnants of the proto-Andean margin. The tectonostratigraphy, style and age of deformation and metamorphism of these rocks, and the relationship between foliation development, folding and thrusting bear on the provenance and tectonic setting of these rocks and how deeply buried rocks flow and accommodate ductile deformation in an A-subduction/collision zone. Our data suggest that an A-subduction/collision zone comprises a regime characterised by early strain localization that transforms to more homogeneously distributed flow in response to the evolving thermal

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doi:10.1016/j.jsg.2010.10.011

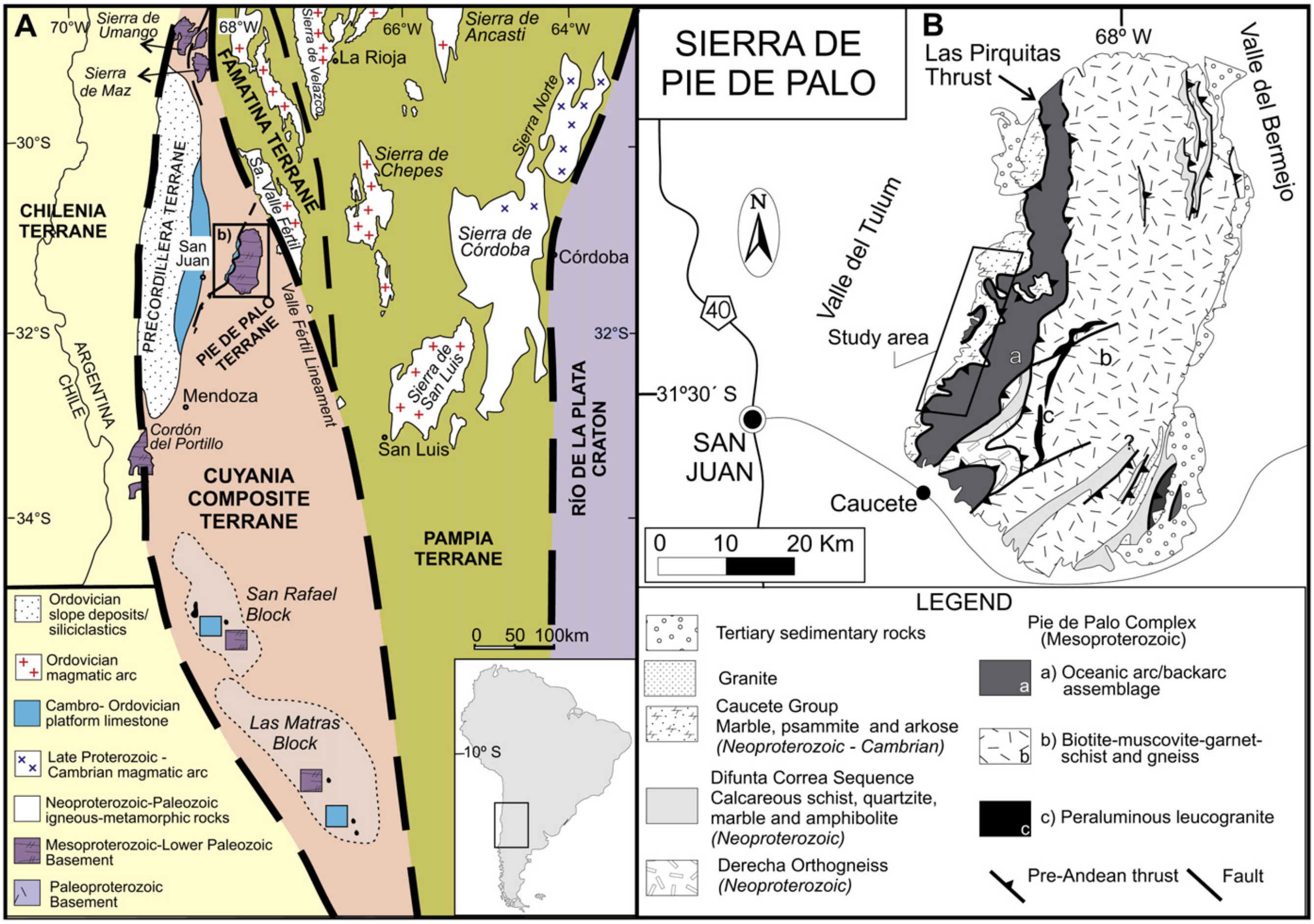

Fig. 1. Map of the Cuyania composite terrane (Precordillera + Pie de Palo terranes) after Ramos et al. (1998, 2010) and map of the Sierra de Pie de Palo after Ramos and Vujovich (2000) and Naipauer et al. (2010a).

structure, and support earlier suggestions that during folding thin ductile thrust sheets formed as a secondary feature by shearing-out of the common, lower limb of overturned folds (e.g. Heim, 1919; Ramsay, 1992).

2. Geological setting

The intensely deformed metamorphic rocks of the Pie de Palo terrane (Fig. 1) lie immediately west of the Valle Fértil lineament (e.g. Chernicoff et al., 2009), generally inferred to mark the suture between the Famatina arc and the exotic Cuyania composite terrane to the west (Ramos et al., 1998; Ramos, 2004). The Pie de Palo terrane, the leading edge of Cuyania, is separated from the Precordillera terrane, which represents Cuyania's trailing part, by a wide ($\sim$50 km) valley (Valle del Tulum) filled with sand and salt flats (Fig. 1). Hence, the relationships between these two Cuyanian terranes are contentious. Early workers inferred that at least part of the rocks in the Sierra de Pie de Palo represented exhumed Mesoproterozoic basement which was assembled into a composite 'Cuyania' terrane during the Grenville orogeny (Ramos et al., 1998; Vujovich and Kay, 1998; Chernicoff et al., 2009). In contrast, Mulcahy et al. (2007) interpreted new radiometric age and isotopic data (Galindo et al., 2004; Mulcahy et al., 2007) as suggesting that the Pie de Palo terrane represents a fragment of imbricated Mesoproterozoic basement to the Famatina forearc. The key to establishing the affinities of the Pie de Palo terrane rocks lies in the metasedimentary rocks of the Caucete Group, which occur along the western fringes of the Sierra de Pie de Palo, and its structural relationships with the structurally overlying Mesoproterozoic rocks of the Pie de Palo Complex (Vujovich et al., 2004). The rocks of the Caucete Group were traditionally correlated with the Cambrian-lower Ordovician platfosrm rocks of the Precordillera terrane (Schiller, 1912) (Figs. 1 and 2). This correlation, supported by tectonostratigraphic studies (van Staal et al., 2002), carbonate isotope data (Galindo et al., 2004) and detrital zircon studies (Naipauer et al., 2010a), implies a direct tectonic linkage between the Precordillera and at least part of the Pie de Palo terranes. Our investigations (Fig. 2) focussed on the Caucete Group, the structurally overlying 1–1.2 Ga ultramafic to intermediate rocks of the Pie de Palo Complex (Vujovich et al., 2004), and the shallow to moderately, east-dipping Pirquitas thrust (Ramos and Vujovich, 2000; Chernicoff et al., 2009) that separates the two units (Figs. 2 and 3). The preserved tectonostratigraphy of the metasedimentary rocks combined with nearly continuous outcrop and significant relief allows elucidation of the complex structure and determination of the relationships between folding and thrusting.

3. Caucete Group

3.1. Tectono-stratigraphy

Rocks of the Caucete Group (Borello, 1969; Vujovich, 2003) were intensely deformed by ductile shear (Fig. 4A) and at least two generations of tight to isoclinal folds (Fig. 4E), which transposed the compositional layering of the rocks into an orientation parallel

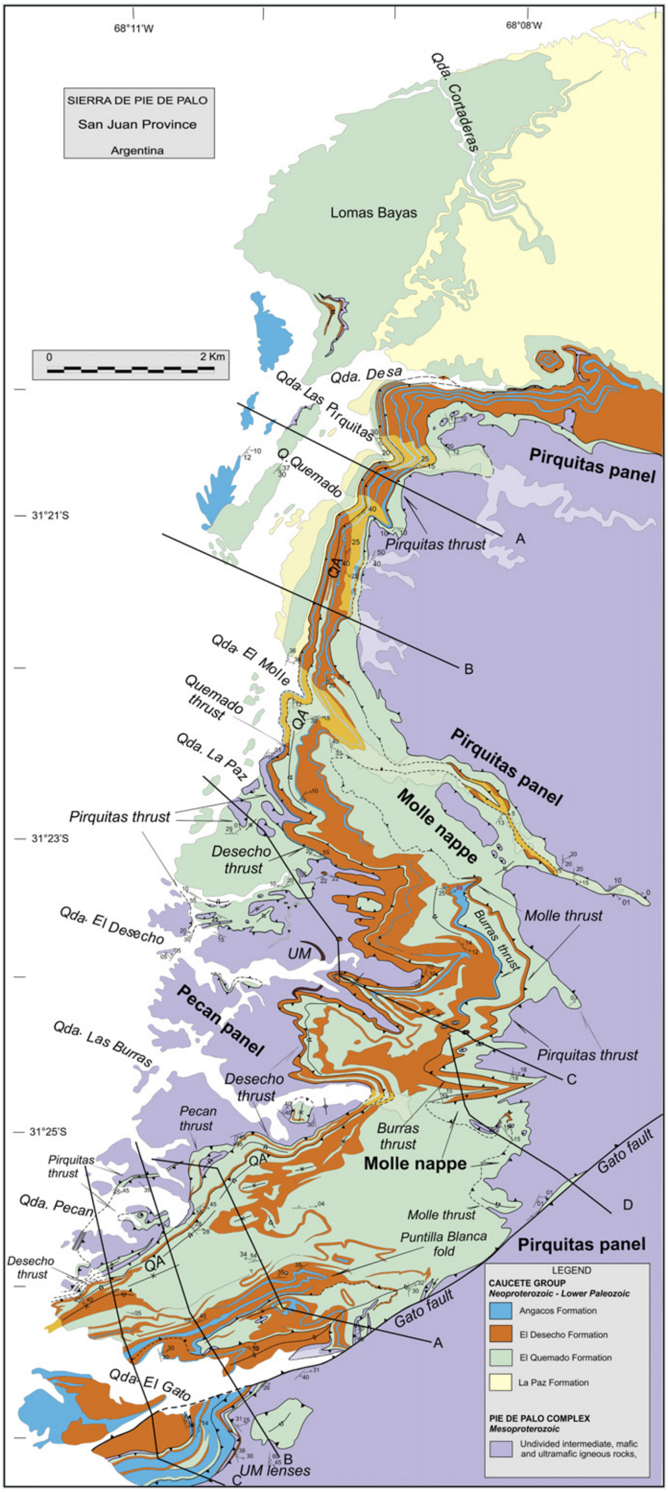

Fig. 2. Geological map of the central-western Sierra de Pie de Palo. Geology was mapped on 1:25,000 air photos and than transferred to a satellite-based topographic map. Where there is little or no outcrop (sand-filled dry creeks and flats) colours are faded or left white. UM = ultramafic rocks.

to a complex, generally shallowly to moderately east-dipping composite fabric. Strain appears high throughout the sequence as documented below. Despite intense deformation, the rocks preserve an easily recognisable tripartite tectonostratigraphy, comprising varicoloured psammite (El Quemado and La Paz formations), poorly sorted arkosic and calcareous red beds interlayered with dolomite (El Desecho Formation), and marble (Angacos Formation). The integrity of the lithological units is generally preserved on map-scale, except in the hinges of large folds, where units are typically complexly structurally interleaved (Fig. 4C) and zones of very high attenuation (Fig. 2). Tectonostratigraphic integrity despite such intense folding is most easily explained if the folds are asymmetrical on all scales such that the overall shallowly dipping enveloping surface to the folded rocks makes a small angle with the compositional layering. All three major units display compositional layering on cm to m-scale (Fig. 4E), which we interpret as bedding. It is difficult to explain layers of such contrasting compositions as dolomite and sandstone in any other way. Some of the layering in the psammites could conceivably be the result of extreme transposition of completely recrystallised felsic sills or dikes, but no evidence for such intrusions is observed where strain is relatively low. Other sedimentary structures are rarely, if ever, preserved (cf. Naipauer et al., 2010a). The overall facing of the tripartite stratigraphy is thus solely based on our correlation with inferred unmetamorphosed lithological and temporal (Naipauer et al., 2010a) correlatives in the much less deformed Precordillera terrane. These correlations are pivotal for our structural and tectonic interpretations and hence are described below.

The psammites comprise the relatively quartz-rich El Quemado Formation (Fig. 4A and D) and the dark and feldspathic La Paz Formation (Fig. 2). These two units are locally intricately interlayered both on outcrop and map-scale, which suggests, but does not require, an original stratigraphic relationship. The La Paz formation, dominant in the northwestern part of the area, rapidly diminishes in proportion to the south, a relation suggestive of either an original facies change or complex folding. We prefer the latter interpretation, but this could not be confirmed due to inadequate outcrop and vertical relief in this part of the area (Figs. 2 and 5). Both units are feldspathic and contain smoky, square-shaped quartz, suggesting input from a consanguineous volcanic source.

The *El Quemado Formation* comprises colour banded, quartz-rich, flaggy psammites, locally called 'quartzites', and mined as roofing slate and building tiles where deformed into platy ultramylonite (Fig. 4A and D). The psammites are feldspathic (microcline and albite) and best described as feldspathic arenites. They contain mm to cm scale bands relatively rich in phyllosilicate, mainly light green phengite and chlorite. Some of these may represent interlayered siltstone or shale, but most formed by strain-induced alteration of feldspar and subsequent metamorphic differentiation to phyllosilicate-rich and quartz-rich layers (Fig. 4B, van Staal et al., 2001). Colours of layers vary from green through yellow to red and black. Green layers generally have the most quartz-rich compositions. Red layers, most common near the contact with the El Desecho Formation are more feldspathic. K-feldspar clasts are commonly transformed into porphyroclasts characterised by deformation bands, twinning and fractures. Contacts of the El Quemado Formation with the other units of the Caucete Group in general are abrupt, although in a few places thin discontinuous dolomite layers are interleaved with psammite near the contact with the El Desecho Formation, probably due to isoclinal folding and associated boudinage, since dolomite is otherwise completely absent from the psammites. The reddening and increase in feldspar content of the psammites suggest an original shallowing sequence culminating in deposition of red beds and dolomite of the El Desecho Formation. We therefore believe that the El Desecho Formation was deposited, possibly disconformably, above the El Quemado and La Paz formations. Detrital zircons indicate that the psammites have a maximum age of 550 Ma (Naipauer et al., 2010a).

The *La Paz Formation* is a dark grey to brown or black, micaceous feldspathic psammite which we interpret as a volcaniclastic or

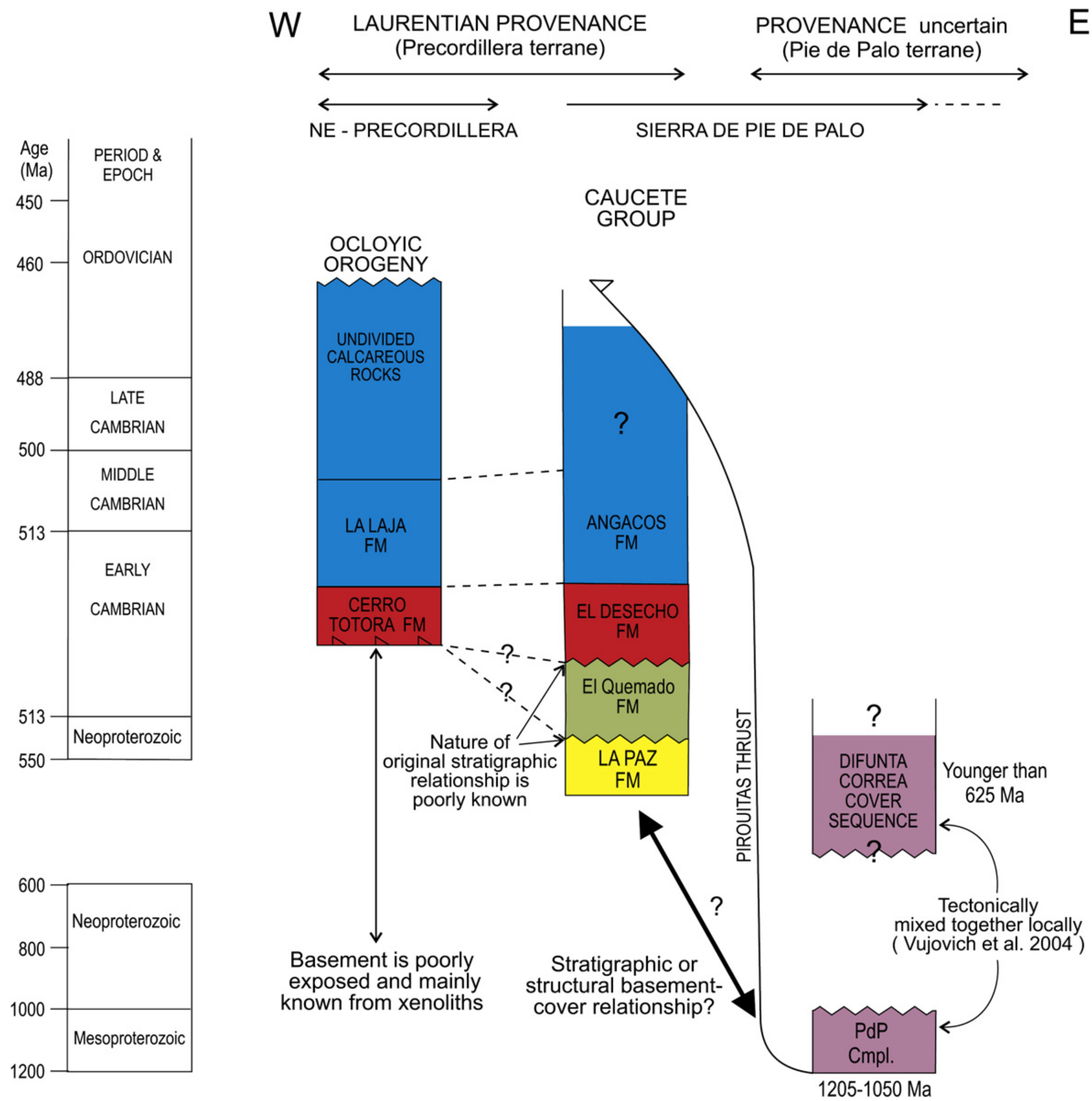

Fig. 3. Schematic tectonostratigraphic relationships and correlations between the various units of the Caucete Group depicted in Fig. 2 and present in the Precordillera terrane. The age relationship between the El Quemado and La Paz formations at the base of the Caucete Group is solely based on our structural interpretations, which are discussed later in the text.

tuffaceous sandstone, because of the abundance of smoky square quartz, typical of high temperatures, and feldspar phenoclasts up to 2–3 cm in diameter. The dark colour of this unit results mainly from the abundance of biotite. Structural interpretations suggest this unit stratigraphically underlies the El Quemado Formation (Figs. 3, 5).

The *El Desecho Formation* comprises poorly sorted red arkose to sandstone beds. In addition to abundant lithic and quartz fragments, the rocks are also relatively rich in calcite, possibly the metamorphosed remains of calcite cement. Some rock fragments are micaceous, suggesting a metamorphic source terrain. The red beds are locally interlayered with white to yellow dolomite (Fig. 4C and E). Detrital zircon studies suggest a Lower Cambrian age for this unit (~530 Ma) (Naipauer et al., 2010a), which is consistent with Sr-isotopic data (Galindo et al., 2004). This unit is distinctive and a key stratigraphic marker.

The *Angacos Formation* comprises varicoloured, well-layered marble, ranging in colour from white to bluish grey to yellow (Figs. 4C and 6A), and in composition from nearly pure calcitic limestone, which was locally mined, to dolomite to a yellowish micaceous marly rock. The last probably represents a mixture of alternating calcareous pelite/siltite and arenite. Naipauer et al. (2010a) interpreted laminated marble consisting of alternating limestone and dolomite laminae as limestone–dolostone rhythmites, suggesting a relatively deep-water setting. Sr and C-isotopic signatures suggest the Angacos Formation is Cambrian (Sial et al., 2001; Galindo et al., 2004), consistent with the presence of possible ichnofossils (Bordonaro et al., 1992). The transition from the El Desecho Formation to the Angacos Formation appears to be transitional and is not always easy to define in the field where deformation has highly attenuated and/or excised part of the unit. We defined the boundary as the point where red beds disappear and calcite marble becomes the dominant lithology.

3.2. Regional correlation and significance of the Caucete Group

The Caucete Group was traditionally loosely correlated with the thick and fossiliferous Cambro–Ordovician carbonate platform

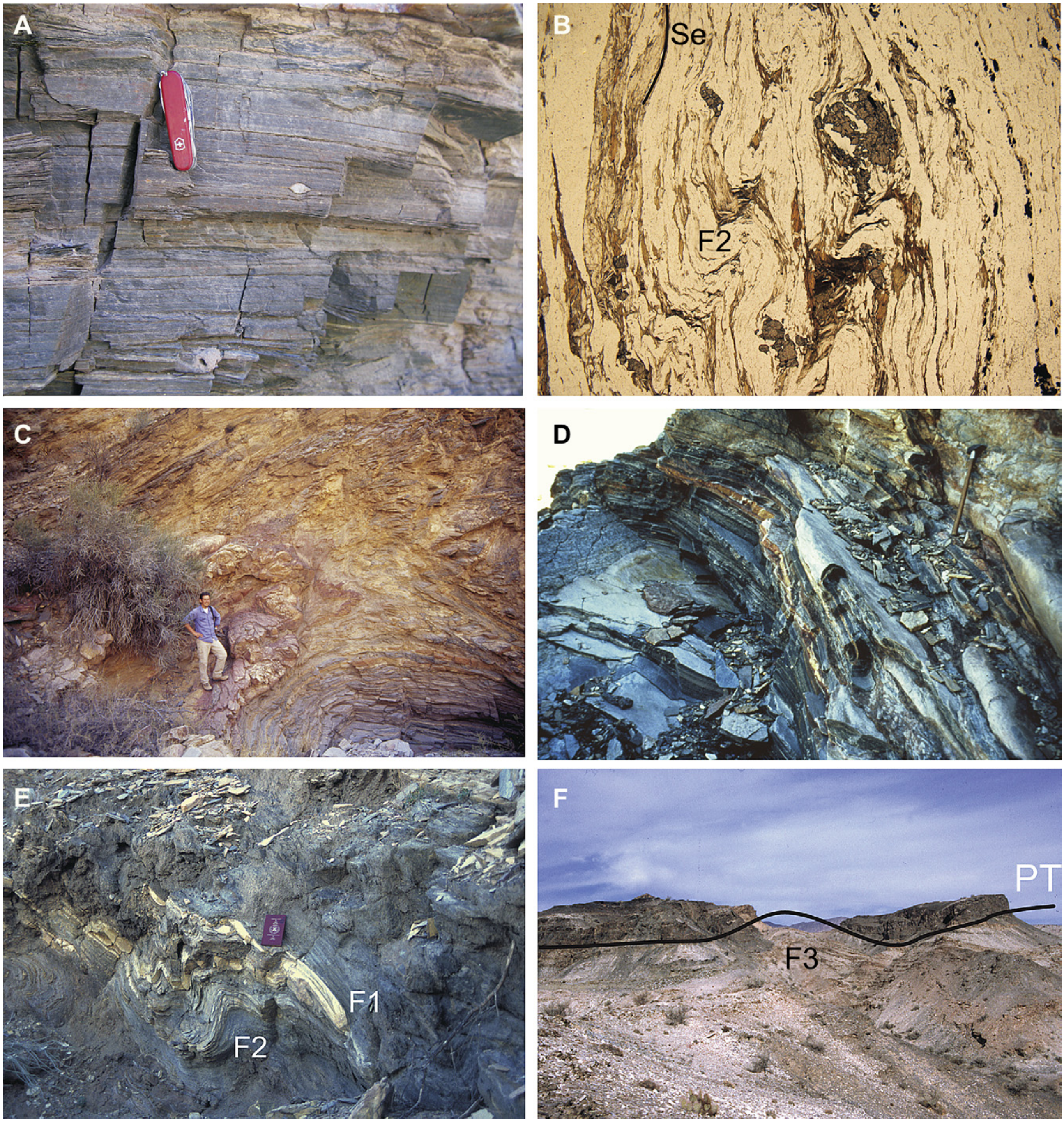

Fig. 4. A) Subhorizontal El Quemado ultramylonite with large winged porphyroclasts of quartz and feldspar (pink) developed from pulled-apart quartz and quartz-feldspar veins. B) biotite–garnet schist (vvl 5), El Quemado Formation, Molle nappe with F_2 microfolds in differentiated S_e. Note that the garnet locally has an internal foliation (S_i) that bends into S_e, width of view is 4 mm; C) disharmonic, nearly symmetrical folds in hinge area of large F_{1-2} fold developed at the contact between the El Desecho (red and white) and Angacos formations (greyish blue). M. Naipauer for scale; D) nest of curvilinear to sheath-like west-verging F_2 folds in flaggy psammite of the Molle thrust zone. Stretching lineation is parallel to pencil (pointing west) and folded by F_2; E) long-limbed recumbent F_1 fold in white dolomite layer refolded by inclined west-verging F_2 folds in purplish to red calcareous siltites of the El Desecho Formation; F) two klippen of the Pie de Palo Complex (Pecan panel) with Pirquitas thrust at the base and overlying El Quemado psammites, separated by open F_3 fold.

succession of the Precordillera terrane, mainly because of the abundance of marble (Angacos Formation). Our recognition of the El Desecho red beds, which closely resemble the redbed, dolomite and minor evaporite (mainly gypsum and anhydrite) strata of the Cerro Totora Formation of the Precordillera terrane forms another lithological link (Fig. 3). The Cerro Totora Formation, the oldest known sedimentary unit in the Precordillera was interpreted as a synrift succession (Astini, 1998). No meta-evaporites have been recognised by us in the El Desecho Formation, but such rocks are unlikely to survive deep burial and regional metamorphism as is seen here. Fine-scale lamination in some dolomite of the Angacos Formation resembles structures found in dolomite of the Cerro Totora Formation. If the correlation of the El Desecho Formation with the Cerro Totora Formation is correct, the Angacos Formation correlates with the Lower Cambrian carbonates of the La Laja Formation or the coeval Los Hornos Formation (Astini, 1998; Keller et al., 1998), which

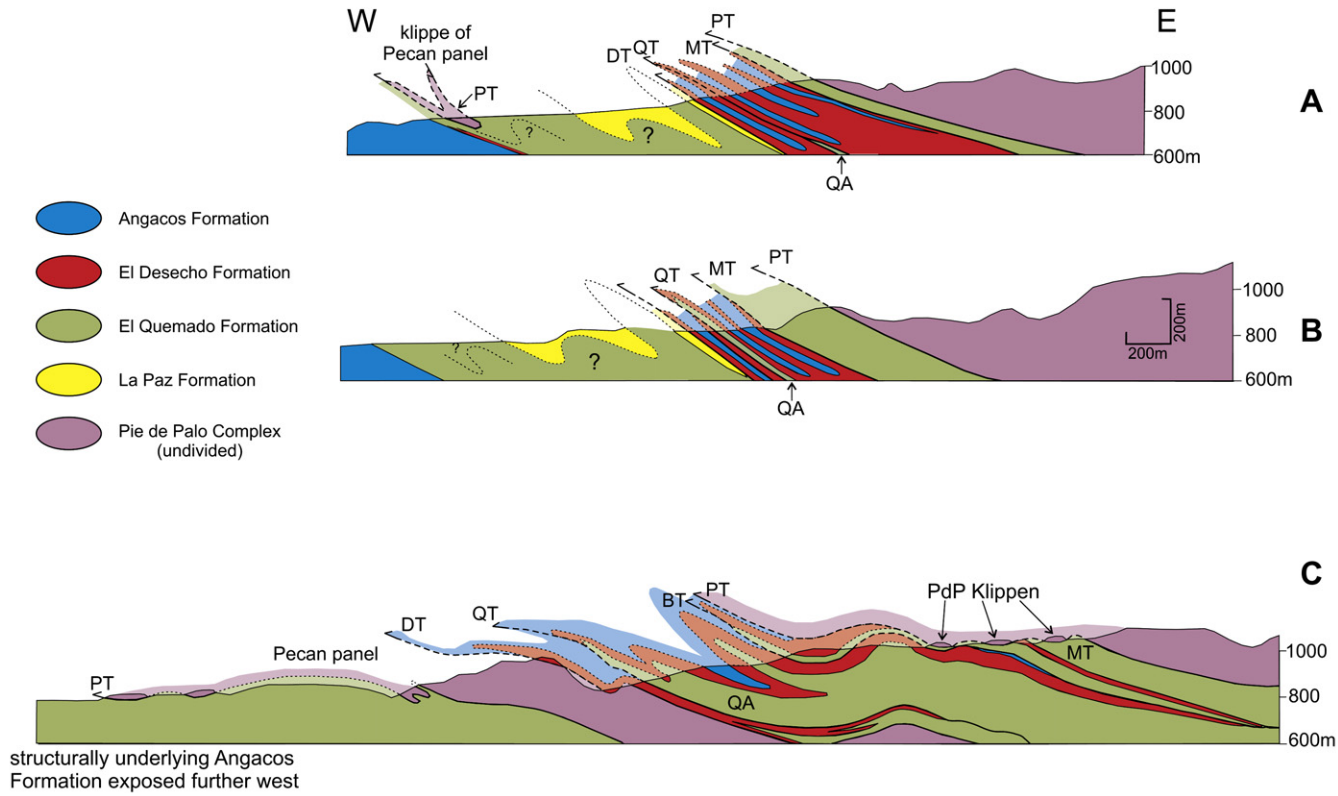

Fig. 5. Structural profiles drawn along lines A, B and C in the northern part of Fig. 2 (north of quebrada Las Burras). Projection of structures to depth is interpretative due to curvilinear nature of F_2 folds. Rocks below the Desecho thrust in sections A and B form part of the downward facing Pecan panel (see section on Large-scale structure of the Caucete Group in text). If correct, our structural interpretation suggests that the La Paz Formation is older than the El Quemado Formation. PT = Pirquitras thrust; BT = Burras thrust; MT = Molle thrust; DT = Desecho thrust; QT = Quemado thrust; QA = Quemado antiform; PdP = Pie de Palo Complex.

stratigraphically overlie the Cerro Totora Formation (Fig. 3) Psammites of the El Quemado Formation are possible equivalents of the sandstones found in the Cerro Totora Formation or a unit underlying the Cerro Totora Formation that is not presently exposed. Equivalents of the volcanogenic sandstones of the La Paz Formation have not been recognised in the Precordillera, but are consistent with a Late Neoproterozoic/Early Cambrian synrift setting in which they would be slightly older than the Cerro Totora Formation. In general, the rifting related units are comparable to other coeval rift-related units along the Iapetan margin of Laurentia, such as the Labrador Group in Newfoundland (e.g. Williams et al., 1995). Detrital zircon provenance studies (Naipauer et al., 2010a) suggest a typical Laurentian provenance for the Caucete Group. Together with the lithological correlations discussed here these data support inclusion of the Caucete Group with the Laurentian-derived Precordillera terrane. We present evidence below that the Pie de Palo Complex may have been stratigraphic or structural basement to the Caucete Group. Regardless whether this is correct the Pirquitas thrust (Figs. 1 and 2) is now regarded as the boundary between the Precordillera and Pie de Palo terranes (Chernicoff et al., 2009), because of the strong correlation between the Caucete Group and the Precordillera rocks.

4. Pie de Palo Complex

The Pie de Palo Complex in our area comprises a tectonic collage of ultramafic to intermediate (e.g. tonalite) meta-igneous rocks, with mafic compositions (amphibolites) dominant, interpreted to represent the metamorphosed remnants of a Mesoproterozoic oceanic arc/backarc assemblage (Vujovich and Kay, 1998; Vujovich et al., 2004). The Pie de Palo Complex structurally overlies the Caucete Group along the shallow to moderately east-dipping Pirquitas thrust (Fig. 4F), which appears to be a fundamental crustal structure (Chernicoff et al., 2009). Our structural data demonstrate a long history of remobilization and it may have initiated as an extensional fault (see below). The rocks of the Pie de Palo Complex were previously considered to have been accreted to the basement of the Precordillera terrane during the Grenville orogeny forming the Cuyania composite terrane (Ramos, 1995; Vujovich and Kay, 1998) thought to form part of the basement to the Paleozoic succession. This hypothesis was challenged recently by Mulcahy et al. (2007) who obtained Late Cambrian (515–510 Ma) $^{40}Ar/^{39}Ar$ hornblende ages from mylonitic amphibolites present along the Las Pirquitas shear zone. They believed such ages to be atypical for Laurentian-derived terranes, and therefore favoured correlation of the Pie de Palo Complex with inferred Mesoproterozoic basement to the Famatinian forearc of the active Early Paleozoic, proto-Andean margin.

Stratigraphic relationships between the predominantly mafic Pie de Palo Complex and the Caucete Group have nowhere been observed. All contacts are faulted and no obvious detritus of the Pie de Palo Complex has been identified in the Caucete Group. Instead the basal psammites of the Caucete Group are quartz-rich with K-feldspar more prominent than albite, suggesting a dominantly felsic rather than a mafic provenance (Vujovich, 2003). However, detrital zircon studies (Naipauer et al., 2010a), Pb-isotope data (Kay et al., 1996) and sediment geochemistry (Naipauer et al., 2010b), are compatible with a sedimentary linkage between the Pie de Palo Complex and the Caucete Group. In addition, the Difunta Correa metasedimentary sequence, with a maximum depositional age of 625 Ma, which is locally structurally interleaved with the Pie de Palo Complex (Vujovich et al., 2004), is generally considered to represent cover to the Pie de Palo Complex (Fig. 3) (Rapela et al.,

Fig. 6. A) F_1 isoclines in Angacos limestone refolded by F_2 folds in hinge area of larger F_2; B) F_1 folds in Pie de Palo Complex amphibolite with tonalitic veins refolded by F_2. Note that F_1 is folding an earlier, spaced foliation (S_e); C) west-verging F_{1-2} tubular sheath fold near Quemado thrust zone; D) west-verging F_2 sheath fold in El Quemado mylonites near where the Burras thrust sheet converges and is truncated by the Molle nappe (see also Fig. 10). M. Naipauer for scale; E) F_1 folded interlayering of amphibole–chlorite schist of the Pie de Palo Complex and Quemado psammite. F_1 fold is overprinted by S_2 and small-scale S-shaped, west-verging F_2 folds; F) large west-verging (right) F_2 fold of the Pirquitas thrust at the base of the Pecan panel. Dark rocks are Pie de Palo amphibolite and light rocks are underlying El Quemado Formation flaggy (mylonitic) psammite.

2005). No stratigraphic relationship is known between the Difunta Correa unit and Caucete Group, but the siliciclastic rocks of both units resemble each other lithologically.

5. Deformation history of the Caucete Group

Rocks of the Caucete Group exhibit a very well-developed, layering-parallel, spaced schistosity (Fig. 4B), folded by at least two generations of tight to isoclinal, asymmetrical early folds (F_1 and F_2) into a composite transposition foliation (S_m) with an overall shallowly east-dipping enveloping surface (Figs. 4C, E, 5 and 6A). S_m is folded into open, upright structures by late (F_3) folds, which are best developed in the southern part of the area (Fig. 4F). The early (F_{1-2}) folds occur on all scales, are generally disharmonic (Fig. 4C) and range from parallel (class 1B) to nearly similar shapes (class1C-3) (Ramsay, 1967, pp. 365–387). Folding thus involved buckling modified by superimposed, more homogeneously distributed strains, which transformed the folds into “flattened” isoclines (Fig. 5). Where early folds have large amplitudes, they define fold nappes, which are commonly spatially associated with regional layer-parallel faults (Fig. 5). Combined, the composite transposition foliation (S_m), the early folds and associated faults have been interpreted as the product of a single progressive deformation, referred to as D_m.

The main composite transposition foliation (S_m) is made up of compositional layering (S_0) and a spaced schistosity (S_e) parallel to it. S_e has no apparent relationship to folding, because it is consistently folded by F_1 and F_2. In thin section, S_e is commonly differentiated into mica-rich domains and quartz and feldspar-rich microlithons (Fig. 4B). The foliation anastomoses around feldspar and quartz porphyroclasts and locally preserves fish-shaped micas and oblique foliations defined by quartz. These characteristics indicate that S_e is a tectonic foliation, not a transposed and metamorphically enhanced bedding structure related to compaction and diagenesis. S_e commonly contains a lineation of streaked-out feldspar, quartz, calcite or mica aggregate, which is parallel to the direction of finite extension, defined by boudinaged and pulled-apart veins. Quartz porphyroclasts are generally completely recrystallised, but their ghost outlines can still be recognised from elongated aggregates of new grains preserving an orientation family. Quartz commonly preserves evidence for a penetrative, pre-F_2 phase of dynamic recrystallization, mainly involving subgrain rotation recrystallization. The quartz fabric also experienced a major post-F_2 phase of grain boundary area reduction, which led to a progressive destruction of the serrated grain boundaries to more elongated polygonal shapes. The phyllosilicates that define S_e (chlorite, phengite and/or biotite) were kinked during both F_1 and F_2 and recrystallised by kinkband boundary migration and subsequent annealing (compare Williams et al., 1977). This process locally led to a new axial plane schistosity, which is typically restricted to the fold hinges (Fig. 4B). Relicts of old kinks are absent within S_m along the long limbs of the folds, suggesting that development of the axial plane foliations and kinking was relatively late with respect to fold formation (see Williams and Jiang, 2001). S_m is thus mainly an old tectonite fabric (S_e) that has been transposed concomitant with recrystallization of the minerals that define it. The overall contribution from newly developed axial plane foliations during F_1 and F_2 thus appears minor.

Quartz and/or quartz-feldspar veins were introduced during the deformation and are relative strain markers, because they are commonly intensely folded and/or extensively boudinaged with quartz- and/or feldspar-rich-boudins transformed into isolated porphyroclasts (Fig. 4A) in zones characterised by high attenuation.

The early folds associated with development of S_m are commonly asymmetrical and occur on all scales. They generally have a westerly vergence. F_1 folds are generally true isoclines and where refolded by F_2, are generally tighter and longer-limbed than the latter (Figs. 4E and 6A). Fold interference patterns vary from fishhook to mushroom types. However, locally both fold generations have the same style and hence can only be separated with confidence where overprinting relationships are present. Where overprinting relationships are missing, the composite folds are referred to as F_{1-2} or early folds. Early folds vary from plunging inclined to rare reclined. Locally sheath-like structures are developed (Figs. 4D and 6D). F_2 folds refold the mineral/stretching lineation (L_m) and are generally curvilinear (Fig. 4D). The F_2 fold profiles are more open and their hinge lines generally more inclined to the stretching lineation than F_1 (Fig. 7). The stretching lineation and $F_{1/2}$ hinge lines define

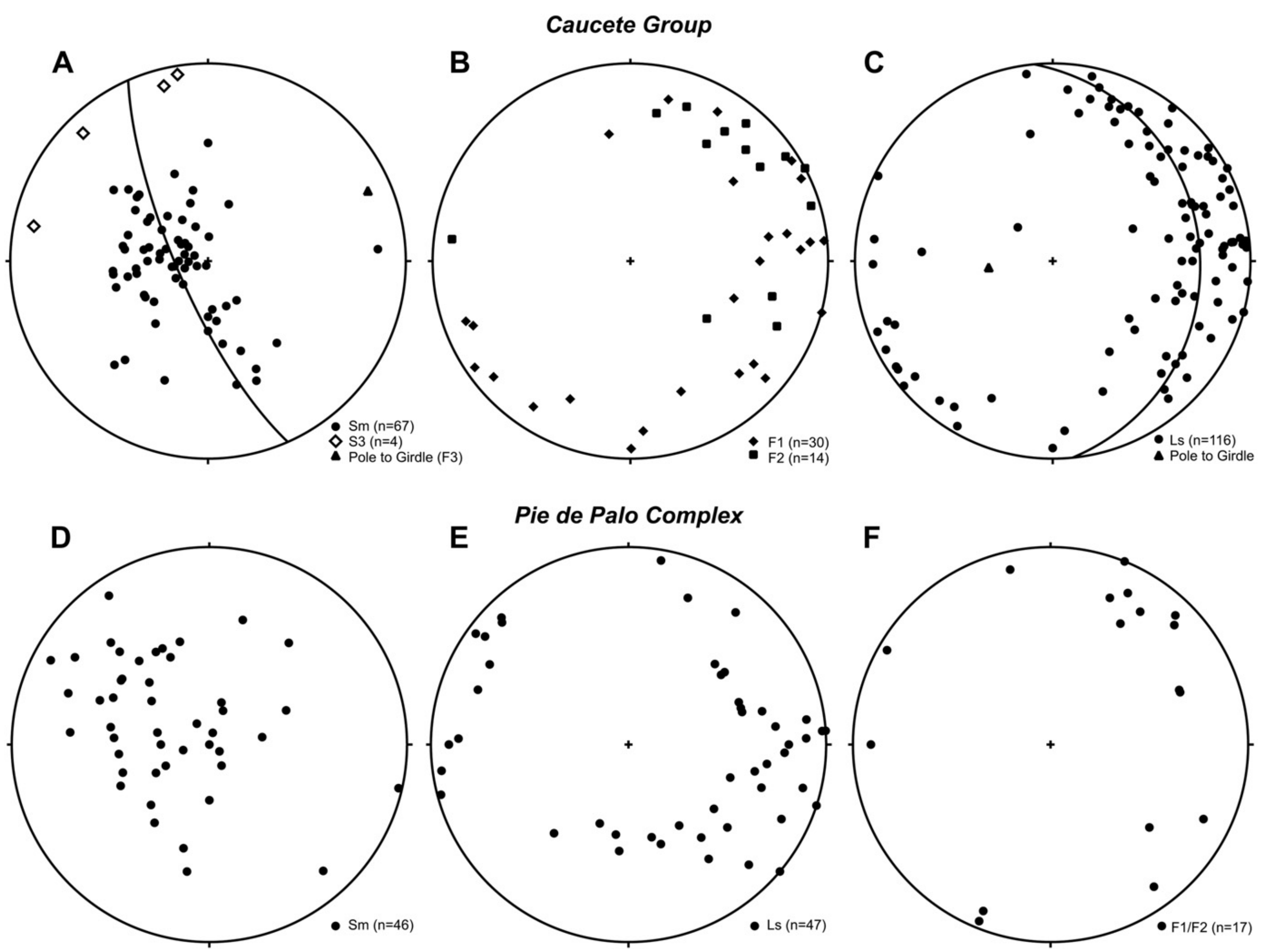

Fig. 7. Lower hemisphere equal area projections with orientation data. A) Poles to S_m forming a partial girdle due to refolding by macroscopic ENE-plunging F_3 folds. S_3 (open diamonds) is the measured orientation of the axial surface of small-scale F_3 folds. A S_3 cleavage generally has not developed; B) plunge of mesoscopic F_1 (diamonds) and F_2 (squares) folds. F_2 folds are generally slightly more open than F_1 and more inclined to the stretching lineation; C) plunge and spread of the stretching lineation (L_s), forming a girdle with its maximum in the eastern quadrant. The pole coincides with the average orientation of S_m ($\sim 20°$ dip to the east). D, E, and F are the same for the Pie de Palo Complex.

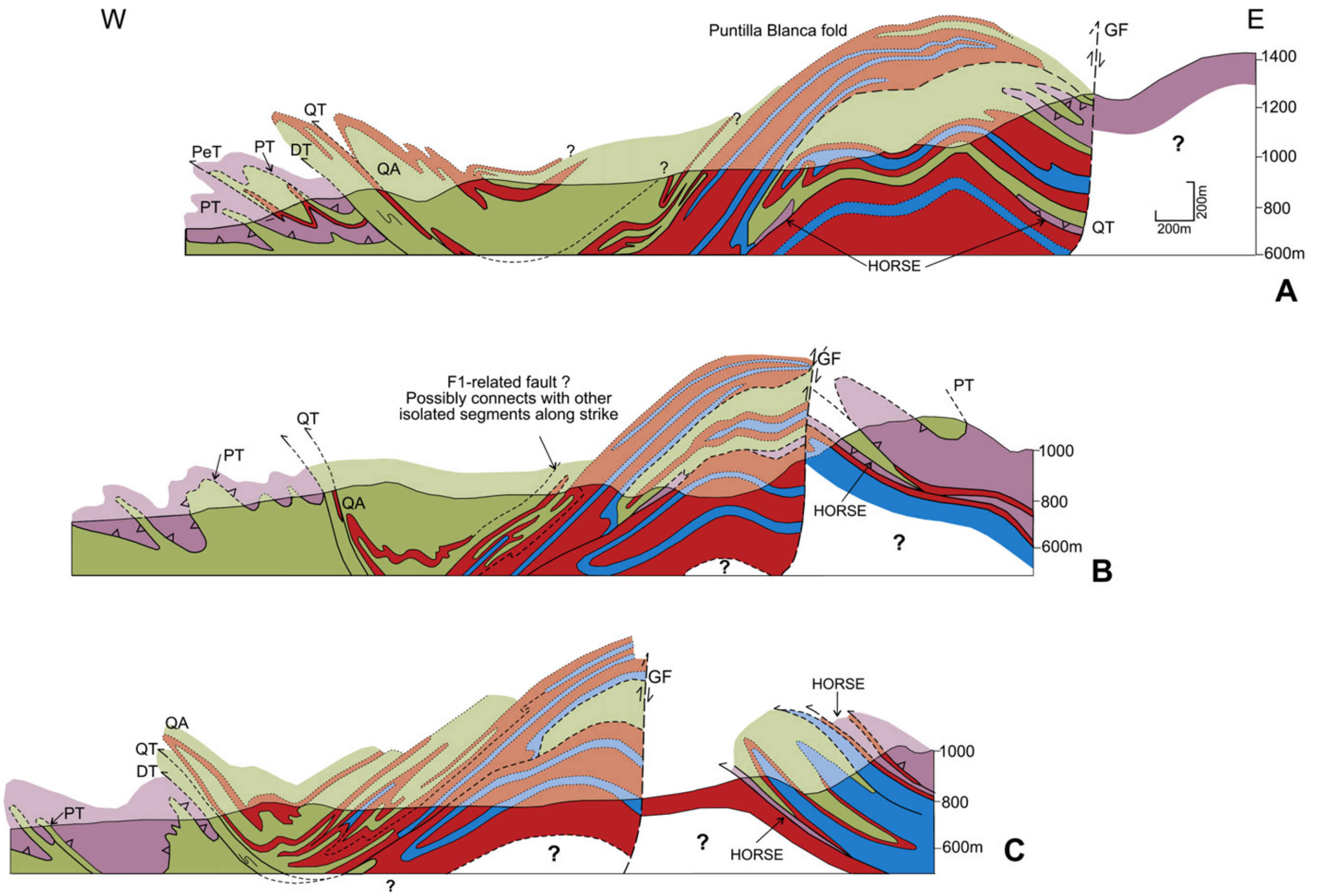

Fig. 8. Structural profiles drawn along lines A, B and C in the southern part of Fig. 2 (south of quebrada Las Burras). Colours of units same as in Figs. 2 and 6. Projections of structures to depth are interpretative. Abbreviations are the same as in Fig. 6. Additional abbreviations: GF = Gato fault; PeT = Pecan thrust (forms part of Pecan panel).

a girdle that lies in S_m, with their orientation becoming more parallel to a stretching/mineral lineation (L_m) where the folds progressively tighten or culminate in sheath folds (Fig. 6C and D). L_m has a maximum in the easterly quadrant (Fig. 7), which we interpret as the orientation of the overall tectonic transport vector associated with the west-directed non-coaxial flow responsible for progressive rotation of the hinge lines and D_m structures in general.

F_3 structures, high-level, upright non-cylindrical open to close, mainly shallowly east northeast plunging folds (Fig. 4F), refold all D_m structures, as reflected in the partial girdle displayed by S_m (Fig. 7). F_3 structures commonly lack an axial plane foliation, and display varying trends, ranging between north and east. In several places this has produced an open dome and basin like geometry in S_m (Figs. 2 and 4F). The dome and basin geometry of S_m combined with the young, rugged topography creates a complex outcrop pattern characterised by numerous outliers and/or klippen that can only be mapped by tracing contacts along their full length. Near the sub-vertical Gato fault, F_3 folds become tighter and trend ENE-WSW parallel to the fault, suggesting F_3 folding and Gato faulting are related. The kinematics of the Gato fault are uncertain due to poor exposure, but the major sand-filled depression, which marks its trace, is spatially associated with hydrothermal mineralization and hot springs, suggesting this fault is still active. The geology on opposite sides of the fault suggests that the amount of strike-slip translation cannot be more than a few kilometres. Spatial relationship between the fault and tightening and rotation of F_3 folds suggests the Gato fault zone accommodated a component of shortening across it, which probably expressed itself by a component of reverse SE-directed motion, which is consistent with the tectonostratigraphic mismatch observed across the fault (Figs. 2 and 8).

6. Deformation history of the Pie de Palo Complex

The Mesoproterozoic rocks of the Pie de Palo Complex are juxtaposed with the Caucete Group along the Pirquitas thrust (Ramos et al., 1998; Vujovich et al., 2004; Chernicoff et al., 2009), a major, shallowly to moderately-steep, east-dipping structure characterised by a belt of highly deformed tectonite and mylonite hundreds of meters thick in the hangingwall. Because it juxtaposes rocks of very different compositions and colour, the thrust dominates the landscape of the western Sierra de Pie de Palo. The rocks of the Pie de Palo Complex in this region consist mainly of dark amphibolites, commonly garnet-bearing, with minor ultramafic lenses and tonalite sills/dykes (Vujovich and Kay, 1998; Vujovich et al., 2004), and rare intercalations of metasedimentary rocks, including marble. Well-developed zones of retrograde chlorite-and/or talc-serpentinite schist and fault gouge occur near its structural base. Thrust-related mylonites contain syn-tectonic muscovite granite and pegmatite sheets, which crosscut S_m in the host amphibolite, but are also cut by it and deformed within it into intrafolial folds and boudins. These granite/pegmatite sheets are absent in the Caucete Group, suggesting they intruded before final juxtaposition of these two units along the Pirquitas thrust. U–Pb zircon dating of metasedimentary intercalations demonstrate that they are generally significantly younger (≤665 Ma) than the enclosing amphibolite (~1200 Ma), indicating that the interleaving is tectonic and probably Paleozoic in age, consistent with radiometric age dating of the metamorphism (Casquet et al., 2001; Vujovich et al., 2004; Mulcahy et al., 2007; Morata et al., 2010). The structural history of the Pie de Palo Complex is similar to that of the Caucete Group, that is a domainal schistosity and stretching lineation folded by two generations of tight to isoclinal asymmetrical folds (Fig. 6B and E). Where the two units occur adjacent to each other, structures in the Pie de Palo complex are coaxial and coplanar with those in the underlying Caucete Group (Fig. 7). In addition, psammites of the El Quemado Formation were locally structurally interleaved with the Pie de Palo rocks on mesoscale during F_1 (Fig. 6E) in the tectonites and mylonites that define the Pirquitas thrust. Emplacement of the Pie de Palo Complex along the Pirquitas thrust therefore appears to form part of the tectonic events responsible for deformation of the Caucete Group.

7. Structure and kinematics of the Pirquitas thrust

Geometrical relationships and other observations discussed in more detail below suggest that the Pirquitas thrust is a long-lived structure that accommodated significant low angle transport, juxtaposing rocks of contrasting age and composition before, during and/or after large scale F_{1-2} refolding and associated shearing. Tectonic repetition, formation of horses and local inversion of the tectonostratigraphy (Figs. 2 and 8), all attest to a long-lived history. As a result of the deformation, the Pirquitas thrust and the Pie de Palo Complex became separated into two major structural panels: the Pirquitas and. Pecan panels (Figs. 2 and 8) and several small horses. The fault is exceptionally well-exposed in quebradas Las Pirquitas, La Paz, El Molle and Pecan and surrounding areas where topographic relief as well as klippen (Fig. 2) indicate at least several kilometres of motion along a low angle detachment (Fig. 5). The Pirquitas thrust was folded locally by large amplitude F_2 folds and finally folded by F_3 into open, large wavelength structures (Figs. 6F and 8). As a result its dip locally varies considerably. However, its overall exposed enveloping surface is shallow (Figs. 5, 7 and 8). Shear sense indicators in mylonites associated with the thrust, such as shearbands, stair-stepping wings, winged porphyroclasts with asymmetrical tails, asymmetry of mesoscopic folds and the obliquity of the finite extension direction of boudinaged veins with respect to S_m confirm the fault accommodated a major component of westerly thrust translation (Fig. 9a and b). However, we also have observed very rare, normal shear sense indicators in schists in a few localities along this fault. These shearbands overprint the early folds and hence, must have formed relatively late. Possibly they are related to exhumation. In the southern part of the area, along the northern arm of quebrada El Gato, rocks of the Pie de Palo Complex occur as small isolated tectonic lenses of meter to hectometer-scale within the Caucete Group along the contacts between its various units (Figs. 2 and 8). These lenses must be tectonic intercalations (horses) and mark old, remobilized movement zones in the Caucete Group. Along the eastern rim of the Pecan panel (Figs. 2 and 8), the Caucete Group was thrust upon the Pie de Palo Complex with its immediate structural footwall (Quemado Formation), exposed in the core of F_2 antiforms, by the relatively late Desecho thrust (see below).

The basal, thrust-related tectonites of the Pirquitas panel were consistently folded with the underlying flaggy El Quemado psammites into west-vergent asymmetrical F_2 folds on all scales. The relative F_2 age of these folds was established on basis of preserved F_1–F_2 overprinting relationships. The asymmetry of F_2 (Figs. 2, 8 and 10) indicates that the Pirquitas panel is situated on the inverted limb of a large west-vergent, highly overturned F_2 fold cored by the Pie de Palo Complex. This structure must refold the original Pirquitas thrust unless the Pie de Palo Complex was the original stratigraphic basement to the Caucete Group (see discussion below). That this inverted limb was reactivated as a thrust, remobilizing part of the pre-existing Pirquitas thrust, is indicated by the truncation of a pre-existing tectonostratigraphy in the underlying Caucete Group, demonstrated by small klippen of Pie de Palo Complex rocks immediately west of the Pirquitas thrust that overstep imbricated units of the underlying Caucete Group (Figs. 2 and 5). Hence, final movement of the Pirquitas thrust must have been relatively late in the deformation history. Part of the late movement history is preserved in strongly retrograde serpentinite and/or chlorite-schists near the base of the Pirquitas panel where shear sense indicators such as chlorite-rich shearbands overprint the higher grade metamorphic assemblage.

8. Large-scale structure of the Caucete Group

We have divided the area occupied by the Caucete Group in our study area into a northern and southern part, roughly separated by quebrada El Molle (Fig. 2), on basis of the dip of the Pirquitas thrust and the enveloping surface of the underlying Caucete Group tectonostratigraphy. In the northern part, the Pirquitas thrust and the underlying Caucete Group tectonostratigraphy dips 25–50° to the east, and formations of the Caucete Group define a linear outcrop pattern. Some of the units observably terminate in highly flattened, isoclinal folds (Fig. 5), suggesting that most repetitions in stratigraphy are also due to such folds. The near-parallelism between the ground surface and the fold hinge lines means that exposed hinges are rarely seen on horizontal surfaces, and generally can only be observed on inaccessible sub-vertical cliffs. Folds alone cannot adequately explain the observed geometry and tectonostratigraphy, which requires a combination of isoclinal folding and thrusting. Thrusts were recognised by (a) marked changes in thickness of units accompanied by low angle truncations in stratigraphy and/or structure (Fig. 2); (b) presence of small, isolated tectonic lenses (horses) of Mesoproterozoic Pie de Palo Complex within Caucete Group rocks (Fig. 8) and (c) evidence of shear sense indicators (Figs. 6c and 9a–d) and/or strain localization where there are relative strain markers such as pulled-apart veins and flaggy/glassy mylonites (Fig. 4A and D). Our interpretation of the structure of the northern part of the area is displayed in Fig. 5. Isoclinal synforms are mainly occupied by marble of the Angacos Formation and antiforms by the El Desecho and Quemado formations, indicating that the structures in this part of the Caucete Group are westward and upward facing according to our stratigraphy. Extrapolation of the structures to depth is poorly constrained because of the curvilinear nature of the folds some of which are probably sheath-like folds. Hence, the cross sections are interpretative at depth. Regional isoclinal folds generally have relatively high amplitudes and short wavelengths, which is consistent with the very high strains recorded by pulled-apart veins and/or other strain markers throughout the Caucete Group. Pulled-apart vein segment show separations exceeding 1000% extension in many places (Fig. 2), suggesting shortening strains in excess of 90 percent in these localities. We interpret these isoclines mainly as F_2 structures, because on a small and regional scale they seem to refold F_1 isoclines. Very low angle truncations and/or excision of units along the limbs of several of these F_2 isoclines (Fig. 9D) indicate strong attenuation and/or faulting. These faults are generally narrow, relatively discrete structures, characterised by very flaggy, in places glassy ultramylonites with little or no evidence for brittle deformation. If these shear zones ever narrowed down into discrete brittle faults, the brittle deformation is now healed. Shear sense indicators, where present, confirm these faults accommodated shear, which generally is thrust-like, with movement preferentially localised along the common, overturned

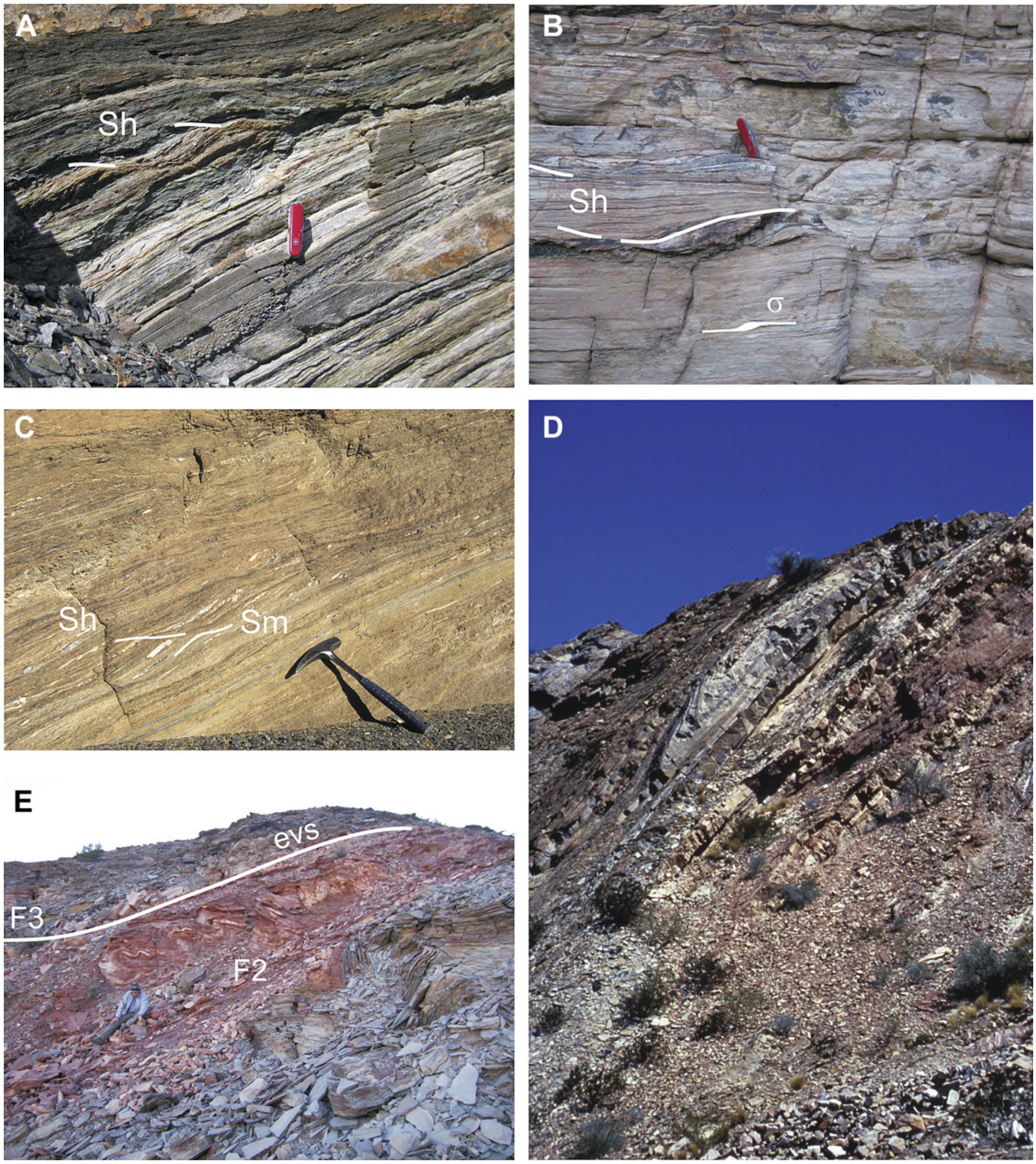

Fig. 9. A) Mafic mylonite of the Pirquitas shear zone (Pirquitas panel). Shearbands (Sh) indicate west-directed tectonic transport (to the right); B) pre-F_2 mylonitic Quemado psammite immediately below Pirquitas thrust, Pecan panel. Shearbands (Sh), oblique foliations and winged σ-type porphyroclasts derived from boudinaged veins indicate westerly transport (written on rocks above knife); C) shearbands (Sh) and fish-shaped boudinaged veins (west to the right) in El Desecho mylonite at contact with overlying Molle nappe; D) truncated F_2 synform in Angacos Formation overridden by minor west-directed (to the right) thrust fault in overlying El Desecho Formation rocks; E) train of nearly upright to recumbent west-verging F_2 folds in El Desecho Formation red beds in the immediate hangingwall of the Quemado thrust, quebrada El Desecho. The enveloping surface (evs-white line) to F_2 is shallowly dipping to the west (left) because of refolding by open F_3 folds (see also Figs. 2 and 6c). Note that El Desecho Formation overlies the Quemado (green) psammites and hence, the folds are upwards facing here according to our stratigraphy. M. Naipauer for scale.

limb of fold pairs. However, in a few places, such as the upper limb of the Quemado antiform (Figs. 2 and 5), we also observed truncation and movement along the normal limbs of the isoclines. We traced the major isoclines and associated thrusts from the northern to the southern part of the area, where on approaching the Gato fault they become progressively refolded by the upright, NE-trending F_3 structures. Our mapping delineated three regional syn- to post-F_2 overthrust zones in the Caucete Group, named after the *quebradas* (dry-creeks) where these structures are relatively well-exposed: as the Molle, Quemado and Desecho thrusts (Figs. 2, 5 and 8), which will be further discussed below. Other thrusts were recognised (e.g. Pecan thrust), but they either accommodate little movement or are subsidiary splays of other thrusts and are not significant for understanding the kinematic evolution of the structures and will not be discussed in detail.

The Molle thrust sheet is situated immediately below the Pirquitas panel and hence is situated in the immediate footwall of the Pirquitas thrust, where this delineates the inverted limb of a large F_2 fold (Fig. 10). It comprises very flaggy, mylonitic psammite of the El Quemado Formation (Fig. 4D) and intercalated rocks of the La Paz Formation, but does not contain rocks of the El Desecho or Angacos formations. The Molle thrust sheet originates at the lower limb of an asymmetrical F_2 fold in the Pirquitas panel as a splay of the remobilized Pirquitas thrust (Figs. 5 and 10). We interpret this

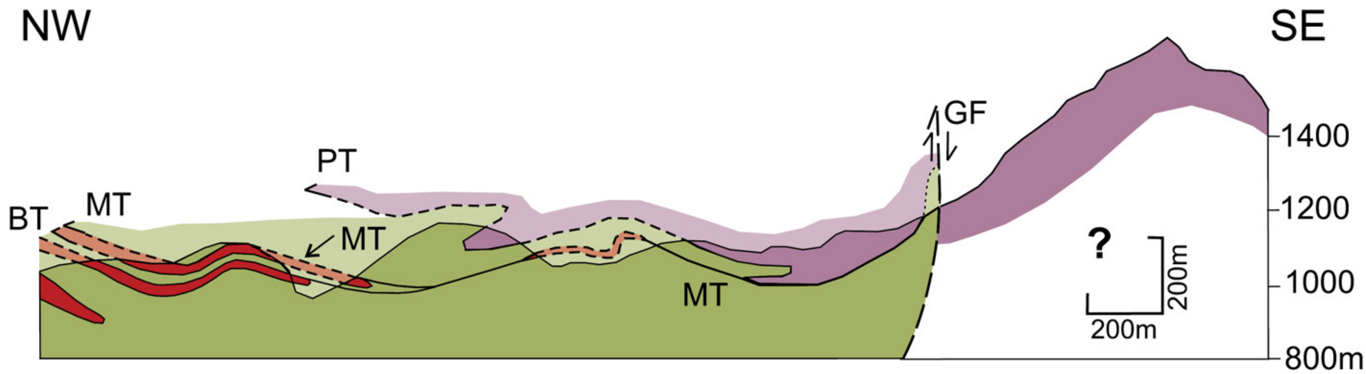

Fig. 10. NW-SE profile (Profile D in Fig. 2) through the Pie de Palo Complex, the underlying Molle nappe and Burras thrust sheet in the southern part of the area. The Burras thrust sheet is truncated by the Molle thrust in a geometry that resembles a rejoining imbricate. Abbreviations and colours of units are the same as in Figs. 2, 7 and 8. The sheath fold of Fig. 5d was mapped where the Burras and Molle thrust sheets become so close to each other that they appear to represent one shear zone.

thrust sheet to be a large horse that was accreted to the base of the Pie de Palo Complex early during D_m, before or during F_2. Combined these relationships suggest that the Molle thrust sheet is a separate nappe, relatively far-travelled with respect to the other F_2-associated structural panels in the Caucete Group.

The structure of the southern area is more complicated than the northern one. One significant complexity is displayed by the west-verging, isoclinal Quemado antiform (Figs. 2, 5 and 8), when traced from north to south. Its isoclinal hinge is exposed on the ridges above quebradas El Quemado, El Desecho and El Gato. F_2–F_1 overprinting relationships suggest that the Quemado antiform is a F_2 structure. Based on our interpreted tripartite stratigraphy, the fold is upwards and westward facing in the northern area, where its lower inverted limb appears to be largely cut-out by the Quemado thrust, although this fault does not appear to have accommodated significant motion (Fig. 5). In the southern part of the area, the Quemado thrust seems to root into the Desecho thrust, suggesting it is a splay. Here, the Quemado antiform changes from upward to downward facing and its inverted lower limb is partially preserved in the ridge above the northern arm of quebrada El Gato, north of the Gato fault (Fig. 2). The latter terminates in a long-limbed isocline, cored by the Desecho Formation and thin, folded bands of Angacos marble (Fig. 8). We call this structure the Puntilla Blanca fold after a nearby, abandoned marble quarry. Its southern, lower limb is truncated by the Desecho thrust. The change from upwards to downwards facing, regardless how the tripartite stratigraphy is interpreted demands that the Quemado antiform refolds earlier attenuated F_1 isoclines unless there are cryptic, complicated layer-parallel faults within the Caucete Group (Fig. 8) that predate F_2. We cannot distinguish between these alternatives with the present data set, but most of the pre-F_2 structural repetitions could be ascribed to large, partly dismembered F_1 folds. We propose that the Puntilla Blanca fold is such a F_1 structure, although we can't prove or disprove this on basis of overprinting relationships.

Structural interpretation of the southern part of the area is complicated by the high angle Gato fault, with poorly known offset, which truncates the F_2 structures in its hangingwall and footwall. However, the major F_2 folds recognised in the southern arm of quebrado El Gato, south of the Gato fault (its interpreted footwall), are also downward facing, whereas the Pirquitas thrust at the base of the Pirquitas panel is still situated on the inverted limb of a large F_2 fold (Fig. 8), which we interpret to be the same structure as is inferred to the north of the Gato fault. In addition, the Caucete Group in the footwall of the Pirquitas thrust in the Pecan panel, which includes the Pecan thrust sheet, is also downward facing on basis of stratigraphy.

9. Metamorphism

Dalla Salda and Varela (1984) made a petrographic and paragenetic study of metamorphism in the southern Sierra de Pie de Palo, dividing the rocks into (1) 'Caucete metamorphics' roughly equivalent to our Caucete Group but also including the Difunta Correa sequence, (2) 'Central schists', approximately equivalent to the mylonites of our Pie de Palo Complex, and (3) granitoid rocks. On the basis of a compilation of experimental data by Winkler (1976) they deduced peak metamorphic pressures of 5–10 kbar, with peak temperatures increasing from west to east from about 450 °C to more then 650 °C.

The dominantly calcareous or quartzose bulk compositions of the metasedimentary Caucete Group produced metamorphic assemblages mainly comprising quartz, feldspar, carbonate, chlorite, muscovite, biotite and epidote. Locally mylonitic psammitic rocks of the El Quemado and La Paz formations, in the Molle nappe contain greenish blue hastingsitic amphibole and and/or Ca-rich garnet (representative analyses in Table 1). Garnet poprhyroblasts grew before the end of F_2, because S_2 is deflected around them in the fold hinges (Fig. 4B). Elsewhere garnets overgrew S_m, which also wraps around them, suggesting that overall they grew during D_m, with peak temperatures probably reached relatively late, during or after F_2, consistent with extensive recrystallization of quartz, feldspar and F_2-kinked biotite and phengite. We found no microstructural evidence of more than one extended period of metamorphism.

Thermobarometric calculations on three samples of the Caucete Group in the Molle nappe containing garnet and amphibole, using compositions of minerals in contact (Table 2) and version 3.26 (2008) of the program THERMOCALC (Holland and Powell, 1998), gave results lying generally within the range 450–600 °C and 8–13 kbar in agreement with the pioneering estimates of Dalla Salda and Varela (1984). A sample with garnet strongly, but continuously zoned from Ca-rich cores (>9.0% CaO) to Ca-poor rims (<5%) contained the assemblage garnet–biotite–muscovite, which is insufficient for complete P–T determination. The rim composition of garnet gave a good T determination of about 540 °C (Table 2). It is uncertain that the calculated P–T conditions are representative for the whole of the Caucete Group, since the Molle nappe (Figs. 2, 5 and 10) appears to have been accreted to the Pie de Palo complex in the Pirquitas panel before the latter was emplaced on the underlying nappes during late F_2 deformation. The underlying nappes may thus have experienced a somewhat different metamorphic history.

Metamorphic conditions of amphibolites of the Pie de Palo Complex in the Pirquitas panel in and above the Pirquitas thrust were tested using four samples of garnet amphibolite from various

Table 1
Representative analyses of minerals of Caucete Group and Pie de Palo Complex. Ferric iron assigned to electron microprobe analyses following the scheme of Holland and Powell (1998).

	Caucete Group, specimen vvl24						Pie de Palo Complex, specimen vvl02				
	Garnet	Amph	Chl	Musc	Plag	Epid	Garnet	Epid	Chl	Amph	Plag
SiO_2	36.39	38.04	23.04	47.38	66.36	37.83	36.37	38.50	23.00	38.45	67.06
TiO_2	0.07	0.25	0.08	0.10	0.00	0.13	0.19	0.16	0.09	0.27	0.00
Al_2O_3	20.40	17.96	20.41	32.46	20.30	27.73	20.70	27.14	19.80	17.43	19.90
FeO	31.99	22.47	31.28	2.49	0.08	6.66	33.75	7.00	31.55	22.51	0.07
MnO	0.81	0.04	0.08	0.01	0.00	0.01	2.63	0.02	0.09	0.06	0.00
MgO	0.63	3.15	9.53	1.55	0.00	0.02	0.77	0.01	8.89	3.69	0.00
CaO	9.08	11.15	0.14	0.07	1.04	23.70	4.62	23.52	0.43	10.75	0.66
Na_2O	0.07	1.84	0.10	0.80	10.89	0.06	0.00	0.01	0.00	1.91	10.88
K_2O	0.03	0.66	0.10	9.85	0.08	0.02	0.00	0.01	0.13	0.70	0.05
Totals	99.77	95.66	84.75	94.72	98.75	96.83	99.04	97.11	83.99	95.99	98.63
Si	2.947	5.981	2.618	3.180	2.942	2.983	2.985	3.025	2.651	6.012	2.969
Ti	0.004	0.030	0.007	0.005	0.000	0.008	0.012	0.009	0.008	0.032	0.000
Al	1.947	3.329	2.734	2.569	1.061	2.578	2.003	2.514	2.691	3.213	1.039
Fe^3	0.165	0.127	0.053	0.002	0.003	0.402	0.003	0.430	0.010	0.241	0.003
Fe^2	2.003	2.826	2.913	0.138	0.000	0.037	2.313	0.031	3.032	2.703	0.000
Mn	0.056	0.005	0.008	0.001	0.000	0.001	0.183	0.001	0.009	0.008	0.000
Mg	0.076	0.738	1.614	0.155	0.000	0.002	0.094	0.001	1.527	0.860	0.000
Ca	0.788	1.878	0.017	0.005	0.049	2.003	0.407	1.980	0.053	1.801	0.031
Na	0.011	0.561	0.022	0.104	0.936	0.009	0.000	0.002	0.000	0.579	0.934
K	0.003	0.133	0.015	0.844	0.005	0.002	0.000	0.001	0.019	0.140	0.003
Sum	8.000	15.608	10.00	7.003	4.996	8.025	8.000	7.995	10.00	15.589	4.979
Oxygen	12	23	14	11	8	12.5	12	12.5	14	23	8
n	14	10	2	2	10	2	11	7	3	22	8

n = number of analyses averaged.
The complete data set is available on request from the authors.

structural levels in the hangingwall tectonites (Table 2). Relationships between deformation and metamorphism mirrors that observed in the Caucete Group. These samples gave P–T estimates in the same range as specimens from the Caucete Group of the Molle nappe. One sample contained garnet strongly but continuously zoned from Ca-rich cores to Ca-poor rims and amphibole slightly zoned in Ca in the same sense. Use of rims with rims and cores with cores gave essentially the same P–T values. Mulcahy et al. (2007) made three determinations on the Pie de Palo complex in the northern part of the area we investigated, which averaged 500 °C ± 20 8.5 ± 0.6 kb. Because the range of P–T in the Pie de Palo Complex brackets conditions in the Molle nappe (Fig. 11), we interpret these results to indicate that at least the Molle nappe, and possibly all of the Caucete Group had been amalgamated with the Pie de Palo Complex prior to peak metamorphism preserved in the rocks and then more or less remained together. This is consistent with our structural interpretations, which require that these two units were amalgamated before or early during F_1 folding and F_2-associated imbrication.

Table 2
P–T estimates from minerals of the Caucete Group and Pie de Palo Complex.

	T	σ	P	σ	
Caucete Group					
vvl2	469	32	8.6	2.1	Mylonite
vvl5	546		9.0		Mylonite
vvl69	452	26	13.2	1.2	Mylonite
vvl82	487	26	12.0	2.1	
Pie de Palo Complex					
vvl24	480	34	10.9	0.9	Garnet amphibolite
vvl61	411	40	12.8	0.8	Garnet amphibolite
vvl72	566	41	8.1	2.7	Garnet amphibolite
vvl102	524	29	10.9	0.7	Garnet amphibolite

P–T estimated using the version 3.26 of THERMOCALC (Holland and Powell, 1998). σ is one standard deviation. Pressure for vvl5 is assumed. dP/dT is 3.7°/kbar.

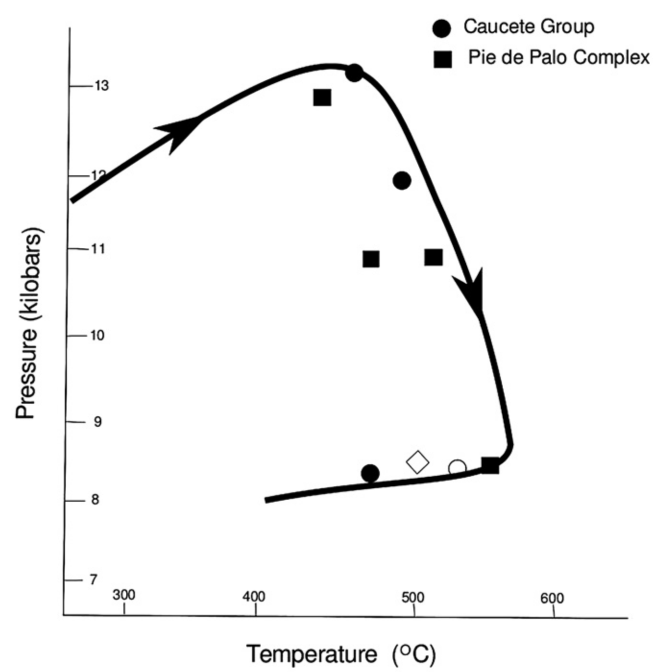

Fig. 11. Part of the estimated P–T path of the Caucete Group (Molle nappe) and Pie de Palo Complex. Dots are from the Molle nappe of the Caucete Group, whereas the squares represent tectonites in the overlying Pirquitas panel of the Pie de Palo Complex (Table 2). The unfilled dot is sample vvl 5, for which only the temperature could be determined. A pressure of 9.0 kbar is assumed. The diamond represents the average of Mulcahy et al's (2007) determinations for the Pie de Palo Complex. Mineral assemblages show that all plotted samples lie in the epidote amphibolite facies of Evans (1990). We believe the epidote blueschist–epidote amphibolite boundary for the Sierra Pie de Palo rocks to be shifted to temperatures lower than those calculated by Evans (1990) due to some combination of very aluminous epidote composition, CO_2 content in the vapour, and oxygen fugacity. Part of the estimated P–T path of the Caucete Group (Molle nappe) and Pie de Palo Complex.

The metamorphic conditions determined by us would lie within, or close to, epidote blueschist facies for iron-rich and aluminum-poor basaltic compositions with a vapour phase poor or lacking in CO_2 (van Staal et al., 2008; Evans, 1990; Fig. 6d–f). The rocks of the Sierra de Pie de Palo examined by us lack the blue sodic amphiboles typical of blueschist facies, although the activity of glaucophane end member in the amphibole is high. In specimen vvl2, for example the activity of glaucophane is calculated to be 0.0231, compared to pargasite 0.0071, ferroactinolite 0.0036 and tremolite 0.0022, the three end members with the next highest activities. We deduce that peak metamorphic conditions lay in epidote amphibolite facies, typified by calcic and aluminous amphiboles, rather than in blueschist facies. Evans (1990) calculated that the P–T range of epidote amphibolite facies is greatly expanded toward lower temperature at expense of the blueschist facies for relatively magnesian amphibole and aluminous epidote. The amphibole compositions measured by us are relatively iron-rich, but the epidote has higher aluminum than any used in Evans (1990) calculations. Evans (1990) also deduced that the epidote blueschist–epidote amphibolite facies boundary would move toward lower temperature as oxygen fugacity decreased and the amount of CO_2 in the vapour phase increased. We conclude that the epidote blueschist–epidote amphibolite facies boundary in the rocks of the Sierra de Pie de Palo lay at temperatures lower than those calculated by us due to some combination of very aluminous epidote composition, CO_2 content in the vapour, and oxygen fugacity.

It is surprising that little-zoned high-pressure assemblages spanning a range of more than 4 kbar are well preserved in a relatively thin package of highly sheared rocks of the Pirquitas panel and underlying Molle nappe. Rejecting the idea of large-scale cryptic dislocations within this thin package, for which there is no observational evidence, these data appear to require that mineral assemblages must have been effectively quenched/locked in at various metamorphic conditions, that is captured various parts of the P–T-t path, due to some combination of dehydration, relatively rapid return to cool, lower-pressure conditions, and progressive localization of deformation, leaving the bulk of the rock essentially impervious to further reaction. Such phenomena have been documented in ultra high-pressure terranes (Ernst, 2001). In such cases, none of the P–T determinations necessarily give the peak metamorphic conditions, but the closest (minimum) approximation would be given by the envelope around the determinations (Fig. 11).

The high pressures and modest temperatures returned by the Caucete Group indicate that metamorphism took place during the subduction of a cold sedimentary slab in an A-subduction zone setting. Plotted in P–T space (Fig. 11), the data indicate a clockwise P–T trajectory reaching a peak pressure of roughly 13 kbar at 450 °C, and then heating as pressure declined, reaching a maximum temperature of roughly 500–560 °C at pressures of 8–10 kbar, indicating relaxation of depressed geotherms associated with subduction. This is simply explained by continuous subduction of a cold sedimentary slab (Caucete Group) after amalgamation with the Pie de Palo Complex in the subduction channel, followed by regurgitation due to the underthrusting of progressively more buoyant Precordillera crust and/or slab breakoff.

We draw attention to the concentration of data in the range 8–9 kbar with T varying from 565 to 465 °C, suggestive of nearly isobaric cooling. Such a trend could be produced by thrusting of the metamorphosed Pirquitas panel and Molle nappe over a cooler slab of Caucete Group, a process which could reactivate metamorphic reaction due to the associated shearing and infiltration by water from the dehydrating underthrusted rocks. Because our data do not capture the lower pressure (<8 kbar) part of the exhumation path of the high-pressure rocks (Fig. 11), we have few constraints on how and when exhumation was accomplished. Marked retrogression of amphibolites and associated ultramafic rocks to chlorite- and/or serpentine-rich greenschists along the base of the Pirquitas thrust and local narrow ductile-brittle or brittle fault gouges (Fig. 6E) suggest some exhumation was accommodated by highly localised deformation at low metamorphic grade. Erosional unroofing was doubtless important, but the relative importance of the various processes is unknown.

Previous studies have presented various metamorphic crystallization and/or cooling ages, ranging from 515 to 396 Ma (Ramos et al., 1998; Mulcahy et al., 2007; Morata et al., 2010). However, metamorphism is most reliably constrained by U–Pb ages of metamorphic zircon, which are restricted to rocks of the Pie de Palo complex and the Difunta Correa unit. Both Casquet et al. (2001) and Vujovich et al. (2004) documented metamorphic zircon rim ages of 460–455 Ma. Considering the evidence for similar P–T paths and their amalgamation early during the metamorphic and deformation history (pre-F_1 and peak metamorphism), these ages should also apply to D_m in the Caucete Group.

10. Interpretation of the macroscopic geometry and evolution of the structures

Structural interpretation of the geometry requires some plausible assumptions, which are as follows: (1) we assume that our stratigraphy and facing of the Caucete Group is correct. (2) We assume that effects of F_3 folding can largely be ignored. Assuming a coaxial deformation path associated with an approximately NNW-SSE shortening, unfolding of these open, generally low strain, upright folds rotates S_m into a tighter cluster with a maximum dipping shallowly to the E or ENE. (3) We assume that all structures formed during a progressive deformation related to east-directed underthrusting (present coordinates) of the Precordillera and Pie de Palo terrane beneath the Famatina arc-forearc system. F_2 folds initially formed with their hinge lines at a high angle to the transport direction and started out as upright folds that were progressively rotated into a more inclined or recumbent position (Fig. 9E) due to accumulating shear strains (Williams and Jiang, 2005). In addition, we ignore minor complications that cannot be resolved with the present data set and possible cryptic structures, such as unrecognised pre-peak metamorphism and annealed faults.

Given these assumptions, any interpretation must explain the following observations. (1) Stratigraphic repetition and overprinting relationships suggest that most mapped macroscopic folds formed during F_2; (2) The geometry and vergence of the large F_2 folds suggest that the Pirquitas panel constitutes the lower limb of a west-verging F_2 antiform, while the structurally underlying Caucete Group is generally upward, not downward facing. The Caucete Group below the Pirquitas thrust in the Pecan panel on the other hand is downward facing and its tectonostratigraphy was assembled before F_2 folding; (3) F_2-related thrusts such as the Desecho thrust locally emplaced young over old; (4) small horses of Pie de Palo Complex occur at the base of a downward facing panel situated structurally immediately below the Puntilla Blanca fold and the Desecho thrust. (5) the Quemado antiform in the southern part of the area changes from upwards to downward facing along the trace of the axial surface. Hence, it locally deformed an already inverted tectonostratigraphy. (6) F_1-related structural interleaving of the Pie de Palo Complex and the El Quemado psammites requires that their juxtaposition (stratigraphic or structural) was in place before the first generation of folding. Two models can be erected to satisfy these constraints.

Model 1 assumes that the Pie de Palo Complex was either the original or structural basement to the Caucete Group (Fig. 12a). This model requires large scale recumbent F_1 folding to create

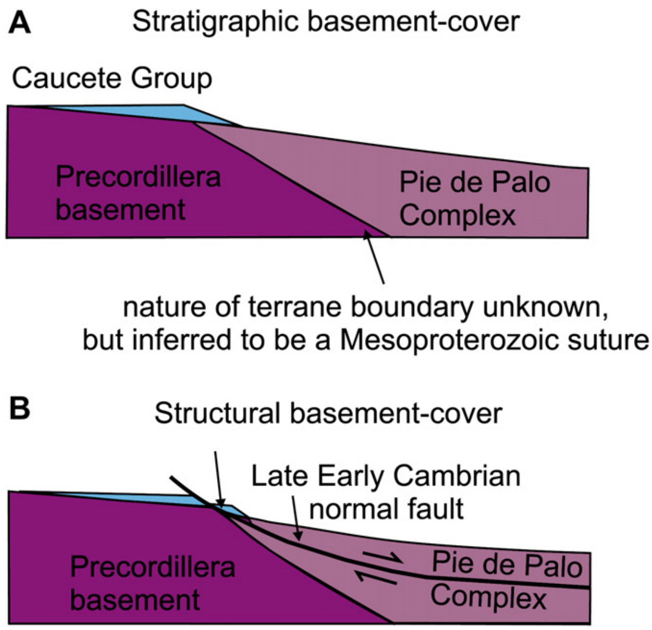

Fig. 12. Two possible scenarios for basement (Pie de Palo Complex) –cover (Caucete Group) relationship necessary for kinematic model 1 (Fig. 13). A) Basement–cover is stratigraphic and the Caucete Group oversteps the inferred Mesoproterozoic suture between the Precordillera and Pie de Palo terranes, which together form Cuyania; B) basement–cover is structural and was established during Early Cambrian extension and rifting that led to departure of Cuyania from Laurentia. Only one extensional fault is shown for simplicity. This extension was in part accommodated at depth by ductile deformation during amphibolite facies metamorphism.

inverted lower limbs prior to F_2 folding. In this scenario, the Puntilla Blanca fold represents a parasitic F_1 structure of the lower limb of a larger recumbent isocline (Fig. 13). The late, F_2-related, Desecho thrust cuts-out parts of the upper limb of the Puntilla Blanca fold and accretes the horses of Pie de Palo Complex to it from a more easterly extension of the Pecan panel. The area east and northeast of the Puntilla Blanca fold is not easily accessible, but exhibits intense attenuation of the Desecho Formation, suggesting the presence of F_1-related faults (Figs. 2 and 13). Although model 1 does not require a thrust at the base of the Pecan panel, the contact is unlikely to represent a basement–cover relationship, as shown by the composition of the Caucete Group psammites, the presence of syn-tectonic muscovite granite sheets in the Pie de Palo Complex tectonites and their absence in the immediately underlying Caucete Group, and the presence of highly sheared rocks everywhere along the contact (Fig. 9B). Either the proto-Pirquitas fault initiated during structural (extensional) underplating of the Pie de Palo Complex to the base of the Caucete Group or initially developed as a thrust along the inverted limb of the west-verging F_1 antiform.

Model 2 assumes that the Pie de Palo Complex was not part of the basement of the Caucete Group. This model assumes that the Pie de Palo Complex was thrust upon the Caucete Group (Fig. 14) prior to F_1 with the pre-F_{1-2} spaced schistosity/differentiated layering S_e developing during this process. The Pie de Palo Complex, the Pirquitas thrust and underlying Caucete Group were folded into large recumbent F_1 isocline(s) akin to model 1 to create an inverted Caucete Group. To place the Pie de Palo Complex of the Pecan panel above the inverted Caucete group on the lower limb of the F_1 folds before F_2, either a pre-F_2 folding phase of imbrication or another generation of folds is required (Fig. 14). In such a scenario, the pre-F_1 asymmetrical west-verging folds could have formed immediately after the early emplacement of the Pie de Palo Complex above the Caucete Group. The rest of the structural evolution of model 2 is identical to the first.

With the present database, we cannot make a definite choice between these two models. Model 2 requires an additional generation of structures for which there is no mesoscopic field evidence. However, taking into account the high strains and structural complexities preserved in the rocks, this would not necessarily be surprising. Model 1 is simple and most consistent with structural evidence, but a stratigraphic basement–cover relationship is not supported by other evidence. Model 1 therefore requires an additional step to generate a structural basement–cover relationship (Fig. 12B). This could be due to extension-related structural underplating prior to subduction, which also has the potential to explain the 515–510 Ma hornblende Ar-ages of Mulcahy et al. (2007) by extension-related amphibolite facies metamorphism of the Pie de Palo Complex.

11. Kinematic model

The metamorphism, geometry and structural relationships require that the Caucete Group and the Pie de Palo Complex were structurally assembled before F_1, either as a result of pre-subduction, Cambrian extension related to rifting and formation of the Laurentian-derived Cuyania microcontinent, or by pre-folding thrusting during the early stages of A-subduction. Subsequent F_1 folding led to large, kilometre-scale fold nappes, the hinges of which are not exposed in our area, and associated parasitic folds such as the Puntilla Blanca fold. These folds probably formed near the time of peak (epidote amphibolite facies) metamorphism. The origin of the pre-folding, penetrative phase of S_m (= S_e) is simply explained by model 2 in which shear related to initial overthrusting of the Pie de Palo Complex, was localised in the proto-Pirquitas thrust zone. The remainder of the two converging units probably deformed by a more coaxial deformation path, which led to formation of the S_e differentiated layering/schistosity as a result of solution transfer creep. S_e was thus analogous to formation of the oblique 'S' fabric of a large S–C structure. Folding during this early thrusting phase could have been inhibited because the rocks were still cold and stiff, making it easier to deform by localised shear on mechanically weakened zones and/or these shear zones also had a thinning (stretching) component. The pre-folding shear model may explain the enigmatic S_1 observed in many orogens. S_e is more difficult to explain in model 1, but could be related to pre-folding shearing, possibly due to remobilization of the postulated proto-Pirquitas fault formed during extension. If such a process took place, it left little or no record in the macroscopic structure. This is not necessarily an argument against it, because such shear zones would have formed prior to peak metamorphism and probably were remobilized and/or completely annealed during F_{1-2} associated dynamic recrystallization and metamorphism. The alternative that S_e could have formed during Cambrian extension and associated vertical thinning is possible for the Pie de Palo Complex, but is highly unlikely for the Caucete Group, which was being deposited during this period (see above). It is difficult to see how the sediments became rapidly buried to sufficient depth in such a scenario to be able to deform by solution transfer creep. The style and nature of F_2 and its associated metamorphism, suggest that they and F_1 form part of a progressive deformation related to ductile flow generated in the A-subduction channel that accommodated underthrusting of Cuyania beneath the Famatina arc. Hence, F_2 folding probably took place after the preceding folds locked-up and were flattened into isoclines. F_2 folds range from upright to nearly recumbent structures reflecting heterogeneous shear strain responsible for rotation of the upright folds into progressively more inclined structures (cf. Williams and Jiang, 2005). The abundance of

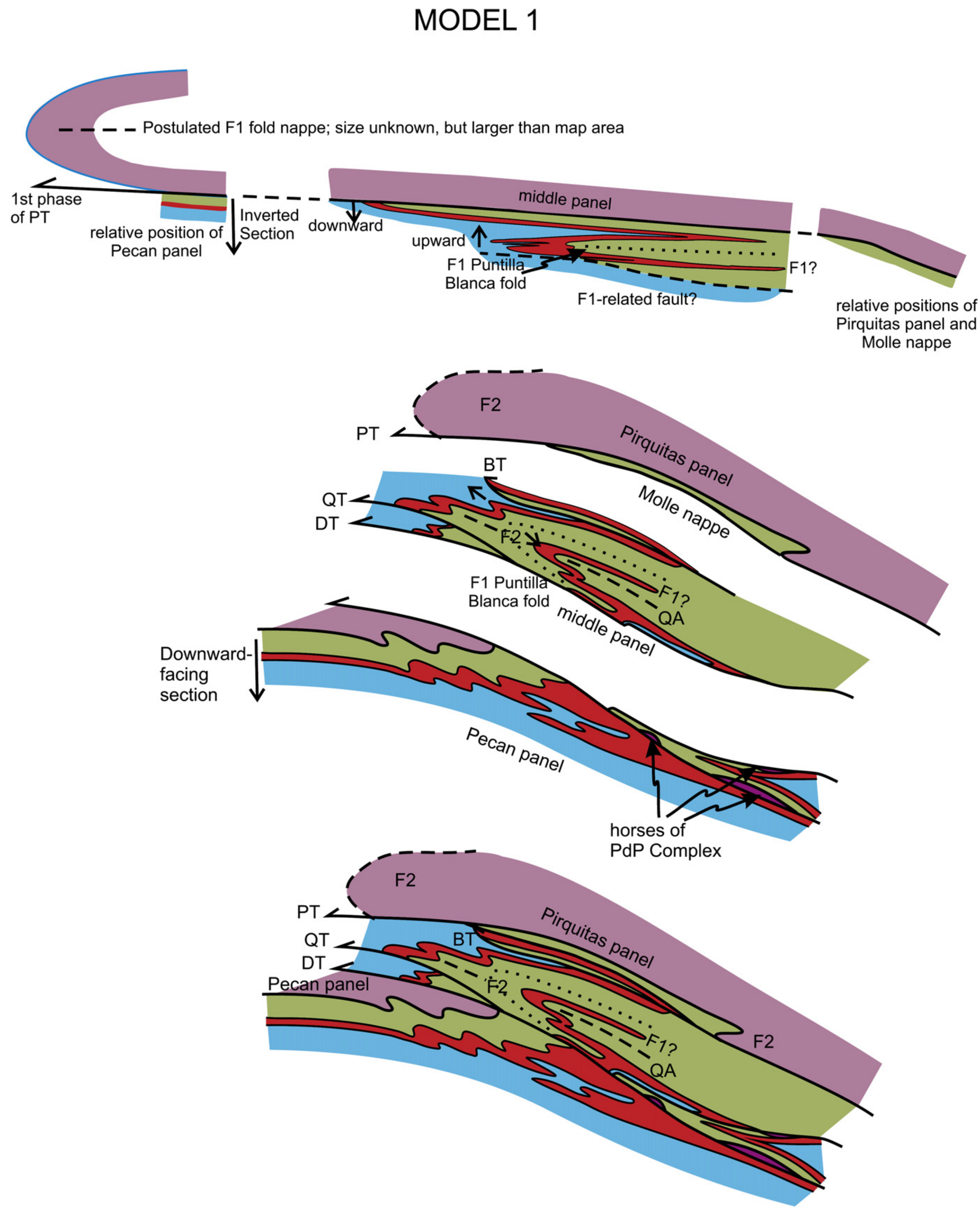

Fig. 13. Kinematic model 1. This model involves formation of a large westward-verging recumbent F_1 nappe to generate an inverted stratigraphy on its lower limb. The structure is schematic and potential complexities introduced as a result of F_1-related boudinage and associated faulting cannot be evaluated and have been ignored. The rocks have been divided into three major panels based on tectonostratigraphy more elaborately discussed in text. The Pecan panel at the base of the thrust stack was situated most westerly on the inverted limb of the postulated F_1 recumbent isocline. The rocks of the Caucete Group thus young downward. The F_2-folded tectonites at the base of the Pie de Palo Complex in the Pecan panel suggest that the Pirquitas thrust (PT) was already active during this deformation phase. The structurally overlying middle panel solely comprises rocks of the Caucete Group. These rocks were deformed into the large Puntilla Blanca fold, which is interpreted to have formed as a parasitic structure on the large recumbent F_1 isocline. The Puntilla Blanca

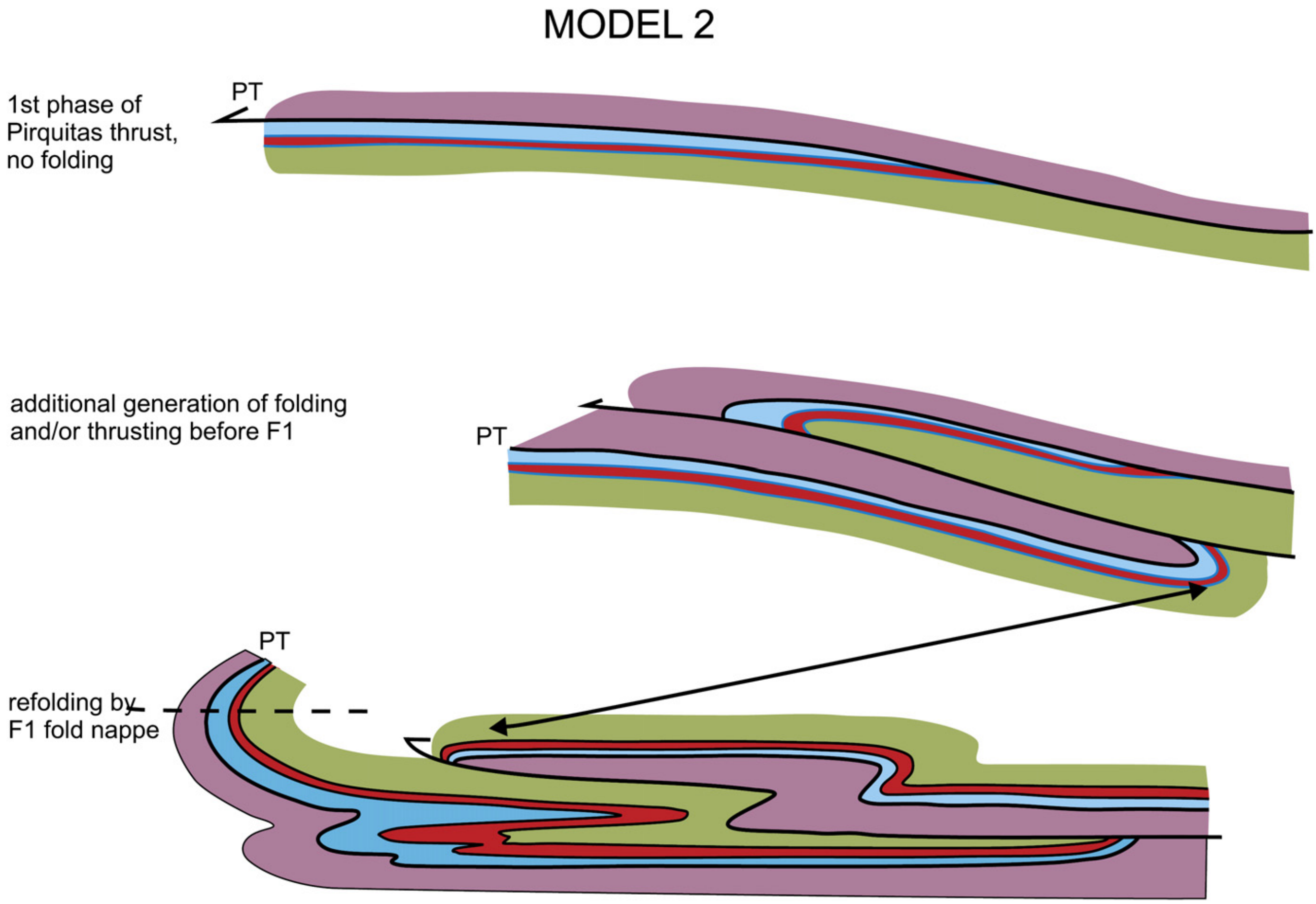

Fig. 14. Kinematic model 2 assumes there is no basement–cover relationship between the Pie de Palo Complex and Caucete Group (Mulcahy et al., 2007). This model is structurally more complex and demands an early phase of thrusting of an exotic Pie de Palo Complex above the Caucete Group (step 1) along the Pirquitas thrust, followed by an extra generation of structures (folding and/or thrusting) to create an inverted stratigraphy beneath the overlying Pie de Palo Complex (step 2). No evidence has been observed on mesoscopic scale for such pre-F_1 structures. Arrows connect the extra generation fold shown in step 2 to its refolded geometry in step 3, which represent F_1 in Fig. 13. The remaining part of this model is similar to that shown in Fig. 13.

parasitic folds along the limbs of the larger structure indicate they unlikely represent drag folds, but rather a phase of layer-parallel shortening induced by increased traction forces generated in a widening subduction channel (van Staal et al., 2009; Fig. 8) following subduction of progressively more buoyant continental material. Thrusts associated with F_2 folds appear at least in part, to have developed as secondary features of folds by shearing-out the common limb of antiform–synform pairs (Heim, 1919; Ramsay, 1992, p. 191). The synforms, where still preserved, such as in the footwall of the Quemado thrust, closely mirror the shape of the hangingwall antiform. Hence, they are not structures formed according to a mid-crustal, ductile variant of the classic upper crust, ramp-flat, foreland fold-thrust mechanism (cf. McClay, 1992; Hatcher and Hooper, 1992). In general, this mechanism is inappropriate to explain overthrusting in highly ductile deforming metamorphic tectonites (e.g. Ramsay, 1992; Casey and Dietrich, 1997; Williams and Jiang, 2005). However, our structural analysis is another example that thin thrust sheets can develop during ductile flow in the deep crust, contrary to the recent assertions of Williams and Jiang (2005) that they generally form by transposition and rotation of pre-existing steep discontinuities.

12. Implications for rheology of the lower-middle crust during collision

Regardless, which of the two discussed models (Figs. 13 and 14) was responsible for the structural evolution in the Sierra de Pie de Palo, the distribution of stain appears to have changed over time. There is ample evidence for continuous remobilization of old structures, such as the Pirquitas thrust, which attests to the significance of strain localization and fabric softening during deformation. However, there is little evidence preserved in the rocks regarding the degree and nature of this strain localization during the earliest phases of deformation, except that it must have occurred. Old, F_{1-2} folded tectonites are locally preserved in the Pirquitas thrust and underlying psammites (flaggy psammites) in areas not much affected by F_2-associated thrusting, such as the Pecan panel (Figs. 6F and 9B). On the other hand, F_2-associated strain is more

fold was subsequently refolded by the F_2 Quemado antiform (QA), creating upward and downward facing sections (indicated by small arrows) and partially decapitated by the Desecho thrust (DT). The Quemado (QT) and Burras (BT) thrust represent two additional thrust sheets in this panel. The Pirquitas panel represents the structurally highest thrust sheet and hence was originally even positioned further east than the middle panel on the inverted limb of the postulated F_1 isocline. The Pirquitas panel accreted the Molle nappe to its base before it was finally emplaced above the middle panel, in the process truncating the underlying Burras thrust sheet. Fold nappes in this schematic model are thought to have started as upright folds and than were rotated into inclined to recumbent positions due to progressive overthrust-related shear toward the west. Thrusts appear to have developed by shearing-out the common limb between antiforms and synforms. Colours of units are the same as in Figs. 2, 7, 8 and 10.

homogeneously distributed in the structurally overlying thrust sheets. Shear sense indicators have developed also outside the thrust zones and the rocks are generally very penetratively deformed into high-strain tectonites, suggesting that these rocks were subjected to a much more homogeneously distributed non-coaxial flow. Strain localization returned after F_2, as is evidenced by formation of the late, retrograde chlorite and serpentinite schists in the Pirquitas thrust zone and brittle-ductile thrusts. Considering that peak-temperature conditions were achieved close to F_2 and muscovite granite and pegmatite sheets intruded synkinematically, the nature and style of deformation appears to have mainly changed in response to an evolving thermal regime (slab breakoff?) in the subduction channel. During F_2, thermal softening dominated over fabric softening, but the relative importance of these weakening mechanisms changed with time.

13. Discussion and tectonic setting of the Sierra de Pie de Palo

The metamorphic history indicates that the Caucete Group and Pie de Palo Complex were incorporated into an A-subduction complex before and/or during the Middle Ordovician, which led to formation of Alpine-like fold nappes and development of several generations of ductile thrusts. Our study supplies additional support for correlation the Caucete Group with platformal sediments of the Precordillera terrane, in accord with earlier interpretations (Ramos et al., 1998) and detrital zircon studies (Naipauer et al., 2010a). The nature of the metamorphism and Laurentian provenance of the Precordillera terrane implies that it was separated by the Iapetus Ocean and a subduction zone from the Famatina margin and hence, cannot have accreted solely by strike-slip motion as suggested by Aceñolaza et al. (2002), Finney et al. (2003) and Finney (2007). Our data thus support the origin of Cuyania as a narrow microcontinent (Ramos, 1995; Astini, 1998; Thomas and Astini, 1996), which probably extended as a single or multiple ribbons along much of the length of Laurentia's Iapetan margin (e.g. Cawood et al., 2001; Waldron and van Staal, 2001; van Staal et al., 2007).The predominantly calcareous composition of the sediments of the Caucete Group makes it unlikely that it could be derived from the active Famatina margin as proposed by Mulcahy et al. (2007). Even if they could, these sediments would somehow have to evade the forearc basinal traps to be incorporated into the trench. Our structural studies favour a pre-orogenic, structural basement–cover relationship between the Pie de Palo Complex and the Caucete Group. The alternative that there was no such relationship is permissible, but requires a more complicated structural history. Such a complicated structural history is not supported by our structural analysis, but evidence possibly could have been erased by the very high strains recorded in the rocks. Hence, the Pie de Palo Complex could be part of the Famatinia forearc basement as was proposed by Mulcahy et al. (2007), in which case, the Pirquitas thrust represents a suture between the Precordillera terrane and the Famatina arc-forearc block. Mulcahy et al. (2007) assumed that 515–510 Ma $^{40}Ar/^{39}Ar$ hornblende ages in Pie de Palo Complex mylonites from the Pirquitas thrust are diagnostic of the active Famatina margin (Pankhurst et al., 1998). We suggest they could have formed in Cambrian low angle shear zones (proto-Pirquitas thrust) formed during Cambrian extension and rifting of the Cuyania microcontinent. Even if this proves incorrect, similar convergence-related Cambrian ages have been documented in peri-Laurentian ribbons equivalent to Cuyania; for example, in the Lushs Bight oceanic tract of the Appalachian-Caledonide orogen in Newfoundland (Dewey, 2002; van Staal et al., 2007) and equivalent rocks in the British Isles (Chew et al., 2010). Thus the 515–510 Ma $^{40}Ar/^{39}Ar$ hornblende ages of Mulcahy et al. (2007) could represent a late Early-Middle Cambrian phase of tectonism in the peri-Laurentian realm of Iapetus, unrelated to mid-Ordovician subduction of the composite Caucete Group-Pie de Palo Complex beneath the Famatina arc. In these models the mid-Ordovician event produced or adjusted mineral compositions to give the observed P–T estimates, but did not erase the 515–510 Ma ages because the relatively low peak temperature did not exceed the closure temperature of amphibole (Mulcahy et al., 2007). In such models, any terrane boundary of the Pie de Palo terrane and by implication also Cuyania, with the Famatinian margin would therefore lie further east during the mid-Ordovician.

Acknowledgements

The authors are grateful to Laboratorio de Tectónica Andina (UBA) and SEGEMAR (San Juan) for logistical support. To CONICET for financial support from PIP 5437 and PIP 0072 (G. Vujovich). Special thanks to Victor A. Ramos for numerous discussions on the local geology. Alex Zagorevski and Bill McClelland are thanked for critically reading the original draft, which combined with the constructive journal reviews by Rudolph Trouw and Victor Ramos improved the paper. The first author (CvS) would like to take this opportunity to express his gratitude to Paul Williams, who persuaded him to follow him to Canada and become his first PhD student at UNB in 1980. This is Geological Survey of Canada publication 20100197.

Appendix. Supplementary material

Supplementary material related to this article can be found online at doi:10.1016/j.jsg.2010.10.011.

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