Tectonothermal evolution in the core of an arcuate fold and thrust belt: the southeastern sector of the Cantabrian Zone (Variscan belt, NW Spain)

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Abstract. The tectonothermal evolution of an area located in the core of the Ibero-Armorican arc (Variscan belt) has been determined by using the conodont color alteration index (CAI), Kübler index of illite (KI), the Árkai index of chlorite (AI), and the analysis of clay minerals and rock cleavage. The area is part of the Cantabrian Zone (CZ), which represents the foreland fold and thrust belt of the orogen. It has been thrust by several large units of the CZ, what resulted in the generation of a large amount of synorogenic Carboniferous sediments. CAI, KI and AI values show an irregular distribution of metamorphic grade, independent of stratigraphic position. Two tectonothermal events have been distinguished in the area. The first one, poorly defined, is mainly located in the northern part. It gave rise to very low-grade metamorphism in some areas and it was associated with a deformation event that resulted in the emplacement of the last large thrust unit and development of upright folds and associated cleavage (S_1).The second tectonothermal event gave rise to low-grade metamorphism and cleavage (S_2) crosscutting earlier upright folds in the central, western and southern parts of the study area. The event continued with the intrusion of small igneous rock bodies, which gave rise to contact metamorphism and hydrothermal alteration. The second event was linked to an extensional episode due to a gravitational instability at the end of the Variscan deformation. This tectonothermal evolution occurred during the Gzhelian-Sakmarian. Subsequently, several hydrothermal episodes took place, in association with local development of crenulation cleavage during the Alpine deformation.

1 Introduction

The Variscan belt defines an arc in the northwestern Iberian Peninsula (Ibero-Armorican Arc), whose core is formed by the Cantabrian Zone (CZ), which represents the foreland fold and thrust belt of the orogen (Fig. 1). This zone consists of Palaeozoic rocks in which two tectonostratigraphic units have been distinguished (Julivert, 1978; Marcos and Pulgar, 1982), whose limit is approximately located by the Devonian-Carboniferous boundary. The preorogenic unit is formed of Cambrian to Devonian rocks consisting of alternating carbonate and siliciclastic formations; they form a wedge that thins towards the foreland. The synorogenic unit is formed by several clastic units, also thinning towards the foreland, which filled foredeep basins generated in the front of the main thrust units of the CZ. In this zone, the Variscan deformation occurred during the upper Carboniferous and gave rise to thin-skinned tectonics, with several large thrust units and associated folds (Fig. 1); the units were emplaced in a sequence towards the foreland. The deformation occurred under shallow crustal conditions, so that diagenetic conditions are dominant in the zone and absence of cleavage in the rocks is also dominant. Nevertheless, there are several areas of the CZ where cleavage and very low- or low-grade metamorphism are present. One of these areas is the southeastern sector of the Cantabrian Zone. It is a foreland basin that occupies the core of the Ibero-Armorican Arc, and has undergone, a complex history of sedimentation, deformation, metamorphism, and to a lesser extent, magmatism.

The present study aims to present a model of tectonothermal evolution for the core of the Ibero-Armorican arc based on conodont colour alteration index (CAI), the Kübler index (KI) of illite, the Árkai index (AI) of chlorite, the analysis of clay minerals and the rock cleavage development.

2 Geological setting

The southeastern sector of the Cantabrian Zone is made up of two units: the Pisuerga-Carrión unit (PCU) and the Valsurbio unit (VU) (Fig. 1). As a consequence of its location in the core of the Ibero-Armorican arc, the PCU has been thrust over successively by the VU, the Central Coal Basin, the Ponga unit and the Picos de Europa unit, (Fig. 1). Thus, the PCU operated as a foreland basin during a great part of the history of the Variscan deformation. This history involved the accumulation of a great thickness of synorogenic Carboniferous sediments, corresponding to clastic wedges associated with the exhumation of the thrust units.

The VU is located to the south of the PCU. Marine facies occur in both units, but from the Emsian, the sediments in the latter unit were deposited in deeper waters than those in the former unit. The VU represents an extension of the southern part of the CZ, and the Devonian succession of both is comparable (Koopmans, 1962). The units within the PCU containing Silurian-Devonian rocks have been interpreted as transported from internal areas of the orogenic belt, specifically from the southeastern extension of the Westasturian-Leonese Zone, currently hidden under the Mesozoic-Cenozoic cover of the Duero basin, and located to the south of the VU (Frankenfeld, 1983; Marquínez and Marcos, 1984; Rodríguez Fernández and Heredia, 1987; Rodríguez Fernández, 1994). These units were named ‘Palentine nappes’ by Rodríguez Fernández and Heredia (1987). The PCU and the VU are separated by the León fault (also called ‘Ruesga fault’ in the study area) (Fig. 2), that crosses most of the Cantabrian Zone and whose meaning is controversial (Alonso et al., 2009 and references therein).

The oldest sediments of the study area are Silurian (Wenlock-Pridoli) sandstones and lutites. The Devonian rocks consist of an alternation of carbonate and siliciclastic formations with the facies differences cited above. Mississippian rocks are mainly limestones in the lower part, especially in the VU; upwards a mostly turbiditic sequence~~s~~ appears with common olistoliths in the northern sector and some carbonate levels. The Pennsylvanian succession is dominantly siliciclastic, with a thickness of several thousand meters and synorogenic character. In relation to this synorogenic sedimentation, several syntectonic unconformities have been described, among which the Curavacas unconformity (early Moscovian) can be highlighted by its structural significance (Van Veen, 1965; Lobato 1977; Alonso and Rodríguez Fernández, 1983; Martín-Merino et al., 2014).

The first deformation events were pre-Curavacas (prior to or earliest Moscovian) and involved the emplacement of the Palentine nappes and the VU. Two generations of thrusts and folds associated with them occurred during this episode (Rodríguez Fernández, 1994), which translated sequences northwards. Further, some back thrusts and normal faults occurred.

The post-Curavacas deformation events involved the development of several generations of thrusts and high-angle reverse faults, folds, cleavages and normal faults. Some thrusts have a trend approximately parallel to the basal thrust of the Ponga unit and are probably related to the emplacement of this thrust unit (Rodríguez

Fernández and Heredia, 1987), which occurred during the late Moscovian. In the same episode that involved the emplacement of the Picos de Europa thrust unit during the Kasimovian-Gzhelian (Merino-Tomé et al. 2009), N – S shortening occurred in the study area, involving the development of thrusts, high angle reverse faults and the reactivation of older faults with a movement dominantly southward (Maas, 1974). In addition, upright folds with E – W axial trace developed; among them, the Curavacas-Lechada syncline is remarkable for its notable dimensions (Savage, 1967; Lobato, 1977; Rodríguez Fernández, 1994).

Several cleavages have been recognised in the study area. Among them, a gently dipping cleavage crosscutting folds is the most relevant and has been described by various authors (Van Veen, 1965; Savage, 1967; Lobato, 1977; Van der Pluijm et al., 1986; Rodríguez Fernández, 1994; Marín, 1997; García-López et al., 2007; among others).

A subsequent N-S shortening episode occurred during the Alpine deformation. It involved tightening of folds, local development of crenulation cleavage and reactivation of some faults. It is responsible for the dome geometry of the VU (Marín et al., 1995; Marín, 1997). Another post-Variscan structure of the study area is the Ventaniella fault, which traverses the whole Cantabrian Zone in a NW – SE direction. It is essentially a dextral, strike-slip fault with a net-slip of 4-5 km (Julivert et al., 1971) whose activity began in the Permian and continues to the present (López-Fernández et al., 2002, 2004).

Outcrops of intrusive igneous rocks are common in the PCU, and their knowledge is important to understand the tectonothermal evolution of this unit. Among these rocks, three granodioritic stocks (Pico Iján, Peña Prieta and Pico Jano; Fig. 2) and many small outcrops can be distinguished. The latter are mainly concentrated in the southern half of the unit.

The stocks of Pico Iján, Peña Prieta and Pico Jano dominantly have granodioritic composition and their intrusion was favoured by the existence of faults (Suárez and García, 1974; Corretgé and Suárez, 1990), having developed a notable aureole of contact metamorphism in the case of the Peña Prieta stock. The porphyroblasts in this aurole are post-tectonic relative to the gently dipping cleavage (Gallastegui et al., 1990; Rodríguez Fernández, 1994). The U/Pb age of the Peña Prieta granitoid is Cisuralian (292+2/-3 Ma after Valverde-Vaquero et al., 1999), and the Lower Triassic rocks appear in nonconformity on the Pico Iján granitoid. The large number of small outcrops of igneous rocks that exist in the southern half of the unit are concentrated in two areas (one in the eastern part and another in the western part) joined by a band whose outcrops of igneous rocks have been related to the León fault (Corretgé et al., 1987; Suárez and Corretgé, 1987; Corretgé and Suárez, 1990). All these southern outcrops have been in general related to fractures and appear as small stocks, probably apophyses of bigger bodies in depth, and as sills or dikes. Their composition is varied and ranges from granodioritic to gabbroic. In some cases, they developed ore bodies close to their contacts (Martín-Izard et al., 1986).

Earlier metamorphic studies in the Cantabrian zone using CAI and/or KI methods have shown the existence of areas with very low- or low-grade metamorphism in the PCU and the VU (Raven and van der Pluijm, 1986; Keller and Krumm, 1993; Marín et al., 1996; Marín, 1997; Köberle et al., 1998; García-López et al., 1999, 2007, 2013; Bastida et al., 2002; Clauer and Weh, 2014; among others). Similar results have been obtained for the southern part of the study area using coal rank and vitrinite reflectance (Colmenero and Prado, 1993; Llorens et al., 2006; Colmenero et al., 2008; Clauer and Weh, 2014). This metamorphism has been described as associated with a late-orogenic extensional event and to the corresponding cleavage (García-López et al., 1999, 2007, 2013; Bastida et al., 2002). Analysis of ore deposits and of the tectonothermal evolution in the neighbouring unit of the

Picos de Europa has defined a subsequent hydrothermal episode during the Permian (Gómez-Fernández et al., 1993, 2000; Bastida et al., 2004). Brime and Valín (2006) have suggested a hydrothermal origin for mineral associations with chloritoid and pyrophyllite found in samples of pelitic rocks collected in the study area. K-Ar dating of illite in samples collected in the southern part of the study area, identified four thermal episodes (Clauer and Weh 2014), namely at: (1) 293 ±3 Ma (Cisuralian), (2) 268 ± 6 Ma (Guadalupian), (3) 243 ± 5 Ma (middle Triassic), and (4) 175 ± 6 Ma (early-middle Jurassic). From apatite fission tracks and zircon (U-Th)/He ages in samples of Westphalian (Bashkirian-Moscovian) sandstones collected in the eastern part of the PCU, Fillon et al. (2016) obtained ages of cooling below ≈180ºC of 37-39 Ma and below ≈110°C of 28-29 Ma. They inferred Cenozoic erosion of a rock thickness between 6.4 and 8 km (assuming a steady-state geothermal gradient of 25ºC km-1).

3 Methods

3.1 X-ray diffraction

A total of 297 mudrocks from various localities (Fig. 2) were studied by X-ray diffraction (XRD) analysis in order to determine their phyllosilicate mineralogy, Kübler Index (KI) of illites, and Árkai Index of chlorites (AI). Preparation of samples and methods for XRD analysis follow the methods described in Brime et al. (2003)

Reaction progress in illitic minerals (*sensu* Środoń 1984) has been widely used to assess the evolution of pelitic lithologies during diagenesis and low-grade metamorphism. Prograde changes can be identified by use of the Kübler Index technique (illite "crystallinity", see Guggenheim et al. 2002) involving quantification of the width of the 10Å peak of illite. This is an indirect measure of lattice reorganization and thickening of illite crystals (Kisch 1983; Merriman and Peacor 1999) with increasing grade. The Kübler Index (KI) is expressed in $\Delta^{o}\ 2\theta$ to minimize variations caused by differences in recording conditions. For this study the KI was measured using a laboratory procedure similar to that outlined by the IGCP 294 working group (Kisch, 1991). The numerical KI value decreases with improving "crystallinity" and is expressed as small changes in the Bragg angle $\Delta^{o}\ 2\theta$, using Cu Kα radiation.

The transient zone between diagenesis and metamorphism (the anchizone of Kübler, 1967) is defined by KI values between 0.42^{o} and 0.25 $\Delta^{o}\ 2\theta$ respectively (Kisch, 1991). The values obtained in our laboratory were correlated with the Kübler scale using a calibration curve based on data obtained from polished slate standards kindly provided by H. Kisch. The diagenetic zone has been subdivided in shallow (KI > 1 $\Delta^{o}\ 2\theta$) and deep (1.0 º > KI > 0.42 $\Delta^{o}\ 2\theta$), using the terms proposed by the IUGS Subcommission on the Systematics of Metamorphic rocks (Árkai et al., 2007). Following Merriman and Peacor (1999) we have divided the anchizone into low (0.42 < KI < 0.30 $\Delta^{o}\ 2\theta$) and high (0.30 < KI < 0.25 $\Delta^{o}\ 2\theta$).

Crystallinity index standards (CIS, Warr and Rice 1994) have also been used to compare the results thus obtained with other published results using that scale. KI values obtained in this work could be converted to the CIS scale by using the calibration equation:

$$KI_{CIS} = 1.505KI_{\text{this work}} - 0.046\ (R^2 = 0.996). \quad (1)$$

For the problems involved in the use of the CIS scale to assess metamorphic grade see Brime (1999) and Kisch et al. (2005).

The KI method does not allow temperature constraints to be placed on the upper and lower boundaries of the anchizone and it is more likely to be a measure of reaction progress than of the thermodynamic equilibrium achieved (Essene and Peacor,1995). However, this method, in combination with others such as fluid inclusions or reflectance of carbonaceous material, indicates that the transition diagenesis–anchizone could be correlated with a temperature of 230 ± 10 ºC whereas the limit anchizone–epizone would be at 300 ± 10ºC (Müllis, 1979; Frey et al., 1980; Frey, 1987; Von Gosen et al., 1991; Müllis et al., 1995; Merriman and Frey, 1999; Ferreiro Mählmann et al. 2002; Müllis et al. 2002).

The presence of illite/smectite (I/S) and paragonite (Pg) and paragonite/muscovite (Pg/Ms) hampers determination of KI of many samples. However, pro-grade changes can also be identified by use of the Árkai Index technique (of chlorite “crystallinity”, see Guggenheim et al., 2002) involving quantification of the width of the 14Å or 7Å peaks of chlorite (Árkai, 1991, Meunier, 2005). The Árkai Index (AI) was determined in the (002) peak using the same instrumental conditions as that for KI measurements. The anchizone limits have been established using samples free of I/S, Pg-Pg/Ms in which the KI measured in the air dried samples has been calibrated with Kisch standards. The AI was measured in the same samples and the regression line obtained allowed the delimitation of the upper and lower anchizone limits using chlorite for AI values of 0.234 and 0.135 Δº2θ respectively. It should be noted that AI values are smaller than the corresponding KI and the method is therefore slightly less sensitive than KI method.

3.2 Conodont colour alteration index (CAI).

Colour changes in conodont elements are related to the progressive and irreversible alteration of the amounts of organic matter within their apatite composition. The CAI method is based on analysis of the colour changes that the conodonts undergo in response of the organic matter to a temperature increase with time. These changes permit construction of a scale of CAI values with eight units that allows the use of the conodonts as maximum paleothermometers for a temperature interval of between 50 and 600ºC (Epstein et al., 1977; Rejebian et al., 1987). It is used mainly in carbonate rocks. Besides colour changes, apatite textural alteration also takes place and can provide complementary information about the thermal conditions. In the present paper the terminology of Rejebian et al. (1987) and García-López et al. (1997, 2006) is used for the textural description of conodonts. In agreement with Rejebian et al. (1987), well preserved conodonts and high CAI values with a wide dispersion are indicative of contact metamorphism. Furthermore, coarse recrystallization and corrosion are related to hydrothermal processes.

Samples were collected from the Pisuerga-Carrión and Valsurbio units. CAI values are based on 5 kg samples of limestone that were treated, with 6% acetic acid solution. Unfortunately, recovery of conodonts from Carboniferous rocks was hindered in some areas by their dominantly siliciclastic character. Sampling was complemented with specimens from collections housed at the University of Oviedo (Spain) and those of the National Museum of Natural History at Leiden (Netherlands) and Institut und Museum für Geologie und Paläontologie in Göttingen (Germany) (Fig. 2). 213 positive samples, corresponding to an age interval from the Pridoli to Ghzelian, were analyzed for CAI determination (Appendix 1 in the supplementary material).

The methodology involved in CAI determination can be found in García-López et al. (1997) and Bastida et al. (1999). Several CAI values were obtained from most samples and the mean of CAI values have been determined for each of them in order to tentatively contour CAI values. Samples with a range higher than 1.5

have not been used to obtain mean CAI values and temperatures. The interpretation of the results is mainly based on the analysis of the CAI isograds and their relationship to the stratigraphic contacts and the main structures of the study area.

For the metamorphic zonation from CAI data, we use the terminology described by García-López et al. (2001), that involves a division in diacaizone (CAI < 4), ancaizone (4 ≤ CAI ≤ 5.5) and epicaizone (CAI > 5.5).

Temperature ranges of the CAI values were obtained from the Arrhenius plot presented by Epstein et al. (1977) and Rejebian et al. (1987). The maximum possible heating time is the age of the rock. Nevertheless, it is possible to place greater limits on this maximum time (García-López et al., 2013). According to the Arrhenius plot a minimum temperature is required to obtain a specific CAI value. For example, in a rock with an age of 400 Ma (Devonian), development of CAI = 5 requires at least 290ºC (point *A* in Fig. 3). Then, it can be assumed that a temperature <290ºC does not contribute to generate a CAI = 5. Hence, to produce a given CAI, the maximum time of heating begins when the rock reaches the minimum temperature necessary to produce that CAI, and it ends when the rock cools down and the temperature becomes lower than this minimum value. Although the heating time can be slightly different depending on the geological location of the samples, we consider that the main heating time corresponds to a late-Variscan period that began at the boundary Kasimovian-Gzhelian and ended at the beginning of the Triassic (heating time of about 50 Ma); this is made in agreement with the age of the metamorphism analyzed below and the igneous rocks. The hydrothermal post-Variscan episodes described by Clauer and Weh (2014) and the Alpine heating (mainly Cenozoic) analyzed by Fillon et al. (2016) probably involved lower temperatures than those reached in the late-Variscan event, in which magmatism and cleavage development are more intense. It must be taken into account that in rocks undergoing more than one heating period, the period to be considered for the development of the CAI is the one which generated higher temperatures. Anyway, due to the geometry of the CAI curves in the Arrehnius plot, for heating intervals such as those involved in the present case, an error of a few Ma in the maximum time of heating has little influence on the results. According to Patrick et al. (1985) and Rejebian et al. (1987) the minimum time of heating assumed here is of 1 Ma.

3.3 Cleavage

Development of cleavage requires mineralogical and also microstructural changes due to ductile deformation, involving mechanisms, such as pressure solution, which require a minimum temperature of about 200ºC for cleavage development in pelitic rocks and 175ºC in limestones (Groshong et al. 1984). Thus widespread presence of cleavage occurs below a certain crustal level (minimum overburden of 5-7 km; Engelder and Marshak, 1985). Furthermore, the relations between folds and cleavages and the overprinting relations between cleavages, play an important role in defining deformation events (Passchier and Trouw, 2005). In addition, cleavage is also a key structure to establish chronological relations between metamorphic crystallization and deformation.

In the context of the study area, we call tectonothermal event to a deformational event with cleavage development and associated metamorphic conditions, and use the term thermal event for metamorphic conditions without cleavage development. Hence, cleavage is considered here as the main reference to ascertain the tectonothermal events of the study area.

4 Results and interpretation

In order to facilitate description, the samples have been mainly grouped in the following areas, namely Liébana, Valdeón, Yuso-Carrión, Pisuerga, Riaño-Cervera and Valsurbio (Fig. 4) (cf. Martín-Merino et al., 2014).

4.1 Clay minerals

4.1.1 Clay mineral assemblages

Mineralogical analysis of the <2 μm fractions shows that dioctahedral K- rich mica-like structures (referred to as illite or muscovite, I-Ms) is present in all the samples with the majority containing also chlorite (Chl) (Fig. 5). Chlorites have poorly developed 14 Å peaks, indicating high iron content suggestive of chamositic compositions (Moore and Reynolds, 1997). Other phases such as ordered illite/smectite (I/S) or paragonite (Pg) and mixed layers paragonite/muscovite (Pg/Ms) are also common. Asymmetry of peaks and sample behaviour after glycolation indicate the presence of ordered illite/smectite (I/S). Absence of random I/S indicate that zone 3 of Eberl (1993) has been reached, suggesting that temperatures exceeded 100ºC.Kaolinite (Kln) and pyrophyllite (Prl) may also be present in some samples and are abundant in a few samples. In addition, chloritoid (Cld) is also present and widespread in the study area. However it is more abundant in samples close to the intrusions and/or faults in which case is found together with chlorite and Pg + Pg/Ms. Only in samples to the E (Pisuerga Area), where it is not as abundant, it may be associated with Prl, Kln or I/S. Finally chlorite/vermiculite mixed layer(C/V) and stilpnomelane (Stp) have been found, in small amounts, in a few samples, and are restricted to samples to the E Pisuerga and E Yuso-Carrión areas.

The I/S is more abundant to the N and E (Valdeón, Liébana, and eastern part of the Pisuerga and Yuso-Carrión areas) and Kln presence is almost restricted to samples to the E (Pisuerga and eastern part of the Yuso-Carrión areas). Prl is common in samples from the central and northeastern parts (Liébana and Pisuerga areas, and eastern part of the Yuso Carrión area) (Fig. 5). Quartz, calcite, feldspars and goethite were accessory phases recognized in some samples.

In general the assemblages found are, in order of abundance of the most frequent phase besides illite (n = 291):

I + **Chl** (n = 215) ± Pg ± Pg/Ms ± Cld ± I/S ± [C/V] ± [Prl] ± [Kln] ± [Stp]

I + **Pg** + **Pg/Ms** (n = 162) ± Chl ± Cld ± [I/S] ± [Prl] ± [C/V] ± [Kln] ± [Stp]

I + **I/S** (n = 112) ± Chl ± Kln ± Prl ± C/V ± Pg ± Pg/Ms ± C/V± [Cld] ± [Stp]

I + **Cld** (n = 93) ± Chl ± Pg ± Pg/Ms ± I/S ± [C/V] ± [Prl] ± [Kln] ± [Stp]

I + **Prl** (n = 56) ± I/S ± Chl ± Pg ± Pg/Ms± C/V± [Cld] ± [Kln] ± [Stp]

I + **C/V** (n = 48) ± I/S ± Chl ± Pg ± Pg/Ms ± Kln ± Prl ± Cld ± [Stp]

I + **Kln** (n = 39) ± I/S ± Chl ± C/V± [Prl] ± [Cld] ± [Pg] ± [Pg/Ms] ± [Stp]

4.1.2 Kübler Index

As mentioned above, determination of KI has been hampered by the presence in some samples of certain types of I/S and big amounts of Pg or Prl, in relation to the amount of illite, that interfere with the 001 peak of illite, therefore rendering their KI values useless for grade determination using KI, even in the glycolated state. As a result, 23 (indicated in *italics* in Appendix 2 in the supplementary material) of the 291 samples studied yielded doubtful KI values (Figs. 6, 7; Appendix 2 in the supplementary material). They are included, nevertheless, as they indicate maximum value of the KI.

Grade ranges from deep diagenetic to epizonal, but deep diagenetic and mainly low anchizonal metapelites are predominant in most of the areas (Figs. 6 and 7). Expandability of the 10 Å peak is only lost at the high anchizone to epizone boundary. Deep diagenetic areas can be found to the north (Liébana and Valdeón areas). The Riaño-Cervera area is mainly low anchizonal with a few samples being diagenetic or deep anchizonal. In the Pisuerga area, the grade ranges from deep diagenetic to low anchizonal (Figs. 6, 7). Higher grade (epizonal) samples may appear in any formation and they are more abundant in the western part of the Yuso-Carrión area, where a big size intrusion is located, and in the Devonian of the Valsurbio area (Fig.7). In both cases, it is in those high grade samples where chloritoid is more abundant (Fig.6).

Work in progress on the variation of the chemical composition of the phyllosilicates of the study area allowed estimation of temperatures using Battaglia's (2004) approach based in the variation in the chemical composition of illites. Temperatures obtained are in the range 230-280ºC, consistent with the anchizonal KI values of the analyzed samples. The observed deficit in layer charge (Brime and Valín, 2006) is characteristic of anchizonal K white micas (Hunziker et al 1986; Livi et al. 1997; Merriman and Peacor 1999; Árkai 2002; Árkai et al 2003).

4.1.3 Árkai Index

The Árkai Index has been measured in 118 samples, most if not all of them, containing various amounts of I/S and/or Pg, Pg/Ms. Of them, 40 yielded diagenetic values, 63 low anchizonal values, 14 high anchizonal values and just one epizonal value. Distribution of these values can be seen in Fig. 6. In those cases in which KI and AI have been determined, the correlation of the grade indicated by both indexes is good ($r = 0.65$; significance level 0.1% $r_{60} = 0.41$) suggesting that both phases were formed under the same conditions, and supporting the reliability of the AI as indicator of grade in those cases in which it is the only index available (Árkai et al., 1995).

The existence of some discrepancies between KI and AI may be caused by the presence of small amounts of I/S or Pg that alters the width of the illite peaks. However, those discrepancies are always small and are usually in samples at the boundary between metamorphic grade zones (Appendix 2 in the supplementary material).

4.1.4 Mineral distribution in relation with grade

Kaolinite is present in deep diagenetic samples and also in some low anchizonal ones. Maximum stability temperature of Kln is 270ºC, according to laboratory experiments (Velde, 1992) and therefore in agreement with its presence in the anchizonal samples. Paragonite, apart from its presence in deep diagenetic samples, is more frequently present in the anchizone and some epizonal samples (Figs. 5 and 6). Pyrophyllite is more abundant in samples from the anchizone but it can also be present in diagenetic samples.

The widespread occurrence of Kln and quartz in the diagenetic rock samples may provide the starting material for the formation of Prl by the reaction

$$1\ \text{kaolinite} + 2\ \text{quartz} \rightarrow 1\ \text{pyrophyllite} + 1\ H_2O, \qquad (2)$$

as suggested in the Glarus Alps by Frey (1978), who considered Prl an indicator of anchizonal regional conditions. In fact of the 53 samples in which Prl is present, Kln is found, and in very small amounts, in only 8 of them. However, the stability field of Prl is strongly influenced by water activity, and thus the formation temperature could be notably lower (Thompson, 1970; Winkler, 1979; Hemley et al.,1980). Its presence in diagenetic samples is not uncommon and could due to the influence of magmatic fluids (Hosterman et al., 1970; Kisch, 1987). According to Kisch (1987) Prl, appears in regional terrains only in the anchizone but in areas of intrusive activity it may appear in lower grade zones. Therefore presence of Prl in samples with diagenetic KI/AI values, as in the eastern part of the Liébana and Yuso Carrión areas, could be regarded as evidence for high geothermal gradients or magmatic heating.

Chloritoid is abundant in samples from the high anchizone to epizone (southeastern Valsurbio area and western Yuso Carrión area), but it can also be present, in smaller amounts, in low anchizonal (1, 3W, 4E, 4W, 5E, 5W) and even diagenetic samples (eastern Liébana, Pisuerga and Riaño-Cervera areas). Cld is Fe rich. The average Mg/(Fe+Mg) found is < 0.12 (Brime and Valín, 2006) similar to that of pelites subjected to intermediate *P*/*T* conditions. It is noteworthy that when this phase is present in the samples (a total of 93 samples have Cld), Prl is absent, or in very minor amounts in a few samples (ten in total), indicating that it could have been formed according to the reaction originally proposed by Zen (1960), which is generally accepted for the formation of Cld during metamorphism of aluminous pelites (Theye et al. 1992):

Pyrophyllite + chlorite → chloritoid + quartz +1 H_2O. (3)

The absence of Cld in the eastern part of the Yuso Carrión area where Prl is abundant, together with Chl, could indicate that the temperature required for its formation by reaction (3) has not been reached.

Presence of some Fe oxides has been detected in samples from the study area. Therefore more Cld could be produced by the reaction suggested by Bucher and Frey (1994):

Chl + 4 hematite = Cld + 4 magnetite + 2 Qtz + 3 H_2O. (4)

However, it has been observed in thin sections that occurrence of Prl is almost restricted to veins and fracture zones, suggesting that Cld could have been formed during the hydrothermal alteration of the pelites following the reaction proposed by Phillips (1988):

Chlorite → chloritoid + Fe rich phase + quartz +1 H_2O. (5)

Presence of Cld in the anchizone has been discussed by Kisch (1983), who concluded that Cld cannot unequivocally be regarded as an indicator of the beginning of the epizone, as previously suggested, because there are occurrences in the anchizone (Árkai et al., 1981). In the study area, Cld is more abundant in the epizonal samples of the Valsurbio (6) and W Yuso-Carrion (3W) areas, but it is also present in low anchizonal and a few deep diagenetic samples from the Riaño Cervera (5E), Pisuerga (4E) or Valdeón (2) areas, thus corroborating the conclusion of Kisch (1983).

Chloritoid and Prl are widespread in virtually all rock types and grade conditions (Appendix 2 in the supplementary material). This occurrence could be related to basin wide alteration by infiltrating hydrothermal fluids (Phillips, 1988; Brime and Valín, 2006). Late to post Variscan fluid flow events have been described in the other areas of the Cantabrian Zone (Ayllón et al., 2003; Gasparrini et al., 2003) and related to a more general Variscan event (Boni et al., 2000).

4.2 Conodont colour alteration index (CAI).

The CAI values are independent of the stratigraphic position of the samples (Fig. 8). These values vary widely, ranging from 1.5 to 7.5, corresponding respectively to intervals of temperatures of < 40-60ºC and 550-590ºC (see Appendix 1 in the supplementary material). However, values equal to or lower than 2 are unusual, being limited to the southeastern sector of the Pisuerga-Carrión unit. Some samples with conodonts having high CAI values and a range of one and a half units, or more, are indicative of contact metamorphism and/or hydrothermal processes. Values ≥ 6 are usually found close to outcrops of igneous rocks. The upper boundary of the ancaizone (CAI = 4) corresponds to a temperature range of 190 - 225°C, while the lower limit (CAI = 5.5) corresponds to the range of 340-375ºC.

The lack of carbonate rocks prevents in some areas the construction of a complete map of CAI isograds; however, it is possible to observe that they crosscut the trend of the Variscan structures. CAI data allow the distinguishing of the following sectors in the study area (Fig. 8):

(a) Northern sector (Liébana and Valdeón areas).This is an ancaizonal area that passes without thermal discontinuity through the basal thrust of the Picos de Europa unit. Inside this unit, the boundary ancaizone/diacaizone appears and the CAI decreases northwards (Bastida et al., 2004; Blanco-Ferrera et al., 2011).

(b) Central-eastern sector (eastern part of the Yuso-Carrión area) with dominance of ancaizonal conditions. Here, in the areas where CAI data exist, a remarkable homogeneity of CAI values appears, mainly in the Devonian rocks of the area located to the east of the Curavacas-Lechada syncline.

(c) Central and western sectors, (western part of the Yuso-Carrión and Riaño-Cervera areas) where the limited CAI data available indicate that epicaizonal areas coexist with ancaizonal areas.

(d) Southern sector. It corresponds to the VU and presents a wide area with epicaizonal conditions (García-López et al., 2013).

(e) Southeastern sector (eastern part of the Yuso-Carrión and Pisuerga areas). In this area, diacaizonal conditions are dominant, but ancaizonal and epicaizonal areas also appear. The latter areas appear adjacent to outcrops of igneous rocks. The greater variation of CAI values is found in this area, with a range from 1.5 to 7.

The apparently chaotic distribution of CAI isograds is probably due to a heat from subsurface intrusions at depth resulting in isotherms having complex geometry. This pattern may be related to a crustal thinning during an extensional episode and to the subsequent intrusion of igneous bodies that emplaced at different levels, generating contact metamorphism and hydrothermal fluids.

In general, conodonts of the study area are undeformed and well preserved. Most of them have granular texture due to apatite recrystallization under high temperature. The apatite crystals do not show preferential orientation and their size increases with temperature. The granular texture is commonly incipient for CAI values between 4 and 4.5 and is widespread for CAI values ≥ 5. Furthermore some conodonts with CAI values between 6 and 7 have coarse recrystallization, corrosion and loss of ornamentation, so that in a few cases they have lost their original morphology ("ghost conodonts"). These alterations of conodonts with CAI values ≥ 5 are indicative of contact metamorphism and hydrothermal processes. Some conodonts with CAI ≥ 4.5 present sets of parallel microfissures, probably related to the rock cleavage. Conodonts with CAI ≤ 4 have occasionally unaltered surfaces, but most of them present a sugary texture (dull, frosted or pitted surfaces).The surfaces of these conodonts show several types of overgrowth of apatite crystals, mainly developed independently of the CAI value (or thermal changes under diacaizonal conditions); they were usually a result of apatite solution and crystallization processes (Blanco-Ferrera et al., 2011).

4.3 Cleavage development and tectonothermal events

Two main cleavages have been found in the study area (Fig. 9). Cleavage S_1 is a rough foliation associated with upright folds and trends approximately E-W; it appears mainly in the northern half of the study area. This cleavage affects latest Carboniferous rocks (Kasimovian-Gzhelian age). Cleavage S_2 dips gently, crosscuts earlier upright folds and is associated with the development of meter-scale open cascade folds. It is especially well developed in the Curavacas-Lechada syncline and in the VU. Both cleavages appear in different areas and have not been observed superimposed. The existence of two cleavages with different age suggests that two tectonothermal events took place in the southeastern sector of the CZ.

The first event, associated with the S_1 cleavage (sub-vertical), is not well defined, since it developed in an area where presence of I/S and Kln and KI and AI values indicate deep diagenesis or low anchizonal conditions, and CAI values dominantly show ancaizonal conditions. According to the age of the latest rocks affected, this event probably occurred during the late Gzhelian. It resulted in crustal thickening produced by the N - S shortening that gave rise to the emplacement of the Picos de Europa unit, the last major Variscan thrust unit that was generated in the foreland fold and thrust belt, and it disassociated with the development of other thrusts and folds to the south of this unit.

The second event produced cleavage S_2 that crosscuts the upright folds in the southern part of the study area (Curavacas-Lechada syncline and the VU). Under the microscope, this cleavage shows evidences of pressure solution and crystallization of oriented muscovite and chlorite with formation of chlorite-muscovite porphyroblasts. X-ray diffraction indicates that the rocks affected by this cleavage present Chl + Pg-Pg/Ms assemblages; KI and AI values indicate high anchizonal to epizonal conditions and CAI values indicate similar conditions. The gently dipping attitude of S_2 suggests that this event was associated with an extensional deformation and the corresponding crustal thinning as a consequence of a late orogenic gravitational readjustment of the orogen in the core of the Ibero-Armorican arc. This interpretation agrees with the kinematic evolution of the arc proposed by Gutiérrez-Alonso et al. (2004, 2011). The event culminated with the intrusion of igneous rocks that pierced the rocks with cleavage and generated a contact metamorphism associated with hydrothermal processes, as indicated by: (1) the widespread presence of Cld and Prl (Fig 5; Brime and Valín, 2006) and low KI and AI values, (2) recrystallization in conodonts (granular texture), (3) high CAI values in samples close to outcrops of intrusive rocks, (4) wide range of CAI in some samples, and (5) irregular variation of the CAI through the area and strong corrosion in some conodonts. The cleavage S_2 developed earlier than the porphyroblasts (biotite, andalusite and chloritoid) formed during the contact metamorphism associated with the granodioritic stock of Peña Prieta (Gallastegui et al., 1990; Rodríguez Fernández, 1994), whose age is Cisuralian (292+2/-3 Ma after Valverde-Vaquero et al., 1999). These data suggest the development of a thermal event that took place near the boundary Carboniferous-Permian and that progressed during the Cisuralian with the intrusion of many small igneous bodies that rose along faults (Suárez and García, 1974; Corretgé and Suárez, 1990).

In some locations, S_2 is gently folded with local development of crenulation cleavage. This may be a result of the Alpine deformation, which is the only post-Variscan compressional deformation described in the area

(Gallastegui, 2000 and references therein), and involves a ductile deformation that required a moderate temperature and gave rise to a dome shape in the Valsurbio unit (Marín, 1997).

The features described above refer to late-Variscan events related to the development of penetrative structures or to the intrusion of igneous rocks. However, the existence of such events does not preclude the development of others subsequently, such as the hydrothermal post-Variscan episodes described by Boni et al. (2000), Muchez et al. (2005), Gasparrini et al. (2006) and Clauer and Weh (2014).

5 Discussion

The distribution of the different grade indicators used in the study area shows, in general, an acceptable correlation between them, although some discrepancies have been observed. All methods coincide in pointing out the location of the areas with higher metamorphic grade, being the CAI and the AI the indicators that tend to give the highest and the lowest grade respectively. All indices point to an irregular distribution of the areas with very low-grade metamorphism. Diacaizonal areas are limited to the southeastern sector. A discrepancy is observed in the eastern Yuso-Carrión area between clay mineral and CAI data. A notable number of CAI values systematically indicate ancaizonal conditions, whereas clay assemblages with abundant I/S and Kln, KI and AI indicate diagenetic conditions.

The correlation among the different indicators that can be used to establish the metamorhic grade is challenging due to several factors, such as the different kinetics of the processes that modify the colour of the conodonts and the transformation of the clay minerals and the different influence of fluids in limestones and pelitic rocks. These processes could explain the discrepancies observed.

In the context of the Cantabrian Zone, the low-grade extensional metamorphism of the PCU extends westwards and allows an elongated area to be defined that can be followed up to the Central Coal Basin (Fig. 1) (Aller, 1981, 1986; Brime, 1985; Aller et al., 1987, 2005; García-López et al., 2007). The biggest width of this zone is in the study area, coinciding with the core of the Ibero-Armorican arc. In the Central Coal Basin, this metamorphism is linked to the occurrence of cleavage associated with crosscutting folds and it has been related to the possible existence of igneous bodies in depth (Aller, 1986) or to the rise of fluids along faults, especially the León fault (Aller et al., 2005). In the metamorphic southern part of the study area (VU), the metamorphism disappears westward, so that the adjacent western unit of the Esla nappe region is not metamorphic (García-López et al., 2013; Valín and Brime unpublished data).

The existence of hydrothermal alteration has been suggested by Brime and Valín (2006) and Clauer and Weh (2014). The common occurrence of Cld and Prl and the irregular distribution of CAI values, the wide range in the high CAI values in some samples and textural alterations of conodonts agree with the occurrence of hydrothermal fluids and possible subsurface igneous bodies. As for the thermal events dated by Clauer and Weh (illite K-Ar; 2014), the first has an age (293 ±3 Ma), comparable to that of the Peña Prieta granitoid, and the others (Guadalupian, middle Triassic and early-middle Jurassic) are probably related to the crustal extension associated with the Basque-Cantabrian basin. Specific structural evidences of these three later events have not been found and their temperatures were probably lower than those of the episode linked to the late-Variscan extensional episode, which, being related to igneous intrusions, probably gave rise to the paleothermal peak.

The zircon (U-Th)/He ages obtained by Fillon et al. (2016) indicate that the Westphalian (Bashkirian-Moscovian) rocks involved in the dating had probably a temperature above 180ºC up to 37-39 Ma ago (Eocene). This is consistent with the occurrence of Alpine ductile deformation, which resulted in a local crenulation cleavage.

6 Conclusions

Study of the low-grade metamorphic rocks and associated structures in the south-eastern sector of the CZ has allowed a model for the tectonothermal evolution of the core of an arcuate orogenic belt to be developed. This core, although it is a part of a foreland fold and thrust belt where diagenetic conditions are dominant, portrays a complex evolution due to its special location inside the belt. It was thrust during the Carboniferous by large units from south, west and north, which resulted in a great accumulation of syntectonic sediments, and development of unconformities and structures. The latter arose as a result of compression in different directions that also generated a crustal thickening. The emplacement of the last thrust unit (Picos de Europa unit) produced a N – S shortening that generated thrusts and associated folds. Shortly afterwards, upright folds with E – W trend and associated cleavage (S_1) developed, mainly in the northern part of the sector. The ductile deformation occurred under thermal conditions which reached the anchizone and the ancaizone in some areas. This represents the first tectonothermal event registered in the southeastern sector of the CZ.

At the end of the Variscan deformation, gravitational instability gave rise to an extensional episode and the corresponding crustal thinning. During this event an increase in the thermal gradient enabled ductile deformation and low-grade metamorphism to take place in some areas (second tectonothermal event), mainly in the central part (Curavacas-Lechada syncline) and the southern part (Valsurbio unit) of the sector. The ductile deformation produced gently dipping cleavage (S_2) crosscutting earlier upright F_1 folds. Some small open cascade folds were also produced. The metamorphism reached epizonal and epicaizonal conditions during this event. The process culminated in the Cisuralian with the intrusion of igneous rocks and the development of contact metamorphism around the larger igneous bodies. In the case of Peña Prieta granodiorite, post S_1 andalusite porphyroblasts developed. Hydrothermal fluids were common during this extensional episode, resulting in the development of Prl and Cld, and textural alteration and high CAI dispersions in conodont samples.

As a whole, the metamorphic grade is independent of the stratigraphic location of the samples and the trend of the main structures, indicating the late-orogenic character of the tectonothermal events. The thermal level decreases progressively northwards inside the adjacent Picos de Europa unit. On the other hand, the metamorphism associated with the extensional episode in the PCU is extended westwards as an elongated area whose development was probably favoured by the rise of fluids along faults, especially along the León fault.

With the development of the adjacent Basque-Cantabrian basin, the extensional regime extended during the Mesozoic, with the probable occurrence of hydrothermal processes. The temperature of the rocks was probably important during Cenozoic times (> 180ºC until the late-Eocene after Fillon et al., 2016, in the eastern part of the study area), so that the Alpine deformation generated locally some ductile deformation with crenulation cleavage affecting the S_2 cleavage.

The evolution described above is summarized in Table 1.

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Variscan deformation	Emplacement of north-directed Palentine nappes (prior or earliest Moscovian) and the adjacent western Cantabrian nappes (late Moscovian) with associated thrusts in the PCU
Variscan deformation (cont.) (N-S shortening)	Emplacement of the south-directed Picos de Europa unit; thrusts and folds in the PCU (Kasimovian-Gzhelian)
	Folds and axial plane cleavage (S_1); first tectonothermal event, with deep diagenetic – low anchizonal and ancaizonal areas in the northern part of the PCU (late Gzhelian)
Late Variscan gravitational readjustment; extensional event	Gently dipping cleavage (S_2) associated with crosscutting folds; second tectonothermal event; very low- or low-grade metamorphism (high anchizone-epizone, and ancaizone-epicaizone) in the syncline of Curavacas-Lechada and the VU. Normal faults (latemost Gzhelian to early Cisuralian)
	Intrusion of igneous rocks, contact metamorphism and wide development of hydrothermal processes (Cisuralian)
Extension linked to the Basque-Cantabrian basin	Permian and Mesozoic hydrothermal episodes
Alpine deformation	N-S shortening, tightening of gentle folds, local crenulation cleavage and tilting of rocks northwards (Cenozoic).

Table 1. Tectonothermal evolution of the southeastern sector of the Cantabrian Zone.

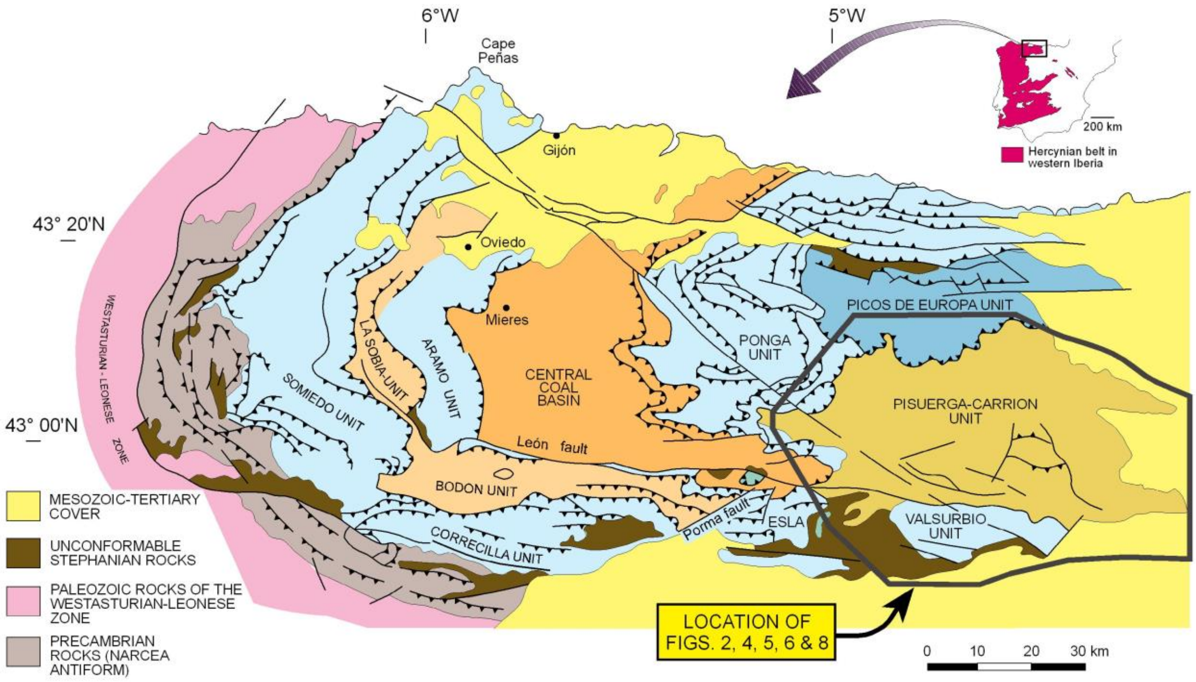


Figure 1. Generalized geological map of the Cantabrian Zone (after Julivert 1971) showing major thrust units and the location of the study area.

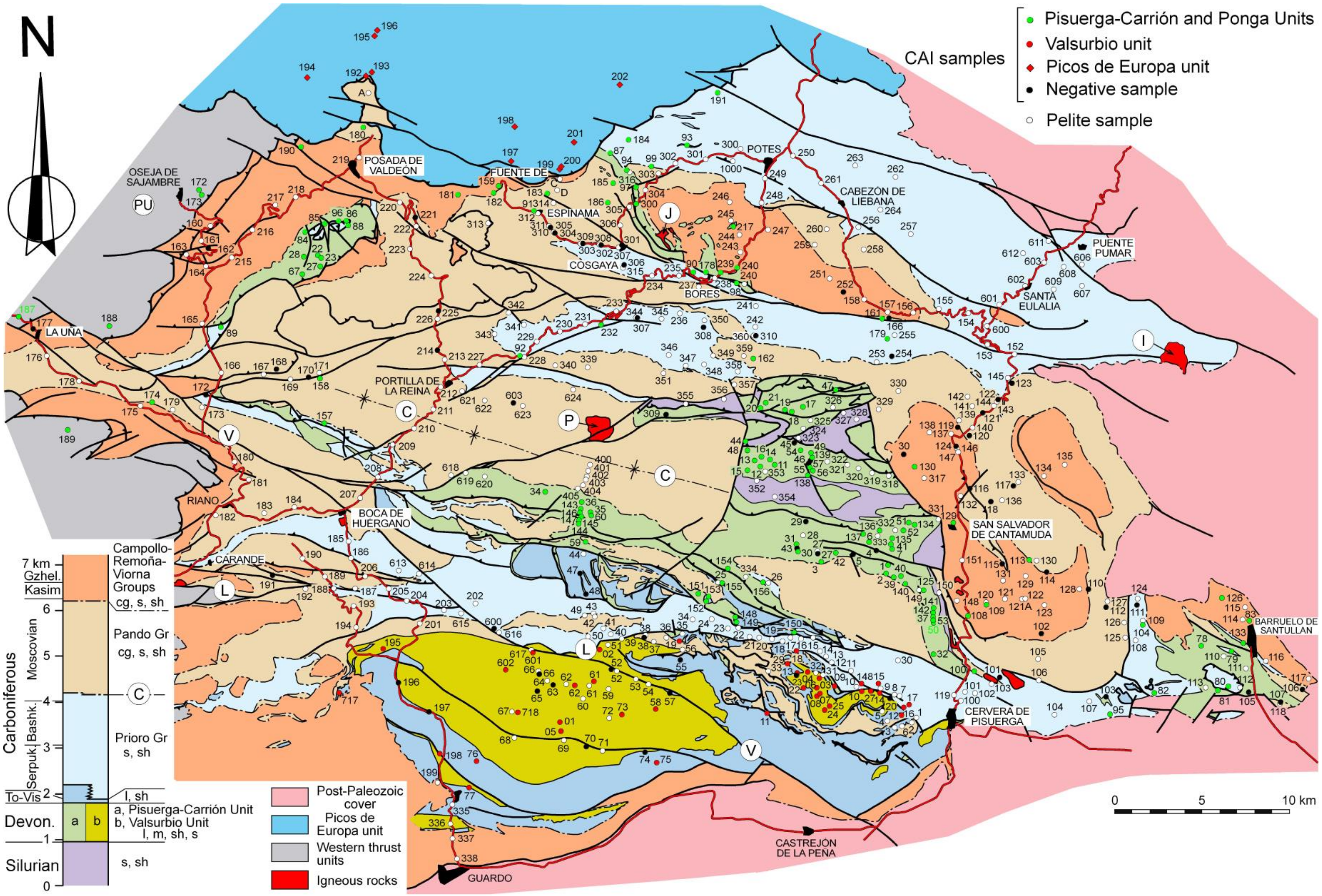

N
CAI samples
Pisuerga-Carrión and Ponga Units
Valsurbio unit
Picos de Europa unit
Negative sample
Pelite sample
POTES
CABEZÓN DE LIEBANA
PUENTE PUMAR
SANTA EULALIA
OSEJA DE SAJAMBRE
POSADA DE VALDEÓN
FUENTE DE
ESPINAMA
CÒSGAYA
BORES
LA UÑA
PORTILLA DE LA REINA
RIAÑO
BOCA DE HUERGANO
CARANDE
SAN SALVADOR DE CANTAMUDA
BARRUELO DE SANTULLAN
CERVERA DE PISUERGA
CASTREJÓN DE LA PEÑA
GUARDO
PU
J
I
P
C
V
L
0
5
10 km
7 km
Gzhel.
Kasim
Moscovian
Carboniferous
Serpuk.
Bashk.
To-Vis
Devon.
Silurian
Campollo-Remoña-Viorna Groups
cg, s, sh
Pando Gr
cg, s, sh
Prioro Gr
s, sh
l, sh
a, Pisuerga-Carrión Unit
b, Valsurbio Unit
l, m, sh, s
s, sh
Post-Paleozoic cover
Picos de Europa unit
Western thrust units
Igneous rocks

Figure 2. Geological map of the southeastern part of the Cantabrian Zone showing sampled localities (composed from Lobato, 1977; Colmenero et al., 1982; Ambrose et al., 1984; Julivert and Navarro, 1984; Martínez García et al., 1984; Lobato et al., 1985; Heredia et al, 1986, 1991, 1997; Rodríguez Fernández, 1994; Rodríguez Fernández et al., 1994). Devonian and Silurian rocks of the PCU form the Palentine nappes. cg, conglomerate; l, limestone; m, marl; s, sandstone; sh, shale. C, Curavacas-Lechada syncline; I, Pico Iján granodiorite; J. Pico Jano granodiorite; L, León fault; P, Peña Prieta granodiorite; PU, Ponga unit; V, Ventaniella fault. Picos de Europa conodont samples after Bastida et al., 2004; Valsurbio conodont samples after García-López et al., 2013.

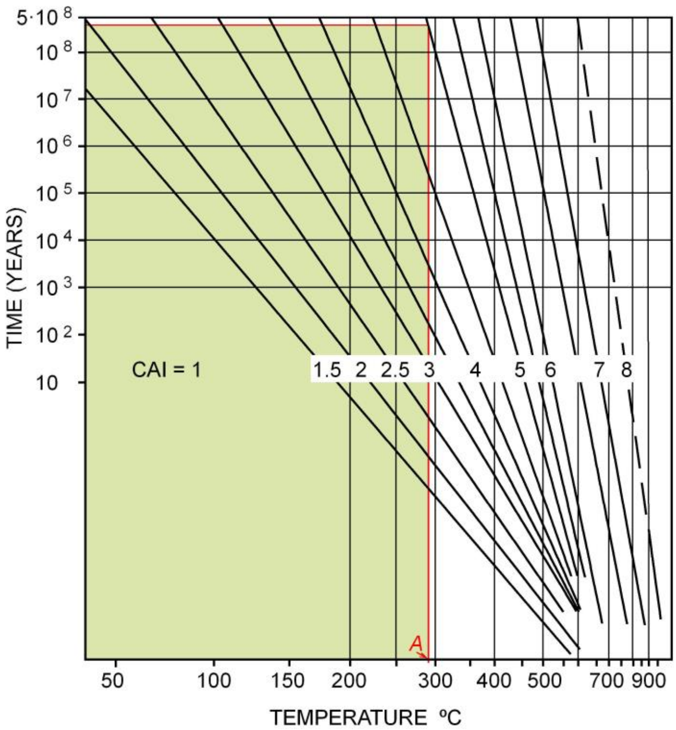


Figure 3. Arrhenius plot to determine paleotemperature from CAI values (on the lines) and heating time (from Rejebian et al., 1987). Point *A* indicates the minimum temperature necessary to obtain a CAI = 5 for a rock with an age of 400 Ma. The green area shows the temperatures and heating times unable to produce CAI ≥ 5 in this rock.

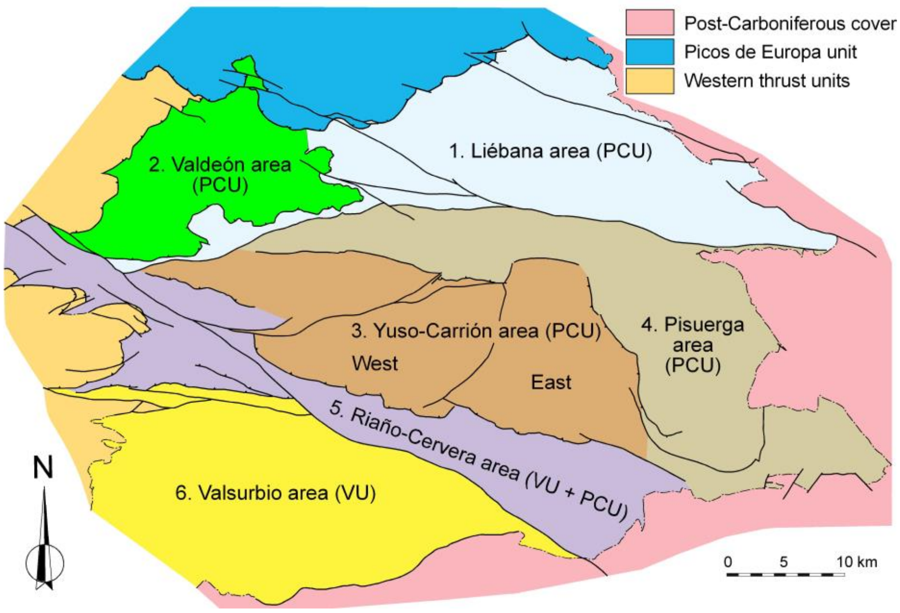


Figure 4. Diagramatic map indicating the areas in which the study units have been subdivided, following Martín-Merino et al. (2014)

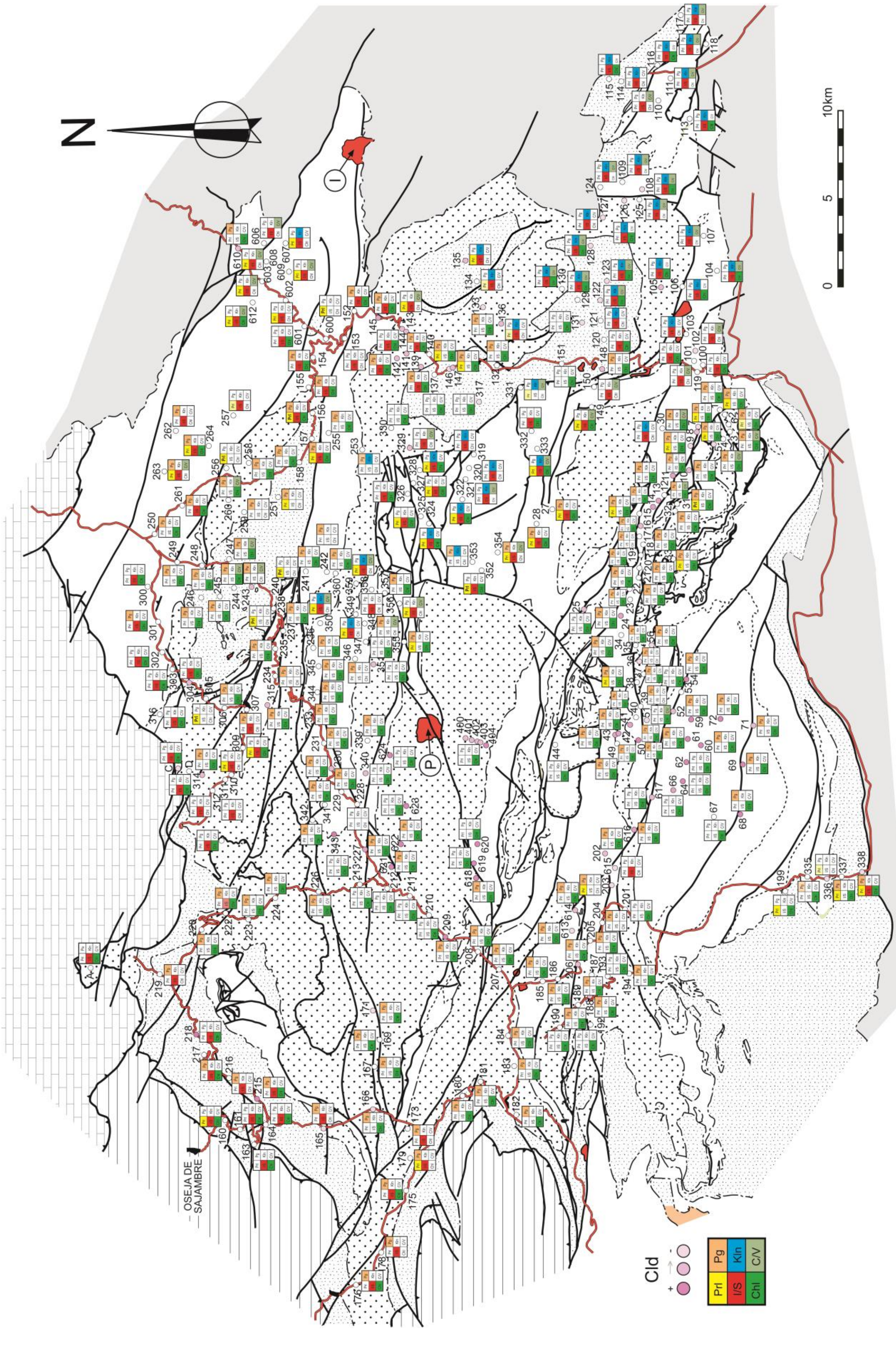

N
0
5
10km
OSEJA DE SAJAMBRE
Cld
Prl
Pg
I/S
Kln
Chl
C/V
P
I

Figure 5. Distribution of clay minerals in the study area. All the samples contain illite and therefore this phase has not been considered in the plot. Presence of a certain phase in the sample is indicated by the colour in the corresponding square. I, Pico Iján granodiorite; P, Peña Prieta granodiorite. For legend see Figure 8.

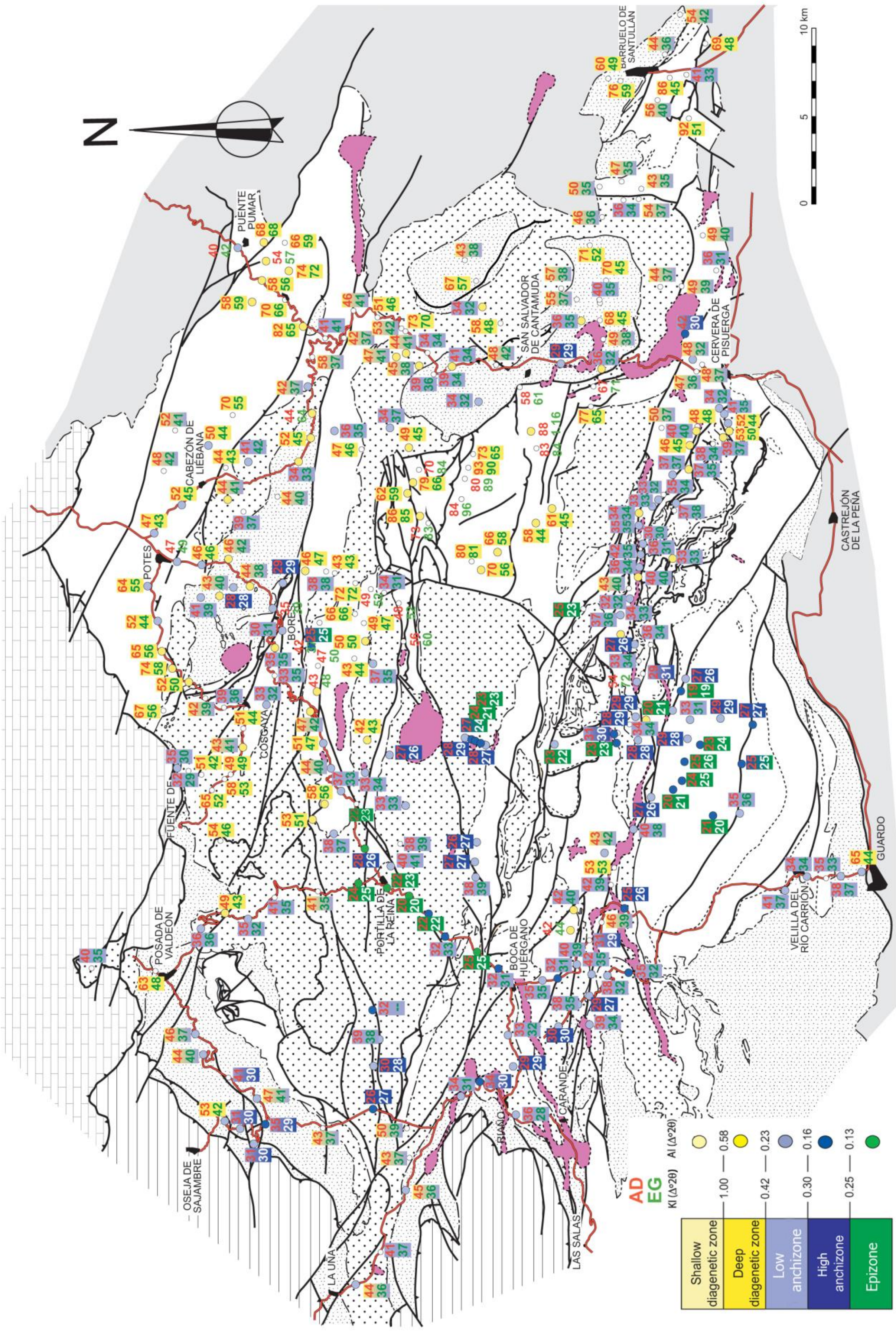

N
0 5 10 km
PUENTE PUMAR
BARRUELO DE SANTULLÁN
CABEZÓN DE LIÉBANA
POTES
SAN SALVADOR DE CANTAMUDA
CERVERA DE PISUERGA
CASTREJÓN DE LA PEÑA
BORES
COSGAYA
FUENTE DE
POSADA DE VALDEÓN
PORTILLA DE LA REINA
BOCA DE HUÉRGANO
VELILLA DEL RÍO CARRIÓN
GUARDO
OSEJA DE SAJAMBRE
LA UÑA
SIERO
CARANDE
LAS SALAS
AD
EG
KI (Δ°2θ)
AI (Δ°2θ)
Shallow diagenetic zone
Deep diagenetic zone
Low anchizone
High anchizone
Epizone
1.00
0.58
0.42
0.23
0.30
0.16
0.25
0.13

Figure 6. Map showing location of Kübler Index (KI) values (Kübler scale). Upper value, in red, air dried sample; lower value, in green, sample treated with ethylene glycol. Árkai Index (AI) is indicated by the colour of the sampling point. Values corresponding to samples with significant amounts of I/S, Prl and/or Pg-Pg/Ms have not been highlighted with grade colours. Areas with small outcrops of intrusive rocks are shadowed with purple colour. For legend see Figure 8.

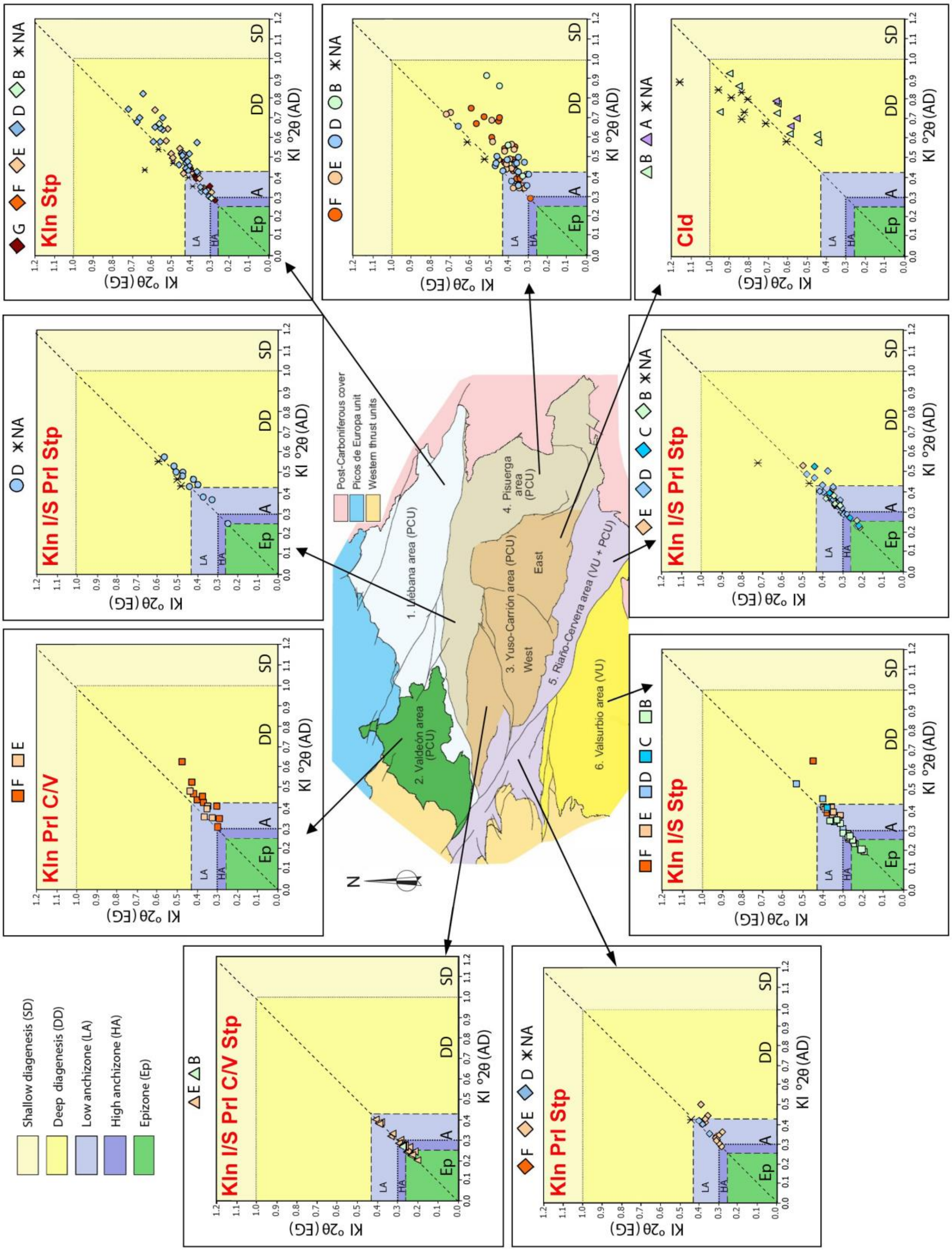
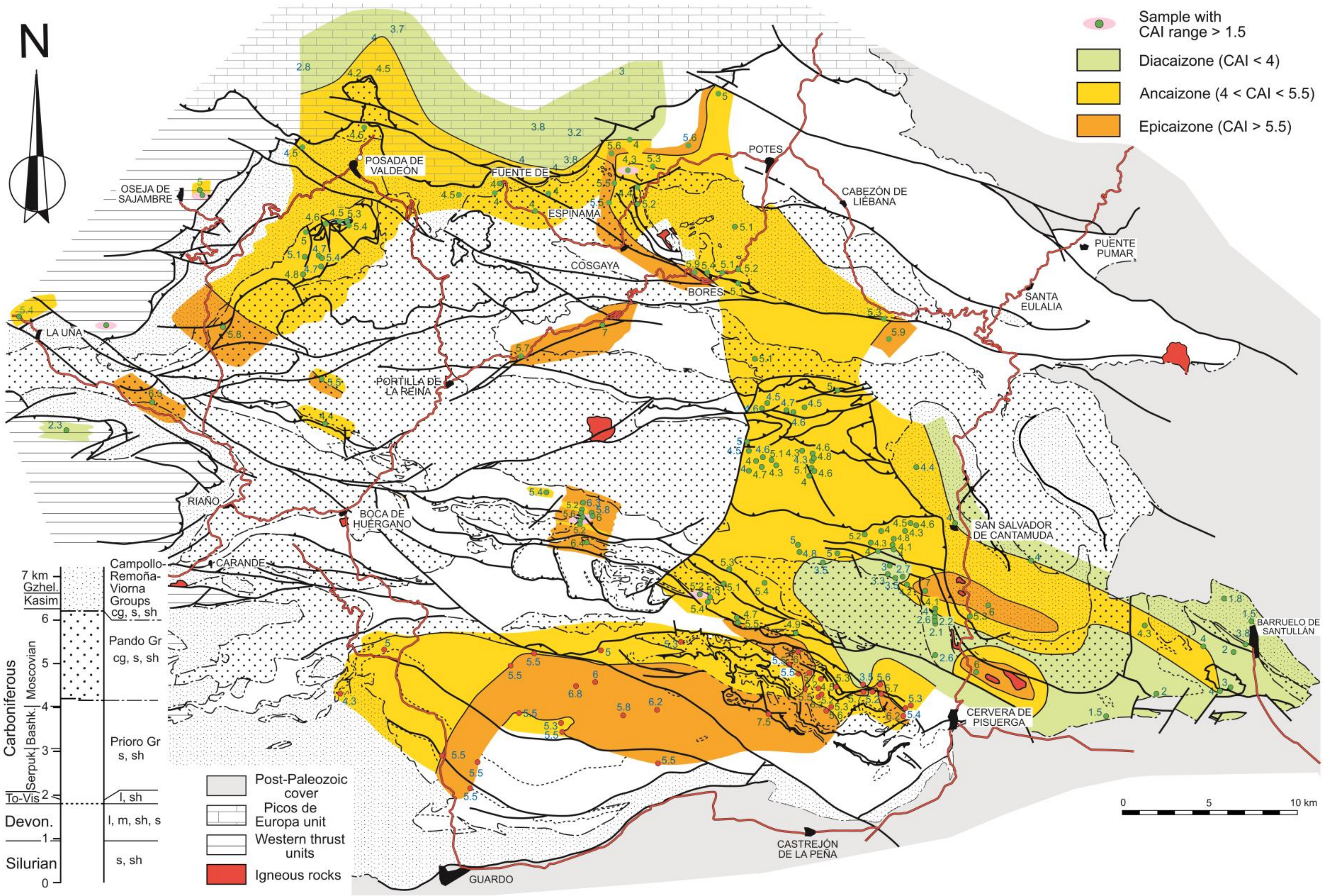


Figure 7. Plot of Kübler Index (KI) measured on air dried (AD) *versus* KI measured on ethylene glycol solvated samples (EG), standarized at Kübler scale. DD, Shallow Diagenesis; LA, Low Anchizone; HA, High Anchizone; Ep, Epizone. Samples are plotted according to the areas outlined in Fig.4 and have been grouped following the divisions of Fig. 2: A, Silurian; B, Devonian; C, Tournasian-Visean; D, Prioro Group; E, Pando Group; F, Viorna Group; G, Campollo-Remoña Group. Samples with significant amounts of I/S,Prl and/or Pg-Pg/Ms are indicated as NA (not applicable). Minerals absent in each of the areas are indicated in red.



N
Sample with CAI range > 1.5
Diacaizone (CAI < 4)
Ancaizone (4 < CAI < 5.5)
Epicaizone (CAI > 5.5)
POSADA DE VALDEÓN
FUENTE DE
ESPINAMA
POTES
CABEZÓN DE LIÉBANA
PUENTE PUMAR
SANTA EULALIA
OSEJA DE SAJAMBRE
COSGAYA
BORES
LA UÑA
PORTILLA DE LA REINA
RIAÑO
BOCA DE HUÉRGANO
CARANDE
SAN SALVADOR DE CANTAMUDA
BARRUELO DE SANTULLÁN
CERVERA DE PISUERGA
CASTREJÓN DE LA PEÑA
GUARDO
0
5
10 km
7 km
Gzhel.
Kasim
Campollo-Remoña-Viorna Groups
cg, s, sh
Pando Gr
cg, s, sh
Moscovian
Bashk.
Serpuk.
Carboniferous
Prioro Gr
s, sh
To-Vis
l, sh
Devon.
l, m, sh, s
Silurian
s, sh
Post-Paleozoic cover
Picos de Europa unit
Western thrust units
Igneous rocks

Figure 8. Map with location of CAI values and delimitation of CAI isogrades. Picos de Europa CAI data after Bastida et al., 2004; Valsurbio CAI data after García-López et al., 2013. Symbols of the CAI samples as in Fig. 2.

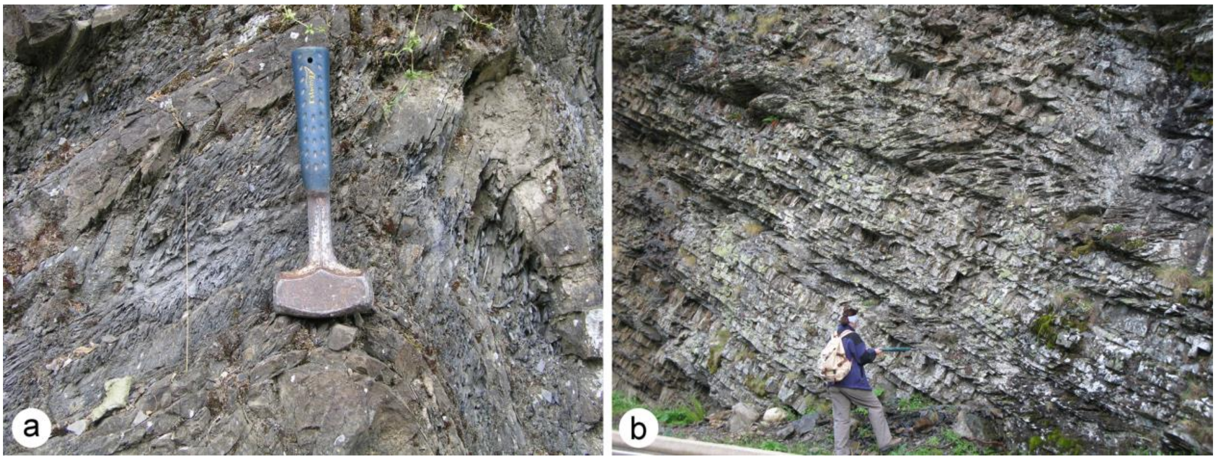


Figure 9. (a) S_1 cleavage associated with a nearly upright fold (eastern part of the Liébana area; north to the right). (b) S_2 cleavage dipping less than bedding in a normal stratigraphic succession (Pando Group; Curavacas-Lechada syncline; north to the left).

Appendices (Supplement)

Appendix 1. Conodont colour alteration index (CAI) values and temperatures inferred from the CAI Arrhenius plot (Epstein et al., 1977; Rejebian et al., 1987). (V: Valsurbio samples; P: Pisuerga-Carrión samples; Po: Ponga samples; Pe: Picos de Europa samples).

Appendix 2. Containing:

1. Values of Kübler Index (KI) measured on air dried (AD) *versus* KI measured on ethylene glycol solvated samples (EG), standarized at Kübler scale. Samples are grouped according to the areas outlined in Fig. 4. Samples with significant amounts of I/S and Pg-Pg/Ms that have not been plotted in Figs 6 and 7 are indicated with Roman letter type of smaller size.

2. Árkai Index (AI) has been measured on air dried samples (AD).

3. Clay minerals present in the samples. Capitals and bold type indicate more abundance of the phase.