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Transition from diagenesis to metamorphism in a calcareous tectonic unit of the Iberian Variscan belt (central massif of the Picos de Europa, NW Spain)

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Abstract – Transition from diagenesis to metamorphism has been characterized in the central part of the Picos de Europa unit (Cantabrian Zone) by conodont colour alteration index (CAI), complemented with Kübler index (KI) data. This unit essentially comprises Carboniferous limestone. The study leads us to deduce two successive tectonothermal events. The first event generated a pattern with palaeotemperatures increasing towards the Pisuerga–Carrión unit, located south of the Picos de Europa unit. The present pattern is the result of an original dip to the north of the isothermal surfaces and the subsequent rising of the Picos de Europa unit along the frontal ramp of a deep Alpine thrust. This episode is interpreted as related to an extensional tectonic regime that occurred close to the Carboniferous–Permian boundary. The second event, which gave rise to thermal anomalies in the pattern of the first episode, was the result of hydrothermal processes in which fluid movement was facilitated by a dense network of fractures in the area close to the eastern section of the studied region. These processes gave rise to numerous mineralizations and have been related to a Permian extensional tectonic regime.

Keywords: CAI, diagenesis, low-grade metamorphism, extension, Variscan.

1. Introduction

Knowledge of the thermal history of rocks located in diagenetic or transitional diagenetic/metamorphic conditions is extremely important for understanding the tectonothermal evolution of orogenic belts. Where basic igneous rocks are not present, the study of such conditions is mainly based on the Kübler index (KI), the conodont colour alteration index (CAI) and the vitrinite reflectance (R). The study of illite ‘crystallinity’ has allowed the definition of an index (Kübler index, KI; see Guggenheim *et al.* 2002, for details about the present use of this term) that decreases with increasing metamorphic grade (Kübler, 1967) and has made possible the definition of the ‘anchizone’ in fine-grained clastic rocks, which marks the transition between diagenesis and low-grade metamorphism. Hence, the KI has become a reference index for the study of this transition. Nevertheless, the use of the KI is restricted to fine-grained clastic rocks, and it is therefore necessary to correlate it with other indices used for studies of low-grade metamorphism.

The CAI method is mainly useful in carbonate rocks, and consequently KI and CAI are mutually complementary methods. The CAI method is based on the analysis of the colour changes of conodont organic matter over time with increases in temperature. These changes have made it possible to construct a value scale with eight units (Epstein, Epstein & Harris, 1977; Rejebian, Harris & Huebner, 1987). The CAI method is a simple and useful tool that covers a large temperature range (50–600 °C). Specific correlations between KI and CAI values have been obtained in several areas (e.g. Kovács & Árkai, 1987; Keller, Lehner & Buggisch, 1993; Gawlick, Krystyn & Lein,1994; García-López *et al.* 1997), and an attempt at a more general correlation has been made by García-López *et al.* (2001). Based on the CAI values that statistically correspond to the KI values which mark the anchizone boundaries, these authors have defined three zones in the transition from diagenesis to metamorphism, named the ‘diacaizone’, ‘ancaizone’ and ‘epicaizone’. The use of these zones enables the transition between diagenesis and metamorphism from CAI data to be characterized exclusively in areas where there are no fine-grained clastic rocks or where KI data are not available. This terminology of zones from CAI data is used in the present paper.

The Cantabrian Zone is located in the core of the Ibero-Armorican arc and is the zone of the southern branch of the European Variscan belt where the characteristics of a foreland thrust and fold belt are

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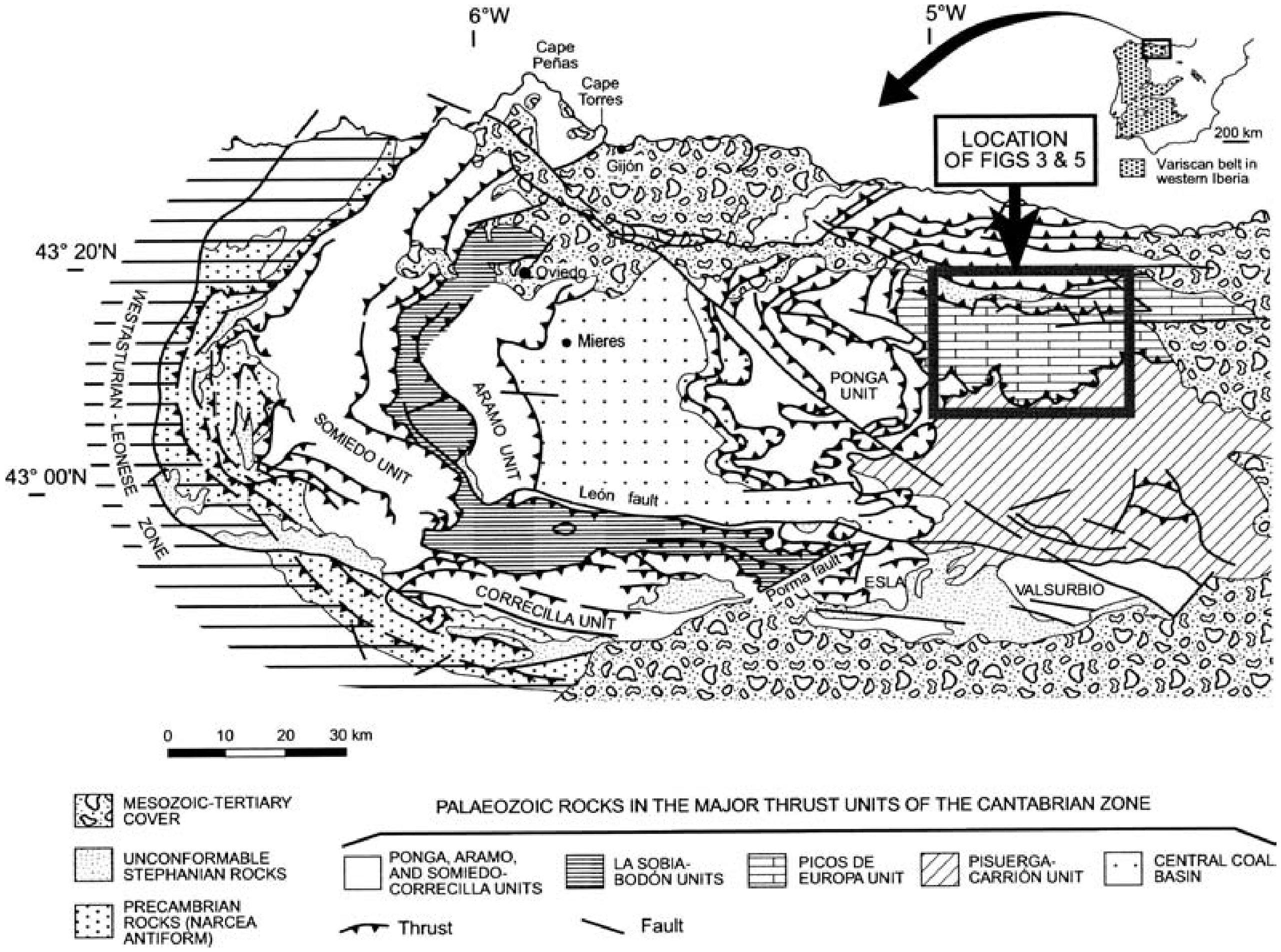

Figure 1. Generalized map of the Cantabrian Zone (after Julivert, 1971) with the location of the study area.

best represented (Fig. 1). It has thin-skinned tectonics and is mostly non-metamorphic. Nevertheless, there are a few areas in the Cantabrian Zone with anchizonal or even epizonal conditions and cleavage development, so this zone is of particular interest in the study of the transition between diagenesis and metamorphism.

Several studies using KI and/or CAI have focused on the tectonothermal history of the western units of the Cantabrian Zone (Brime & Pérez-Estaún, 1980; Keller & Krumm, 1992, 1993; García-López *et al.* 1997; Bastida *et al.* 1999; Brime *et al.* 2001). A few areas of the southern part of the Cantabrian Zone have also been analysed by the KI method (Aller & Brime, 1985; Brime, 1985; Aller *et al.* 1987). In addition, review papers on the metamorphism in the Cantabrian Zone have been published by Raven & van der Pluijm (1986), Suárez & Corretgé (1987), García-López *et al.* (1999) and Bastida *et al.* (2002). In accordance with the latter authors, four Variscan episodes of low-grade metamorphism can be distinguished in the Cantabrian Zone:

(a) *Orogenic*. This is well represented in the internal zones of the Variscan Iberian belt and slightly penetrates a few areas of the Cantabrian Zone.

(b) *Burial*. This appears in the basal part of some thrust units and pre-dates thrust development.

(c) *Metamorphism associated with an extensional episode* (diastathermal *sensu* Robinson, 1987). It appears in the central and southeastern parts of the Cantabrian Zone. It is mainly anchizonal, although the epizone is reached in a few areas. A subhorizontal or moderately N-dipping cleavage is associated with this metamorphism.

(d) *Contact metamorphism around small intrusive bodies*. This episode can reach higher-grade conditions than the other episodes.

Episodes (a) and (b) are probably mutually related and represent two manifestations of Variscan regional metamorphism. Episodes (c) and (d) occurred near the boundary between the Carboniferous and the Permian and can be considered as late Variscan events.

Currently there are some areas in the Cantabrian Zone where thermal history of the rocks is poorly understood. This is the case of the Picos de Europa unit (Fig. 1), and the purpose of this paper is to study the transition from diagenesis to metamorphism from data mainly obtained along two sections through this unit: the Cares river section (or western section) and the Duje river section (or eastern section). The thermal conditions will be related to the lithology and the structure to establish a model of the thermal evolution of the study sector. Since the rocks involved are primarily limestone, the CAI method is mainly used, but it has been complemented with some KI data obtained from the scarce pelitic rocks in the area.

2. Geological setting

The Picos de Europa unit is located in the core of the Ibero-Armorican arc (Fig. 1) and is mainly formed of Carboniferous limestone (Figs 2, 3). It is overthrust by the Ponga nappe unit to the west and it thrusts over the Pisuerga–Carrión unit to the south (Fig. 1), which mainly consists of synorogenic siliciclastic Carboniferous rocks, although Silurian and Devonian rocks are also present. The structure of the Picos de Europa unit is formed by an imbricated system of thrusts (Figs 3, 4). According to the interpretation by Marquínez (1989), Farias & Marquínez (1991) and Farias & Heredia (1994), the thrusts are S-directed listric faults that converge towards a basal thrust. This thrust is mainly located in the lower levels of the Carboniferous succession, reaching Ordovician rocks in the northern part of the section. The development of a great number of thrusts gave rise to a multiple repetition of the Carboniferous carbonate succession.

The structure is mainly a result of the Variscan deformation, although the development of the thrusts occurred in the last stages of the forward thrust sequence of the Cantabrian Zone. In the Picos de Europa unit, the lower Gzhelian rocks are involved in the deformation and affected by thrusting (Marquínez, 1978; Martínez-García & Villa, 1998, 1999; Sánchez de Posada *et al.* 2002). Similarly, in the juxtaposed Pisuerga–Carrión unit, the synorogenic succession may reach Gzhelian times (Stephanian B–C) (Heredia *et al.* 1991; Rodríguez-Fernandez *et al.* 1994; Colmenero *et al.* 2002; Rodríguez-Fernández, Fernández & Heredia, 2002). However, in the rest of the Cantabrian Zone the equivalent Stephanian rocks are unconformable and are not affected by the thrusts. This structure was modified by the Alpine deformation which gave rise to the reactivation of some thrusts and the development of faults. In addition, geological and geophysical data indicate the existence of a deep Alpine thrust system with large ramps along which the Palaeozoic rocks of the Cantabrian Zone thrust southwards onto the Mesozoic–Tertiary cover (Alonso *et al.* 1996; Gallastegui, 2000). The movement of this thrust probably increased the northward dip of the Picos de Europa basal thrust.

Ore deposits and ore showings are common in the Picos de Europa unit (Fig. 5). They are mainly Zn–Pb mineralizations, but other elements, such as Fe, Mn, Cu, Ba and Hg can also be present (Martínez-García, 1983; Martínez-García *et al.* 1991; Gómez-Fernández *et al.* 1993, 2000; Martín-Izard, Paniagua & Arias, 1995; Gutiérrez-Claverol & Luque, 2000). Gómez-Fernández *et al.* (1993, 2000) interpreted the Zn–Pb deposits as epigenetic hydrothermal mineralizations

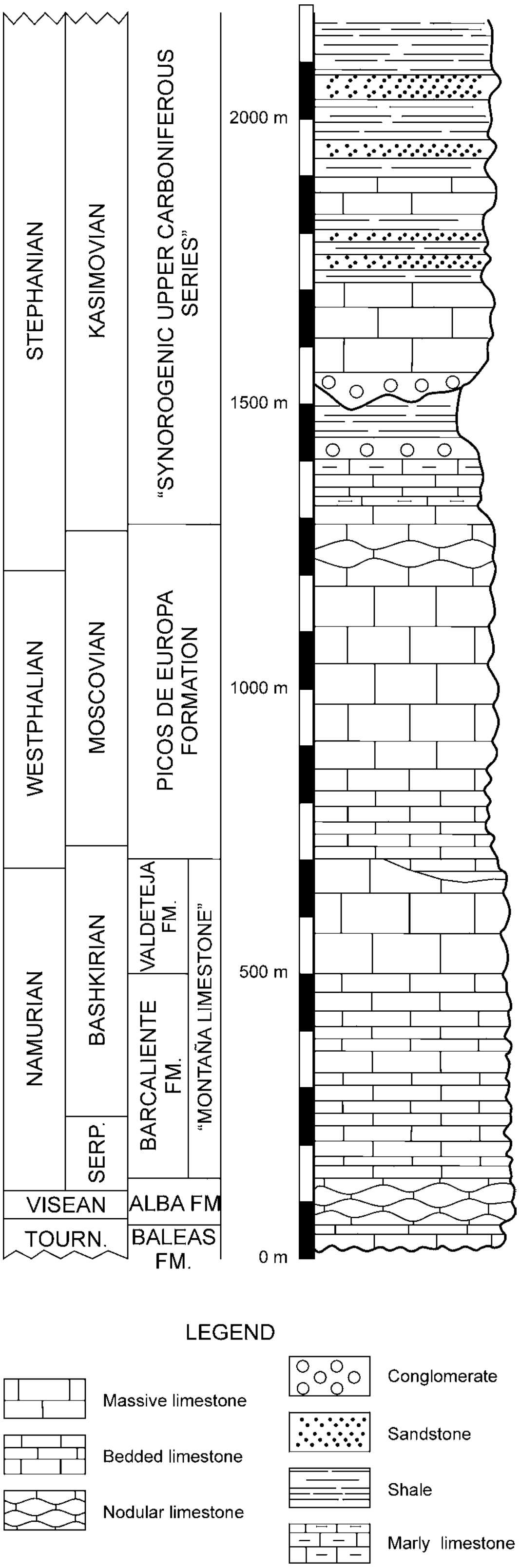

Figure 2. Synthetic stratigraphic column of the rocks cropping out in the study area.

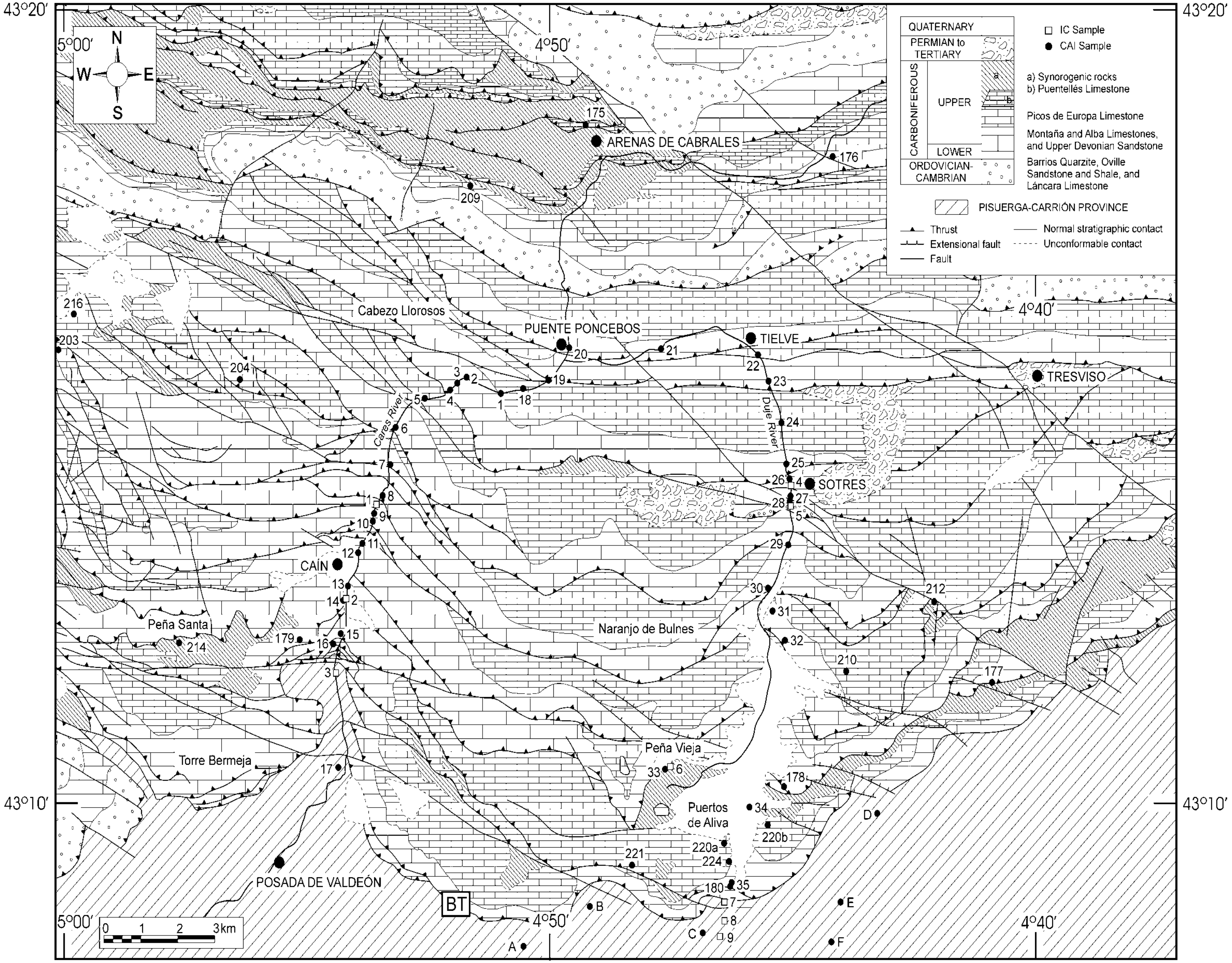

Figure 3. Geological map of the study area with location of samples (geology after Marquínez, 1989). Samples A–F, after Raven & van der Pluijm (1986, fig. 2); BT – Picos de Europa basal thrust.

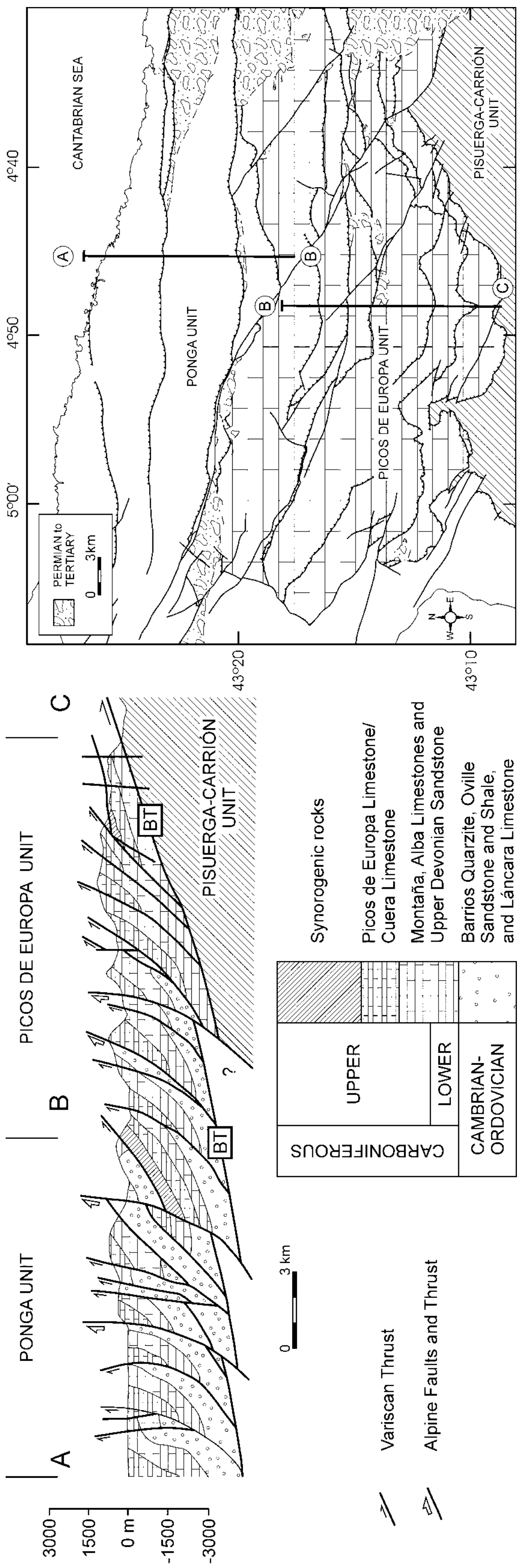

Figure 4. Geological cross-section through the Picos de Europa unit (after Marquínez, 1989). BT – Picos de Europa basal thrust.

formed at moderate temperatures (about 170–200 °C) from formation water of the sediments of the Pisuerga Carrión and Picos de Europa units; the fluids would have migrated through late Variscan fractures during a Permian extensional episode.

Previous data related to the thermal conditions of the rocks in the Picos de Europa unit are very scarce. Nevertheless, to the south, in the Pisuerga–Carrión unit, CAI data indicate anchizonal or even epizonal metamorphism in some areas (Raven & van der Pluijm, 1986; García-López *et al.* 1999). A moderately N-dipping cleavage is associated with this metamorphism that cuts most of the folds in the area (Rodríguez-Fernández, 1994; J. A. Marín, unpub. Ph.D.thesis, Univ. Oviedo, 1997). This metamorphism occurred between the Kasimovian and the Early Triassic, probably near the Carboniferous–Permian boundary (García-López *et al.* 1999; Bastida *et al.* 2002).

3. Methods

Samples from 35 localities were collected along the study sections to obtain CAI values, but only 21 yielded conodonts. In addition, the CAI from 10 conodont localities from the collections of the Oviedo University was evaluated, and the CAI values of 12 samples obtained previously by Raven & van der Pluijm (1986) were used (six of them were revised). CAI values were determined by comparison with a standard set prepared under the direction of A. G. Harris at the U. S. Geological Survey (Reston, Virginia). Conodont textures were observed under the scanning electron microscope in order to infer thermal changes or other types of processes. Temperature ranges corresponding to CAI values were obtained from the Arrhenius plot presented by Epstein, Epstein & Harris (1977) and Rejebian, Harris & Huebner (1987). The minimum heating time considered is 1 Ma, according to Epstein, Epstein & Harris (1977), and the maximum heating time considered is the difference between the age of the rock and the beginning of the Triassic (*c.* 250 Ma), since rocks of this age appear in non-conformity on the igneous rocks that post-date the low-grade metamorphism. After the beginning of the Triassic, the studied Palaeozoic rocks were not exhumed until the Alpine rise of the Cantabrian Zone; none the less, the CAI values were not influenced by temperatures much lower than those of the thermal peak (García-López *et al.* 2001).

It is common for conodonts from a single sample to have dispersed CAI values. Dispersion ranges ≤ 1 are due to normal variability in the amount of organic matter of the different morphotypes of the sample and, in order to plot CAI data on a map and construct a metamophic zonation, the mean CAI values have been used in these cases. When the dispersion range is > 1, and a single CAI modal interval exists, the presence of fluids is probable. In these cases, the two

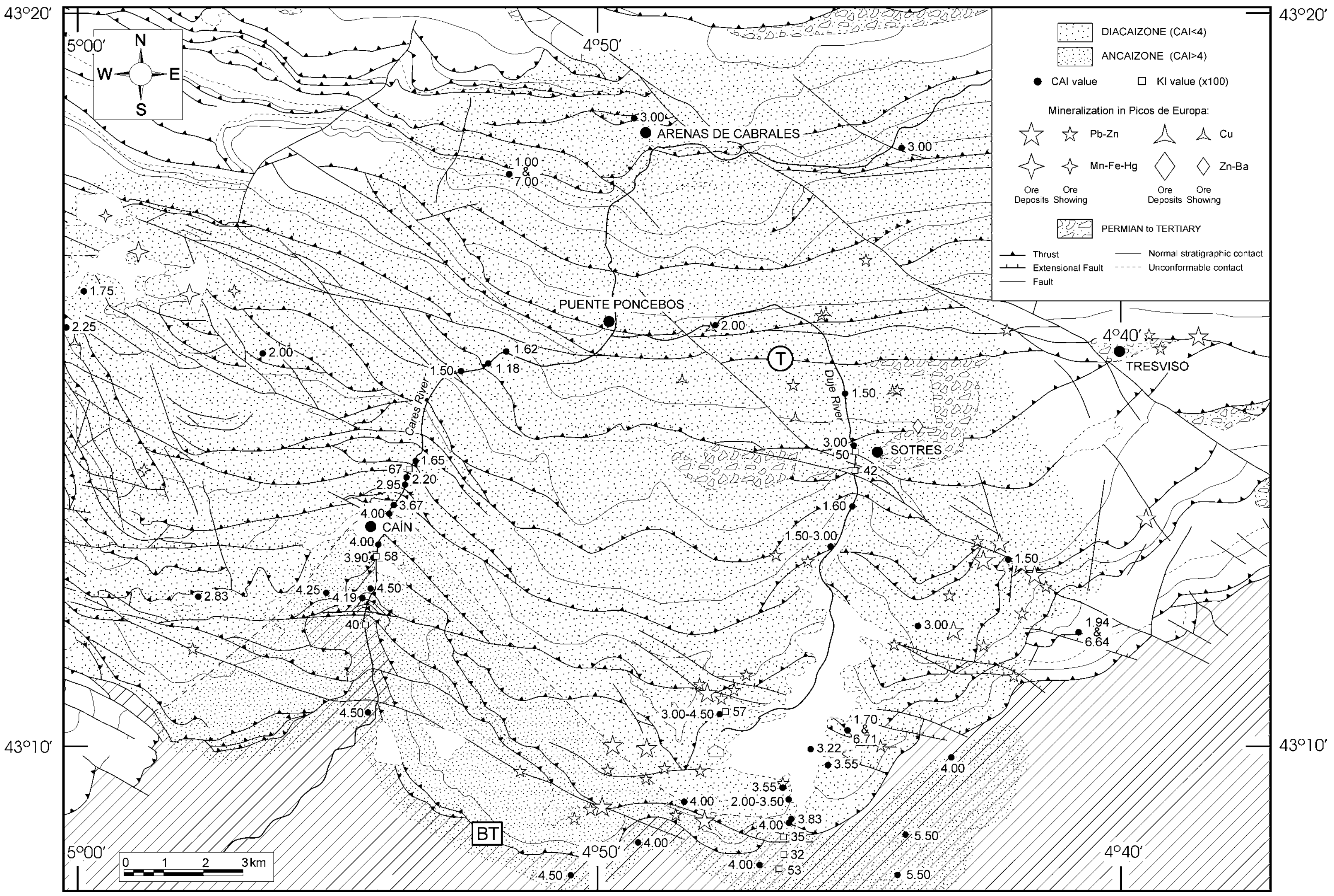

Figure 5. Map with location of conodont colour alteration index (CAI) values and Kübler index (KI) values and boundaries of the diacaizone and ancaizone. BT – Picos de Europa basal thrust; T – Tresviso thrust.

extreme CAI values of the range have been represented on the map. A range of > 1 with two CAI modal intervals is always due to hydrothermal processes; in these cases two mean values have been determined and represented on the map. In all cases with a range of > 1, the presence of corroded surfaces in conodonts is another distinctive feature of hydrothermal alteration; then, CAI values cannot be used to assess temperatures, although they may serve as a valuable indicator of potential mineralization (Rejebian, Harris & Huebner, 1987).

To complement the CAI method, only nine samples could be collected to obtain the Kübler Index due to the scarcity of fine-grained clastic rocks in the area. The samples for XRD analysis were dispersed in deionized water and disaggregated before separation of the < 2 μm fraction by settling in a water column. This clay fraction was smeared on glass slides and air dried in atmospheric conditions.

X-ray diffraction patterns were obtained using a Philips automated PW1730/10 X-ray diffractometer, with CuKα radiation and graphite monochromator operating at 40 kV and 30 mA, with intervals of 0.02° 2θ for at least 2 s. The identification of the mineral phases was determined from diffractograms of orientated air-dried mounts, after glycolation and heating to 300 and 550 °C. Preparation of samples and determinations of the Kübler Index followed the recommendation of the IGCP294 working group (Kisch, 1991). The KI values obtained were converted to the Kübler scale with anchizone limits of 0.42°/0.25° $\Delta°2\theta$, using a set of samples provided by H. J. Kisch (Ben-Gurion University of the Negev, Israel).

4. Results

The results obtained from the CAI data are shown in Table 1 and on the map in Figure 5, in which a metamorphic zonation has been established. In the western section, along the Cares river canyon, CAI values increase progressively southwards from 1 to 5, suggesting a temperature range between 50 and 275 °C (Table 1). These values indicate thermal conditions ranging from the diacaizone to the ancaizone (Fig. 5), with a transition zone in which mean CAI values are close to 4. Ancaizonal values appear in the basal part of the Picos de Europa unit and in the footwall of this unit, that is, in the Pisuerga–Carrión unit. The three complementary KI values agree with the tendency of the CAI values, with an anchizonal value in the Pisuerga–Carrión unit (Fig. 5). The conodont elements mainly present a sugary texture with dull surfaces. Incipient granular texture only appears in a few conodonts with CAI = 5 located in the southern part of the Cares section and it corresponds to the beginning of apatite recrystallization. The dispersion of CAI values in the Cares section is low, although there is a locality to the northwest of this section (locality 209 in Fig. 3) where low and high CAI values coexist in a single sample.

In the eastern section, along the Duje river valley and neighbouring areas, the CAI value distribution is more complicated. In any case, the higher CAI values are found in the southern part of the section, with values of 4 (diacaizone/ancaizone boundary) near the Picos de Europa basal thrust. To the north of the Tresviso thrust (Fig. 5), there are several localities with CAI values of 2–3, higher than at some localities south of this thrust. A relatively high CAI value (CAI = 3) also appears near the village of Sotres (Fig. 5). The CAI dispersion is low, except for a few localities (30, 33, 177, 178 and 224 in Fig. 3 and Table 1) in which the conodonts have a sugary texture with dull and corroded surfaces. The six KI values (Fig. 5) measured in this section are compatible with the CAI values. Two of these values, located in the Pisuerga–Carrión unit, are anchizonal, and one, located near Sotres and the locality with the abnormally high CAI value cited above, corresponds to the diagenesis/anchizone boundary.

In both sections the mineralogical analyses of the < 2 μm fraction of the pelitic rock samples show that illite is the principal clay mineral phase present in all samples. Minor amounts of chlorite and mixed-layer illite/smectite are common.

5. Interpretation and discussion

All the samples have a similar stratigraphic position; hence, the variation of the CAI (and KI) values cannot be explained by a burial effect, but must be a result of tectonic processes. On the other hand, the pattern of CAI is different in the two study sections.

The western section is suggested to be controlled by a thermal event that increased towards the basal thrust of the Picos de Europa (Fig. 5). Near this thrust, the ancaizone appears both in the hanging-wall and the footwall; in the latter, an anchizonal KI value is also present. Hence, this very low-grade metamorphism continues without apparent discontinuity in the Pisuerga–Carrión unit, where it is widespread, indicating that the metamorphism post-dated the main tectonic movement along the basal thrust of the Picos de Europa unit during Kasimovian–Gzhelian times. On the other hand, the progressive character, with no apparent discontinuities in the increase of the CAI values southwards, indicates little or no displacement along the thrusts during the Alpine deformation. The increase of the CAI values and the topographic height of the localities southwards gives rise to the pointing-northwards ‘V’ shape shown by the diacaizone/ancaizone boundary trace in the southern part of the Cares river canyon (Fig. 5), and it suggests a northward dip of the isothermal surfaces. It can be in part an original feature of these surfaces and in part due to a southward rise of the Picos de Europa unit after the

Table 1. Conodont colour alteration index (CAI) values and temperatures inferred from the CAI Arrhenius plot (Epstein, Epstein & Harris, 1977; Rejebian, Harris & Huebner, 1987) according to the heating interval of the rocks

Tectonic unit	Locality number	Formation	Age	CAI (number of specimens)	Mean value	Standard deviation	Temperature range (°C)	Texture
Picos de Europa	2	Alba	Visean	1.5(19); 2(6)	1.62	0.22	<50–60	Sugary, bleached
Picos de Europa	4	Alba	Visean	1–1.5(5); 1(2)	1.18	0.12	<50	Sugary, corroded, bleached
Picos de Europa	5	Picos de Europa	Moscovian	1.5(1)	1.50	–	<50–57	Sugary
Picos de Europa	8	Alba	Visean	1.5(47); 1.5–2(28); 2(13)	1.65	0.18	<50–62	Sugary, smooth
Picos de Europa	9	Alba	Visean	2(4); 3(1)	2.20	0.45	55–85	Sugary
Picos de Europa	10	Alba	Visean	2.5(2); 2.5–3(3); 3(30)	2.95	0.13	115–155	Sugary
Picos de Europa	11	Barcaliente	Serpukhovian	3.5(4); 4(2)	3.67	0.26	155–195	–
Picos de Europa	12	Barcaliente	Serpukhovian	4(1)	4.00	–	185–225	–
Picos de Europa	13	Alba	Visean	3.5(3); 4(48); 4.5(4)	4.00	0.18	185–225	Sugary
Picos de Europa	14	Barcaliente	Serpukhovian	3(2); 3.5(1); 4(22)	3.90	0.29	180–220	Sugary
Picos de Europa	15	Alba	Visean	4.5(1)	4.50	–	238–275	Fragmented, cleavage
Picos de Europa	16	Alba	Visean	4(22); 4–4.5(18); 4.5(10)	4.19	0.19	195–230	Sugary, bleached
Pisuerga–Carrión	17	Valdeteja	Bashkirian	4(2); 4.5(1); 5(2)	4.50	0.50	240–275	Sugary, some recrystallized
Picos de Europa	21	Barcaliente	Visean	2(3)	2.00	0.00	50–80	Smooth
Picos de Europa	24	Picos de Europa	Moscovian	1.5(1)	1.50	–	<50–57	Sugary, bleached
Picos de Europa	26	Picos de Europa	Moscovian	3(4)	3.00	0.00	<118–155	Sugary
Picos de Europa	29	Barcaliente	Serpukhovian	1.5(4); 2(1)	1.60	0.20	<50–60	Sugary, smooth
Picos de Europa	30	Alba	Visean	1.5(91); 2(29); 3(16)	–	0.49	–	Sugary, corroded
Picos de Europa	33	Picos de Europa	Moscovian	3(10); 3.5(31);4(58); 4–4.5(17); 4.5(1)	–	0.36	–	Sugary, corroded, dispersed organic matter
Picos de Europa	34	Picos de Europa	Moscovian	3(6); 3.5(5)	3.22	0.25	130–165	Sugary, corroded, ductile strain
Picos de Europa	35	Barcaliente	Serpukhovian	3.5(1); 4(2)	3.83	0.24	150–205	–
Picos de Europa	175	Upper Carboniferous series	Kasimovian	3(2)	3	0.00	115–155	–
Picos de Europa	176	Upper Carboniferous series	Kasimovian	3(3)	3	0.00	115–155	–
Picos de Europa	177	Alba	Visean	1.5(10); 2(9); 2.5(7); 6.5(5); 7(2)	1.94 & 6.64	–	–	Sugary, bleached, grey patina
Picos de Europa	178	Alba	Visean	1.5(15); 2(10); 6.5(4); 7(39)	1.7 & 6.71	–	–	Sugary, bleached, grey patina
Picos de Europa	179	Alba	Visean	4(2); 4.5(2)	4.25	0.29	210–240	–
Picos de Europa	180	Baleas	Tournaisian	4(3)	4	0.00	185–225	–
Picos de Europa	203	Picos de Europa	Moscovian	2(4); 2.5(4)	2.25	0.27	62–100	–
Picos de Europa	204	Picos de Europa	Moscovian	2(4)	2	0.00	52–80	Sugary
Picos de Europa	209	Picos de Europa	Moscovian	1(1); 7(1)	1 & 7	–	–	Sugary, corroded
Picos de Europa	210	Picos de Europa	Kasimovian	3(3)	3	0.00	115–155	–
Picos de Europa	212	Picos de Europa	Moscovian	1.5(2)	1.5	0.00	<50–57	–
Picos de Europa	214	Upper Carboniferous series	Kasimovian	2.5(1)–3(2)	2.83	0.29	110–150	Grey patina
Picos de Europa	216	Picos de Europa	Moscovian	1.5(1); 2(1)	1.75	0.35	50–70	Smooth, sugary, grey patina
Picos de Europa	220	Picos de Europa	Moscovian	3(4); 3.5(8); 4(6)	3.55	0.38	155–185	Sugary, grey patina
Picos de Europa	221	Picos de Europa	Moscovian	4(2)	4	0.00	185–225	–
Picos de Europa	224	Alba	Visean	2(7); 2.5(3); 3(5); 3.5(11)	–	0.64	–	Sugary, corroded, grey patina

thermal event. An Alpine uplift of the Picos de Europa unit could be related to the southward displacement of this unit along the frontal ramp of a deep Alpine thrust (Alonso *et al*. 1996; Gallastegui, 2000).

The variations in the CAI distribution throughout the eastern section are associated with several different geological features of this section as compared to the western section. These include faults, often extensional, cutting the thrusts, an abundance of ore deposits and ore showings, and some thrusts cutting post-orogenic unconformable Permian sediments (Martínez-García, 1981*a*; Martínez-García & Villa, 1999). In accordance with the above features, the high dispersion of CAI values in some localities (30, 33, 177, 178 and 224 in Fig. 3 and Table 1), and the existence of dull and corroded surfaces and grey patinas in conodonts of the eastern section can be explained as a result of a hydrothermal episode. According to Gómez-Fernández *et al*. (1993, 2000), the fluid circulation and the development of metallic mineralization would have been favoured by the high density of extensional fractures in the area. These authors consider that the development of the mineral deposits could have occurred during Permian times. A good example of an ore deposit formed during this period is the Hozarco Pb–Zn–Hg deposit (Martínez-García *et al*. 1991).

The relatively high values (CAI = 2–3) located to the north of the Tresviso thrust suggest a relative upward movement of this thrust sheet, together with other thrust sheets located northward, subsequent to the thermal events which gave rise to the CAI values. This is probably an Alpine movement, since the Tresviso thrust cuts post-orogenic sediments. Westwards, CAI values decrease in the northern part of the area, suggesting a decrease in the rise of rocks along this thrust. Likewise, the relatively high KI and CAI values found near Sotres appear in a small area where there are several crossed faults, which have enabled the existence of deeper rocks outcrops, among which Cambrian rocks are included.

A model explaining the CAI distribution found in the Cares and Duje river sections involves the development of a first thermal episode which would have given rise to a progressive southward transition from diagenesis to metamorphism that reached the ancaizone in the basal part of the unit. Subsequently, a second thermal episode of hydrothermal character gave rise to local variations in CAI values modifying the previous thermal pattern. The latter episode would have affected mainly the eastern section. Finally, Alpine deformation gave rise to the northward tilting of the thermal pattern and to simple modifications in it by movements along faults. While it is difficult to test this model with data restricted to the study area, the regional geology provides useful information.

The progressive southward metamorphism, more clearly observed in the western section, subsequent to the basal thrust of the Picos de Europa unit and extended into the Pisuerga–Carrión unit, is associated in the latter unit with the development of a subhorizontal or moderately N-dipping cleavage, penetrative in the pelitic rocks, and cutting most of the folds (van Veen, 1965; Savage, 1967; Lobato, 1977; van der Pluijm, Savage & Kaars-Sijpesteijn, 1986; Rodríguez-Fernández, 1994). In this unit, the cleavage is pre-tectonic with respect to the high-temperature minerals of the contact metamorphism produced by a granodiorite intrusion (Peña Prieta stock). The age of this intrusion, based on the U–Pb geochronology of Valverde Vaquero *et al.* (1999), is 292 ± 2/3 Ma. Hence, this thermal event was interpreted by García-López *et al.* (1999) and Bastida *et al.* (2002) as a late Variscan extensional episode dated near the Carboniferous–Permian boundary. The moderate northward dip of the cleavage can be explained by the rise of a deep Alpine S-directed thrust (Alonso *et al.* 1996), which agrees with the northward dip of the CAI isogrades mentioned above.

A late Palaeozoic hydrothermal episode gave rise to many mineralizations formed in the Cantabrian Zone at moderate temperatures. Like the Hozarco deposit mentioned above, many mineralizations of the Cantabrian Zone, mainly fluorspar deposits, appear in the Permian post-orogenic sediments, but never in the Mesozoic cover (Martínez-García, 1981*b*, 1983; Martínez-García & Tejerina, 1985). These mineralizations have been interpreted by these authors as originating at the beginning of a post-Variscan continental rifting episode during Permian times. K–Ar ages of about 270 Ma in hydrothermal illite, obtained by Weh *et al.* (2001) in the Pisuerga–Carrión unit, also suggest a Permian thermal episode.

In the El Valle–Boinás deposit (Western Cantabrian Zone), K–Ar dating of micas from 14 samples of granitoids, skarn and dykes and a whole-rock diabase–andesite by Martín-Izard *et al.* (2000) gave a quasi-continuous age range from 308 to 233 Ma. These authors distinguish three age groups. The older ages (average age of 303 Ma) are from granitoids and the skarn (somewhat older than the U–Pb ages between 297–290 Ma obtained by Valverde *et al.* 1999 for the granitoid outcrops of the Cantabrian Zone). The other two groups have mean ages of 285 and 255 Ma and correspond to intrusions of porphyritic rocks and diabasic dykes respectively; both types are associated with the development of faults, and their ages correspond to Permian thermal episodes.

The above data suggest that the Picos de Europa unit was affected by a late Variscan progressive southward thermal episode associated with extension in late Carboniferous–early Permian times. Subsequently, during the Permian, post-Variscan hydrothermal processes, also in extensional regime, gave rise to ore deposits and the textural alteration in conodonts, producing changes in the CAI that involved anomalous values and a notable dispersion in some localities. The extensional deformation shown by the study area and the adjacent Pisuerga–Carrión unit is moderate, although it is relatively high in the context of the external zone of an orogen, probably due to its location in the core of an orocline.

6. Conclusions

The Picos de Europa unit mainly consists of Carboniferous limestones forming an imbricate system of Variscan thrusts. The basal thrust places this unit on the Pisuerga–Carrión unit, located to the south, and both form the core of the Ibero-Armorican Arc. Both CAI and KI values were obtained mainly in two cross-sections (the Cares and Duje rivers) through the Picos de Europa unit. CAI variation is a result of thermal events of tectonic origin, and KI values agree with CAI data in both sections. Each section offers a specific pattern of variation.

The Cares river section (or western section) shows a pattern of progressive transition from diagenesis to metamorphism involving an increase in temperature towards the basal part of the Picos de Europa unit, where the ancaizone appears. The present distribution of CAI values is probably due to an original dip of the isothermal surfaces northwards and to a southward rising of the Picos de Europa unit along the ramp of a deep Alpine thrust. Ancaizonal values are widespread within the Pisuerga–Carrión unit and the basal thrust does not give rise to a perceptible metamorphic break. Therefore, the thermal event was subsequent to the emplacement of the Picos de Europa unit and occurred near the boundary between the Carboniferous and the Permian, and it is a very low-grade, late Variscan metamorphism. In addition, the presence of subhorizontal cleavage associated with the metamorphism and abundant small igneous bodies in the adjacent Pisuerga–Carrión unit suggests that the thermal event was the result of a late Variscan extensional episode.

In the Duje river section (or eastern section), the thermal pattern is similar in outline to that of the western section, but it is notably modified by the existence of anomalies resulting from Permian hydrothermal processes. The higher topographic level of the eastern section has resulted in lesser penetration of the ancaizone in its southern part than in the western section, where erosion has reached a deeper level.

The thermal evolution of the Picos de Europa unit involves two different successive episodes. The first is heating, related to an extensional late Variscan deformation that appears better reflected in the Pisuerga–Carrión unit and whose age is near the Carboniferous–Permian boundary. The second one is a hydrothermal post-Variscan episode that could be related to the beginning of the Alpine cycle in this part of the Cantabrian Zone.

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