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Organic matter maturation vs clay mineralogy: A comparison for Carboniferous to Eocene sediments from the Alpine – Dinaride junction (Slovenia, Austria)

Odsevna sposobnost organske snovi v primerjavi z mineralno sestavo glinenih mineralov: Primerjava sedimentov nastalih od karbona do eocena iz Alpsko – Dinarskega stika (Slovenija, Avstrija)

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Abstract

Clay mineral diagenesis of Carboniferous to Paleogene rocks within the Alpine-Dinaric junction was studied and compared to vitrinite reflectance. Generally, there is a good fit between clay mineral diagenesis and VR. However, clay mineral alterations lag behind maturation in some Ladinian and Carnian rocks (e.g. northern margin of the Dinaric Platform). Most probably, the lag in clay mineral diagenesis reflects an highly varying geochemical background in these stratigraphic horizons. Carboniferous deposits are late diagenetic to anchimetamorphic. Mesozoic deposits cover the range from middle diagenesis to the anchizone. Triassic to Cretaceous rocks in the SB and the Sava Folds reach the anchizone. Differences in diagenesis/metamorphism are mainly due to different maximum burial in Paleogene time.

Kratka vsebina

Preučevali smo diagenezo glinenih mineralov v sedimentih nastalih od karbona do eocena iz Alpsko – Dinarskega stika (Slovenija, Avstrija) in jo primerjali z odsevno sposobnostjo vitrinita (VR). V splošnem se rezultati med mineralno sestavo in VR zelo dobro ujemajo. Spremembe mineralne sestave glinenih mineralov nekoliko zaostajajo v nekaterih ladinijskih in karnijskih kamninah (severni rob Dinarske karbonatne platforme). Zaostanek v diagenezi glinenih mineralov najverjetneje odraža zelo spremenljivo geokemično okolje v teh stratigrafskih enotah.

Karbonski sedimenti so poznodiagenetski do anhimetamorfni. Mezozojski sedimenti so v območju od srednje diageneze do anhicone. Triasne do kredne kamnine v Slovenskem jarku in Posavskih gubah dosežejo anhicono. Razlike v diagenezi/metamorfizmu so večinoma zaradi največjih razlik v največjih obremenitvah in temperaturah v času paleogena.

Introduction

Correlations between inorganic and organic thermal indicators have been discussed by many authors (e.g. Kisch, 1987; Underwood et al., 1992; Sachsenhofer et al., 1998). These papers show that a universal statistical correlation between Vitrinite Reflectance (VR) and Illite "Crystallinity" (IC) cannot be established, because the two indices respond to different sets of variables. The present paper provides a comparison between organic and inorganic indicators of diagenesis to anchimetamorphism in the Alpine-Dinaric transition zone.

Geological setting

The study area is formed by different geotectonic units. The Eastern Alps are situated north of the Periadriatic Lineament (PL), whereas the Southern Alps and the Dinarides occur south of it (Fig. 1). The eastern continuation of the Alps and Dinarides is covered by Cenozoic rocks of the Pannonian Basin.

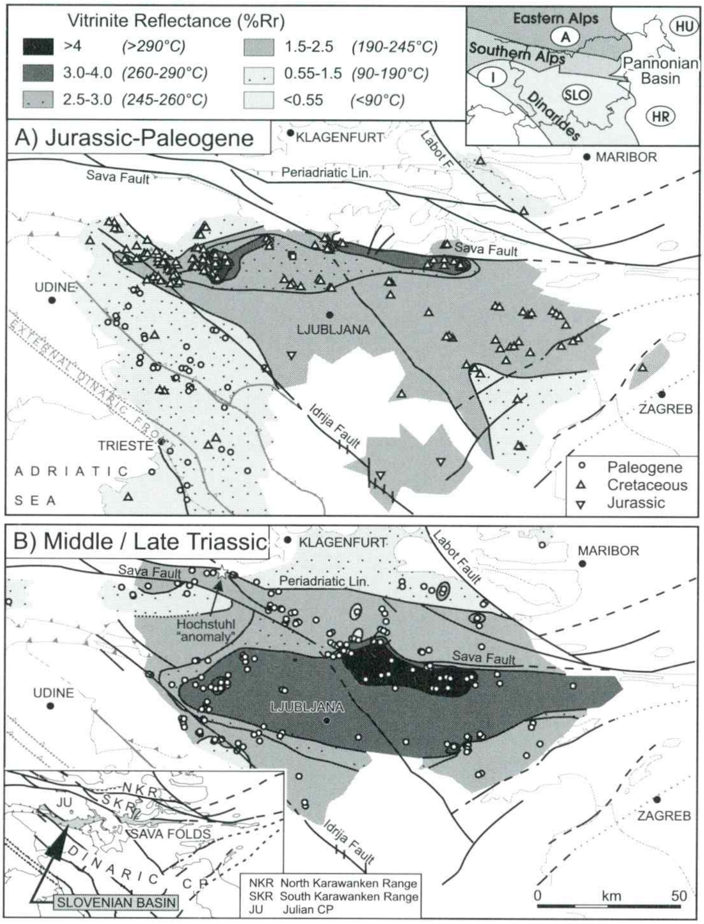

Fig. 1: Vitrinite Reflectance maps for (a) Jurassic to Paleogene rocks and (b) Middle to Upper Triassic rocks. The tectonic sketch map follows Placer (1998). Barker´s (1988) correlation is used to estimate paleo-temperatures (see legend).

The North Karawanken Range (Eastern Alps) is composed of a 3 to 4 km thick Permo-Mesozoic succession that rests unconformably on metamorphic Austroalpine basement. Within the Southern Alps and the Dinarides, the pre-Variscan sedimentary cycle is terminated by Lower Carboniferous flysch. The post-Variscan sequence is represented by Upper Carboniferous to Lower Permian molasse and thick marine Upper Permian to Triassic deposits. During the Ladinian the uniform carbonate platform disintegrated and the Slovenian Basin (SB) formed between the Julian carbonate platform (CP) to the north and the Dinaric CP to the south (Buser, 1987). The Julian CP and the South Karawanken Range preserved the characteristics of a carbonate platform till Liassic times. Cretaceous rocks occur as local remnants (Jurkovšek et al., 1988/89). In the SB deep marine facies persisted until the Paleogene. The Dinaric CP remained at shallow water depth from Late Triassic to Cretaceous times. Minor lateral facies changes occurred in the SB during Ladinian and Carnian times. In contrast, rapid changes in depositional environments occurred at the northern edge of the Dinaric CP (Buser, 1987). The Dinaric CP disintegrated during the Maastrichtian. The Paleogene „Dinaric“ phase deformed the Southern Alps and the Dinarides by SW vergent thrusts. The depocenter of the SB was shifted to the south onto the northern margin of the Dinaric CP (early Eocene). From the Late Miocene onward the Southern Alps were affected by S-SE vergent „Alpine" thrusting (Castellarin & Cantelli, 2000).

Methods

Vitrinite reflectance (VR): Random VR (% R_r) of ~1000 whole rock samples (slates, marls) representing Carboniferous to Eocene horizons and different geotectonic units was measured using standard procedures (e.g. Taylor et al., 1998).

Clay mineralogy: Clay mineral assemblages, the smectite to illite transformation, and Illite-"Crystallinity" (IC) have been used by many authors to subdivide the diagenetic/low-grade metamorphic zone (e.g. Frey, 1987 cum. lit.). The smectite to illite transformation comprises three stages. Stage 1 (early diagenesis) is characterised by the presence of discrete smectite. In stage 2 (middle diagenesis) smectite disappears and illite-smectite mixed layer minerals (I/S) are formed. In stage 3 (late diagenesis) the mixed layer peak merges with the illite peak resulting in the formation of diagenetic illite. IC values (width at half peak height of the first illite basal reflection) of diagenetic illite decrease with increasing thermal overprint. The anchizone is defined by the limiting values of 0.42 and 0.25 $\Delta°2\Theta$ (Kübler, 1984).

Air-dried and ethylene glycol-solvated preparations from 130 samples were studied. Sample preparation and experimental conditions are in accordance with the recommendations of Kisch (1991) and Warr & Rice (1994). Measurements were performed using a Phillips X-ray diffractometer, operated at 40 kV and 30 mA (Ni-filtered Cu-K? radiation). The identification of clay and non-clay minerals was carried out using the methods of Moore & Reynolds (1989). IC raw data were corrected to CIS (crystallinity index standard) data (Warr & Rice, 1994).

Results and Discussion

Thermal maturity of the organic matter

A detailed discussion of the thermal history of Slovenia will be presented in a forthcoming paper (Rainer et al., in prep.). Only some general maturity trends are presented here, in order to compare organic maturity and clay mineralogy.

No difference in VR was observed across the Variscan discordance in Carboniferous rocks. Therefore, the post-Variscan thermal overprint was at least as high, as the pre-Variscan one. Maturity maps based on VR of Middle/Upper Triassic and Jurassic to Paleogene samples are presented in Fig. 1. VR in Permo-Mesozoic strata is highly variable and depends on the geotectonic and stratigraphic position. The SB features the highest levels of maturity with VR values >4 % R_r in Ladinian to Lower Cretaceous rocks. The high thermal overprint of Upper Cretaceous sediments in the central Sava Folds and the SB (>3.7 % R_r) and low VR in Oligocene rocks (~0.5 % R_r; Sachsenhofer et al., 2001) suggest a Paleocene or Eocene thermal overprint. The Eastern Alps and the Southern Alps are characterized by lower VR values. Maturity in the Dinaric CP increases northwards.

The observed maturity pattern is controlled mainly by the depth of sedimentary burial and by different heat flows. This is supported by the observation that thrusting events generally post-date the thermal overprint (Rainer et al., in prep.).

A local thermal anomaly caused by Oligocene magmatic activity overprints Scythian and Anisian strata in the South Karawanken Range near the dextral Hochstuhl fault (Fig. 1b; Rantitsch & Rainer, subm.).

Mineral assemblages in the clay-size fraction

The mineralogical composition varies according to the sampled lithology, but illite, chlorite, quartz and plagioclase are mostly dominant. Calcite and dolomite occur in marls. Proportions of K-feldspar are generally low.

Pyrophyllit, an indicator mineral for late diagenesis and anchizone, was detected in the Upper Carboniferous of the South Karawanken Range. Rare occurrences of paragonit in Carboniferous slates from the Sava folds (containing graphitisized organic particles) are indicative for the higher anchizone and the epizone.

Smectite to illite transformation and Illite-"Crystallity" (IC)

The regional distribution of samples with diagenetic and anchizonal overprint is presented in Fig. 2. The zone of early diagenesis (stage 1) characterised by the occurrence of discrete smectite was observed only in Eocene marl from the Adriatic CP (southwest of the external dinaric front).

Illite-smectite mixed layer minerals (I/S) with 10–30% smectite (stage 2) were detected in Ladinian marls of the northern margin of the Dinaric CP (Wengen beds) and Carnian marls of the South Karawanken Range (Raibl beds). I/S minerals with <10 % smectite (stage 2) occur in various stratigraphic levels of all Alpine and Dinaric geotectonic units, but are missing in the SB and the central Sava Folds.

Burial conditions resulting in late diagenetic stage 3 (IC >0.42 $\Delta°2\Theta$) and the anchizone (IC 0.25 – 0.42 $\Delta°2\Theta$) were reached in the South Karawanken Range, the Sava folds, the northernmost part of the Dinaric CP (Carboniferous to Middle Triassic) and in the SB (Middle Triassic to Cretaceous). The epizone (IC <0.25 $\Delta°2\Theta$) was not detected in the study area.

Illite-"Crystallinity" (IC) versus Vitrinite Reflectance (VR)

Discrete smectite occurs in a single sample with a VR of 0.56 % R_r. The lowest VR of a sample with a stage 2 mineralogy is 0.83 % R_r. The transformation of stage 2 to 3 occurs in a VR range of č1.4 to 1.7 % R_r. However, Ladinian and Carnian marls from the northern margin of the Dinaric CP (stage 2; <10% smectite in I/S) reach VR >2.5 % R_r. Anchimetamorphism starts at č2.5 % R_r (Fig. 3).

IC and VR data are crossplotted in Fig. 3. Data from the SB and the Sava Folds show a general trend of decreasing IC with increasing VR. This trend is very well defined for Carboniferous, Middle Triassic, Jurassic and Cretaceous strata (Fig. 3a; correlation coefficient R = 0.81).

Data from Upper Triassic slates of the SB ("Amphiclina beds") and Carboniferous to Upper Triassic slates and marls from the northern margin of the Dinaric CP are added in Fig. 3b. It can be recognised that Carboniferous and Lower Triassic samples fit well into the overall trend, whereas Ladinian (Dinaric CP) and Carnian (Dinaric CP + SB) samples show a poor statistical correlation. Obviously, the clay mineralogy of these samples shows a delay in illitisation reaction relative to organic maturity. A similar "Carnian anomaly" (Nußbaum, 2000) was detected in the Southern Alps of the Friuli area (Italy), where IC values of (Ladinian and) Carnian rocks are significantly higher than in older and younger strata. Nußbaum (2000) explained this by a shallower burial depth of Carnian levels. This interpretation cannot be adopted for our study area, because Carnian deposits and overlying Jurassic to Cretaceous rocks (with "normal" VR – IC correlations) are characterized by similar burial histories.

Therefore, we attribute the delay of clay mineral diagenesis to factors other than temperature. VR and IC correspond to different sets of external variables (Frey, 1987). A

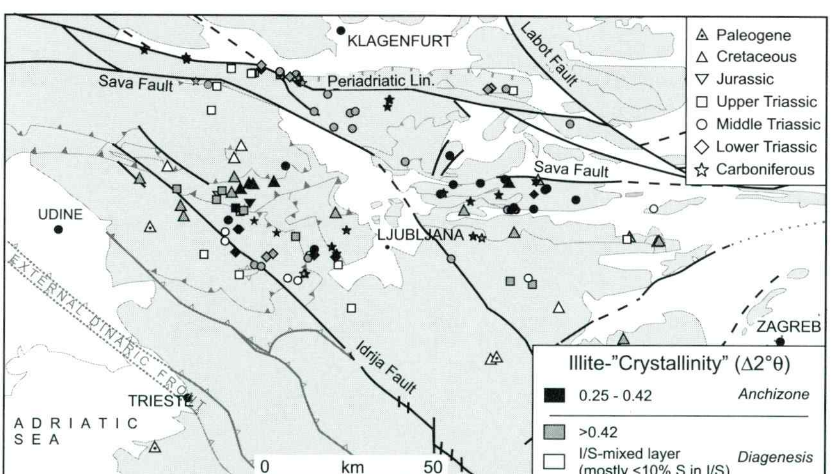

Fig. 2: Map of Illite "Crystallinity".

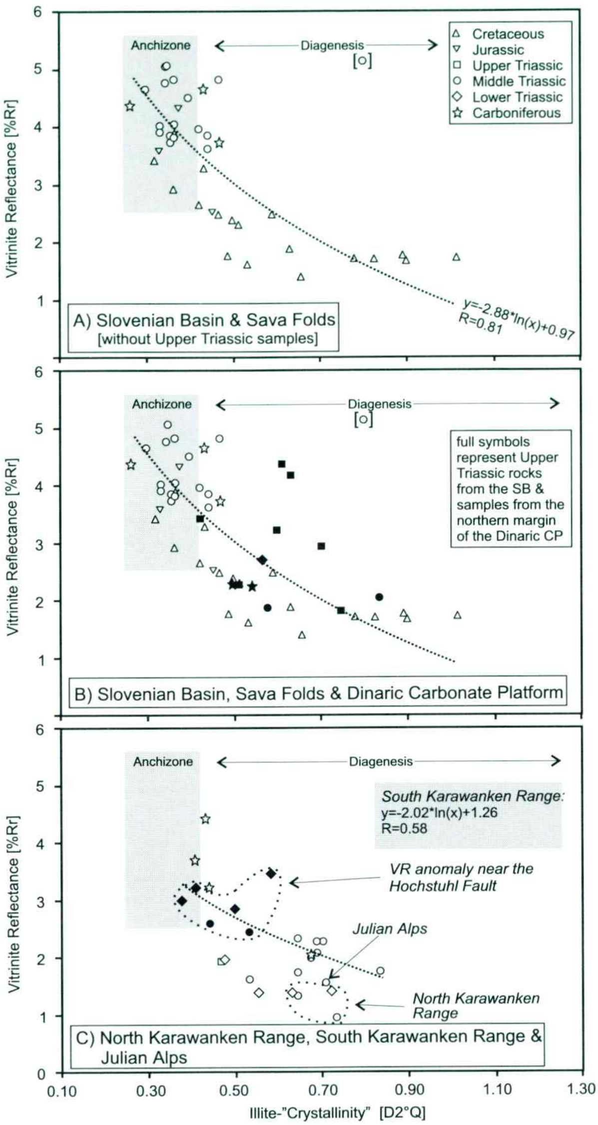

Fig. 3: Vitrinite Reflectance versus Illite "Crystallinity" of rocks from different geotectonic units and stratigraphic horizons. Boundary values for the anchizone are adopted from Kübler (1984).

bad fit can be caused by differences in the precursor clay-mineral assemblages or the bulk geochemistry of the diverse host rocks (Underwood et al., 1992). A lag in clay mineral diagenesis has been noted in tuffs (Frey, 1987; Merriman & Roberts, 1990), in bitumen-rich rocks (Krumm et al., 1987) or in areas with abnormally high geothermal gradients (e.g. near igneous intrusions; Kisch, 1987). The Ladinian and Carnian of the northern margin of the Dinaric CP is dominated by carbonates, but contains a wide variety of rock types including cherts, bituminous marls, coal seams and volcanic rocks. Although the lithology of the studied samples is similar (marls, slates), the highly varying geochemical background may lead to pronounced fluctuations in the chemical composition of pore fluids, which might explain the observed scatter in the data set.

IC and VR data from the South Karawanken Range are presented in Fig. 3c. Higherrank samples of the thermal anomaly near the Hochstuhl Fault fit well the regression line for the entire data set. The thermal overprint caused by Oligocene magmatism was sufficiently long in duration to allow equilibration of both VR and IC with the temperature field. Only few samples from the North Karawanken Range and the Julian Alps (1 – 1.7 % R_r) yielded IC results. Data are included in Fig. 3c and plot slightly below the regression line for the South Karawanken Range.

Conclusions

- Generally, there is a good fit between clay mineral diagenesis and VR in the transition area between Eastern Alps, Southern Alps, and the Dinarides (Slovenia / Austria).
- Clay mineral diagenesis shows a lag in relation to organic maturity in Ladinian (northern margin of the Dinaric CP) and Carnian (northern margin of the Dinaric CP and SB) rocks. Similar observations by Nußbaum (2001) in the Italian Southern Alps indicate that this is not a local phenomenon. Most probably, the lag in clay mineral diagenesis reflects the highly varying geochemical background in these stratigraphic horizons.
- Carboniferous deposits are late diagenetic to anchimetamorphic
- Mesozoic deposits cover the range from middle diagenesis (stage 2) to the anchizone. Triassic to Cretaceous rocks in the SB and the Sava Folds reach the anchizone.
- Differences in diagenesis/metamorphism are mainly due to different maximum burial in Paleogene time.

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