Diagenesis and very low grade metamorphism in a 7,012 m-deep well Hongcan 1, eastern Tibetan plateau

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Abstract This study uses clay mineral assemblages, illite "crystallinity" (IC), chlorite "crystallinity" (CC), illite polytypes, the *b* cell-dimension of K-white mica, mineral geothermo-geobarometers and homogenization temperatures of fluid inclusions to investigate the transition from diagenesis to metamorphism in a 7 km thick Triassic flysch sequence in the well Hongcan 1, eastern Tibetan plateau. The 7,012.8 m deep borehole penetrated flysch of Upper to the Middle Triassic age and represents a unique chance to characterize low temperature metamorphic processes in an unusually thick sedimentary sequence developed on thickened continental crust. Mineral assemblage analysis reveals a burial metamorphic pattern with kaolinite and chlorite/smectite mixlayer phases present in the upper 1,500 m, and illite/smectite mixed-layer phases extending to a depth of 3,000 m. The metamorphic index mineral, graphite, was detected in sedimentary rock below 5,000 m using Raman spectroscopy. There exists a good correlation between IC and CC within the prograde burial sequence; with CC anchizonal boundaries of

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0.242 and $0.314^{\circ}2\theta$ (upper and lower boundaries, respectively) corresponding to Kübler's IC limits at 0.25 and 0.42°2 θ . Illite polytypism also shows an increase in the $2M_1$ polytype with increasing depth, with ca. 60 % $2M_1$ abundance compared to the 1M type at the surface, to 100 % $2M_1$ at the bottom of the borehole. Fluid inclusion analysis show HHC-rich bearing fluids correspond to the diagenetic zone, CH₄-rich bearing fluids appear at transitional zone from diagenetic to low anchizone and H₂O-rich bearing fluids mark the high anchizone to epizone. Based on chlorite chemical geothermometer, calcite–dolomite geothermo-barometers as well as homogenization temperature of fluid inclusions, a paleotemperature range of 118–348 °C is estimated for the well with a pressure facies of low to intermediate type.

Keywords Diagenesis · Very-low-grade metamorphism · Illite crystallinity · Triassic flysch · Tibetan plateau

1 Introduction

The Triassic flysch of the Tibetan plateau preserves an important stage of tectono-thermal evolution that spans the closure of Paleo-Tethys and the formation of the Himalayas. The state of diagenesis and metamorphism of the Triassic flysch has been investigated largely by the thin section study of samples from surface outcrops (Dong et al. 1986). However, a detailed analytical study of unweathered samples from depth has not yet been undertaken. X-ray diffractometry based methods (e.g. Kübler 1964; Frey 1987) suitable for characterizing mineral assemblages in more detail have only been applied to 5 samples located far from the Hongcan 1 borehole (Xia 1993).

Since 2002 the eastern Tibetan plateau has been chosen as a new target area for oil and gas exploration, and

therefore the diagenetic to low temperature metamorphic history of the Triassic flysch is of economic importance (Yang and Liu 2005). Currently, many aspects concerning the state and cause of metamorphism in the Triassic flysch are debated, with options ranging from a complete lack of metamorphism (Yang and Liu 2005) to diagenetic metamorphism (Chen et al. 2001), anchimetamorphism (Xia 1993; Wang et al. 2008), local metamorphism in the area of the Danba dome (You et al. 2006; Zhou et al. 2008), regional subgreen schist-facies metamorphism (Dong et al. 1986), regional low-temperature dynamic metamorphism (Bureau of geology and mineral resources of Sichuan province 1991) and low-grade regional dynamic metamorphism (Xu et al. 1992). Such metamorphic anomalies have been attributed to the circulation of hydrothermal fluids related to tectonic deformation, such as activity along the Longmenshan fault (cause great Sichuan earthquake on May 12, 2008) and other detachments in the Triassic flysch (Xu et al. 1992, 2007). Also unclear is the relationship between metamorphism and magmatic activity since the Mesozoic (Chung et al. 2005; She et al. 2006).

A 7.012.8 m deep well called Hongcan 1 was drilled during 2005-2006 in order to probe the depth of the Tibetan plateau as well as to explore for oil and gas in that area. The well Hongcan 1 is located within the Hongyuan County, north of Sichuan province, on the eastern margin of Tibetan plateau. Triassic flysch occurs throughout the well and represents the typical flysch sequence (200-245 Ma) of the Qingzang-Dianxi fold region located on the northern Tibetan plateau, western China $(>410,000 \text{ km}^2$, see Fig. 1). The purpose of this paper was to investigate the diagenetic to very low grade metamorphism overprint of this particularly thick Triassic flysch sequence in the well Hongcan 1 using a range of accepted geothermal indicators which have been widely used by many researchers since 1980s. Based on these new analytical results the thermal evolution of the Triassic flysch of the Tibetan plateau is addressed.

2 Geological setting

Tectonically the Triassic flysch in well Hongcan 1 has a complex geological history, belonging to the Songpan-Garzê orogen, which is limited by the north China, south China and Indian blocks (Xu et al. 1992, 2007; Roger et al. 2008, 2010). From Early Paleozoic to Devonian times, the Songpan area was characterized by a large carbonate platform that extended towards the SE onto the Yangtze craton. By the end of Devonian, the area underwent extensive crustal stretching with the development of ocean crust (Nie et al. 1994; Zhou and Graham 1996; Weislogel et al. 2006; Weislogel 2008). Continent–continent collision

between the North and South China blocks during the Triassic resulted in the formation of the Qinling-Dabie orogen and caused the closure of the Paleo-Tethys Ocean (Pullen et al. 2008). Large-scale foreland basins such as the Sichuan and the Songpan basins in the south developed on both sides of the collisional belt with syn-orogenic filling and closure of the basins. In the Carnian stage (T_{2-3}), deep sea turbidites were deposited in the Songpan basin (Zhang et al. 2008). Granitoid melts intruded into the flysch series during the late Triassic to early Jurassic period (Hu et al. 2005). Early magmatism preceded deformation (Xiao et al. 2007; Weislogel 2008) or was simultaneous with folding of the Triassic strata (Hu et al. 2005). Ongoing crustal thickening and shortening finally resulted in uplift of the crust (Arne et al. 1997; Wang and Cai 2007).

Based on geophysical surveys and investigation of surface samples around Zoigê between 2002 and 2005, it was expected that the locality of the well Hongcan 1 would be in a centre of diagenetic zone and about 6 km below the surface the lower Triassic-upper Permian carbonaceous rocks would occur in which large gas reserves were found in the neighboring Sichuan basin (Ma et al. 2005, 2007). However, after drilling the borehole was discovered to be dominated by the upper-middle Triassic flysches in a sequence of alternating shales, silt- and sandstones with only minor carbonates. The current geothermal gradient of the borehole measured is 30 °C/km. The tectono-thermal evolution of the Songpan-Garzê orogen since the Mesozoic reflects the interactions between Indian and the South China and North China blocks, which was characterized by both magmatic activity and limited uplift occurred during the Mesozoic, as well as large-scale uplift and rapid cooling during the Tertiary Himalayan orogen (Huang et al. 2003).

3 Methods

This investigation is based on the study of 234 samples from well Hongcan 1, which including 31 core samples taken from 31 core sections. Sample preparation of clay rich rocks followed the recommendations of the IGCP 294 (Kisch 1991). Clay-sized fractions were separated using a HITACHI CR-22G centrifuge.

For XRD analyses, all measurements were performed with an X'Pert Pro MPD diffractometer with CuK α radiation and operating conditions of 40 kV and 40 mA. The slit system was set with a 1° divergence, an anti-scatter slit of 2° and a 6.6 mm receiving anti-scatter slit for the X'celerator detector. The step size was set at 0.017° 2 θ and the count time was 20 s. Mounts of randomly oriented bulk powder were used for mineral phase identification measured in the range of 4–75° 2 θ . Oriented slides of the Fig. 1 Tectonic map of China (from Ma et al. 2002). Grey area represents the Qingzang-Dianxi fold region. Filled triangle marks the location of well Hongcan 1. UHP ultrahigh pressure metamorphic belt. Lower part is the geological sketch around the well. Filled triangle marks the locality of the well Hongcan 1



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Jurassic

Table 1 EN	MPA dati	a of chlor	ite, muscovi	te, illite and c	alcite measure	d from rock's	matrix and b	cell data o	f K-white	e mica of	part cor	e sample:	s and the	ir depths			
No	HW- 591-3	HW- 698-3	HW- 699-4	HW- 699-5	HW- 733-2	HW- 733-5	HW- 733-6	HW- 734-1	HW- 589-2	-WH 698-7	-WH -8-669	HW- 732-4	HW- 733-4	HW- 734-6	HW- 589-3	HW- 591-1	HW- 698-1
Depth (m)	4945.2	5847.5	6006		6543.7			7011.2	4375.1	5847.5	6006	6073.2	6543.7	7011.2	4375.1	4945.2	5847.5
Phase	Chlorite								Illite	Muscov	te				Calcite		
SiO_2	26.33	25.83	24.86	24.93	24.5	24.78	24.88	24.40	52.41	45.92	46.77	48.12	46.56	45.6	0.14	0.05	0.07
TiO_2	0.02	0.05	0.05	0.09	0.12	b.d.	0.08	0.10	0.43	0.35	0.19	0.30	0.44	0.24	0.04	b.d.	b.d.
Al_2O_3	21.49	23.78	21.57	21.35	21.24	21.67	21.99	24.27	30.22	33.7	34.33	33.05	32.33	35.90	0.02	0.03	0.07
Cr_2O_3	b.d.	0.12	0.07	0.04	0.02	b.d.	0.08	0.02	b.d.	b.d.	0.04	0.09	0.34	0.02	b.d.	b.d.	b.d.
FeO	25.24	26.59	29.16	29.19	27.43	27.84	27.28	30.64	2.47	1.63	1.26	1.76	1.99	1.00	1.02	1.00	1.39
NiO	0.06	0.03	0.03	0.04	0.05	b.d.	0.02	b.d.	b.d.	0.02	b.d.	b.d.	b.d.	b.d.	0.02	b.d.	b.d.
MnO	0.05	0.07	0.06	0.04	0.03	0.13	0.05	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.03	1.73	0.22	0.18
MgO	13.37	12.76	11.39	11.91	13.37	12.83	13.55	8.91	1.69	1.25	0.82	1.24	1.48	0.32	0.36	0.57	0.46
CaO	0.27	0.08	0.13	0.15	0.11	0.04	b.d.	0.18	0.04	0.03	0.06	0.05	b.d.	b.d.	52.11	54.12	52.55
Na_2O	b.d.	0.03	b.d.	b.d.	0.03	b.d.	b.d.	b.d.	0.14	0.30	0.65	0.32	0.26	1.22	b.d.	b.d.	b.d.
K_2O	0.17	0.43	0.02	0.04	b.d.	b.d.	0.02	0.22	9.13	10.64	10.29	10.23	10.66	9.80	b.d.	0.04	0.02
Total	86.99	89.76	87.33	87.78	86.89	87.32	87.95	88.76	96.53	93.86	94.4	95.17	94.07	94.13	55.45	56.04	54.75
Based on	28 O								11 0						1 0		
Si	5.576	5.332	5.371	5.361	5.284	5.319	5.280	5.210	3.387	3.103	3.128	3.189	3.145	3.056	0.002	0.001	0.001
Ti	0.003	0.008	0.008	0.015	0.019		0.013	0.016	0.021	0.018	0.010	0.015	0.022	0.012	0.001		
AI	5.364	5.785	5.492	5.411	5.398	5.482	5.500	6.107	2.302	2.684	2.706	2.582	2.574	2.836	0.000	0.001	0.001
Cr		0.020	0.012	0.007	0.003		0.013	0.003			0.002	0.005	0.018	0.001			
Fe*	4.470	4.590	5.268	5.249	4.947	4.997	4.842	5.471	0.120	0.083	0.063	0.088	0.101	0.050	0.014	0.014	0.020
Ni	0.010	0.005	0.005	0.007	0.009		0.003			0.001					0.000		
Mn	0.009	0.012	0.011	0.007	0.005	0.024	0.009							0.002	0.025	0.003	0.003
Mg	4.221	3.926	3.668	3.818	4.298	4.105	4.287	2.836	0.163	0.126	0.082	0.123	0.149	0.032	0.009	0.014	0.012
Ca	0.061	0.018	0.030	0.035	0.025	0.00		0.041	0.003	0.002	0.004	0.004			0.948	0.966	0.963
Na		0.012			0.013				0.018	0.039	0.084	0.041	0.034	0.159			
K	0.046	0.113	0.006	0.011			0.005	0.060	0.753	0.917	0.878	0.865	0.919	0.838		0.001	0.000
T(°C)			213	237	348	328	317								264	316	293
X_{Mg}	0.486	0.461	0.410	0.421	0.465	0.451	0.470	0.341							$0.938^{\$}$	$1.424^{\$}$	$1.179^{\$}$
Al ^{IV}	2.424	2.668	2.629	2.639	2.716	2.681	2.720	2.790	0.613	0.897	0.872	0.811	0.855	0.944			
Al ^{VI}	2.94	3.117	2.863	2.772	2.682	2.801	2.78	3.317	1.689	1.787	1.834	1.771	1.718	1.892			
ΣOcta	11.631	11.633	11.799	11.839	11.927	11.903	11.909	11.624	1.972	1.996	1.979	1.982	1.968	1.974			
K+Na									0.770	0.956	0.962	0.906	0.953	966.0			
R1									0.283	0.209	0.145	0.210	0.250	0.082			
R2									0.934	0.956	0.967	0.953	0.944	0.974			

(2009)

Calculated by Inoue et al. (2009) method, those parameters a1, a2, a3 and a4 for temperature calculation are given in the eighth decimal and their meanings refer to Inoue et al.

Table 1 continued

No	- MH	- MH	HW-699-4	HW-699-5	HW-733-2	HW-733-5	HW-733-6	-WH	-WH	- MH	-WH	-WH	HW-	- MH	- MH	- MH	-WH
	5-160	6-860						/34-1	7-680	1-860	049-8	152-4	133-4	/ 34-0	5-680	1-160	098-1
a1¶			0.00036783	0.00046595	0.00092126	0.00070864	0.00090551										
a2¶			0.00244637	0.00271166	0.00431985	0.00381852	0.00460479										
a3¶			0.05127978	0.04885852	0.03564009	0.03889698	0.03319854										
a4 ¹			0.00762870	0.00607520	0.00310834	0.00349319	0.00420941										
ΣOcta octi	thedral oc	cupancy,	, $RI = Mn + M_{\odot}$	g+Fe, R2 ^{VI} A	$l^3/(^{VI}Al^3 + ^{VI})$	Fe ³), b.d. Blee	ow detection 1	imit									
* For mus	scovite an	id illite th	he FeO is treate	ed as Fe ₂ O ₃													
§ vCc																	

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<2 um fraction were measured from 4 to 35° 2 θ for clav mineral identification and IC and CC measurements. Because nearly all samples contain quartz, this mineral was used as an internal standard to make peak shift corrections.

For chemical composition analysis of minerals, electron microprobe analyses (EMPA) were performed using a JXA-8100 electron microprobe at 15 kV acceleration voltage and 10 nA beam current, a 1 µm beam diameter, a PRZ correction, and calibration against 53 minerals standards of SPI Corp. Ltd, USA. All Fe was calculated as FeO. The thin sections for EMPA were oriented perpendicular to the rock fabric in order to reduce the influence of neighboring mineral grains.

Fluid inclusion analysis was performed with a MXM850 heating-cooling stage installed on an Olympus microscope system. The temperature was adjustable from room temperature up to 400 °C with a temperature resolution of 0.1 °C. The objective lens used was 32X. Thin sections were prepared from those flysch samples containing a quartz veins lying parallel or subparallel to the bedding fabric.

Raman spectra were obtained with a confocal micro Raman system Reshan-1000 and an excitation wavelength for 514.5 nm line for an Ar ion laser operated at 50 mW. The scanning range was $3,000-500 \text{ cm}^{-1}$ with 10 s counting time. Each spectrum was measured with a $20 \times$ objective and in single accumulation mode. The resolution was $\pm 1 \text{ cm}^{-1}$. Inorganic carbonaceous materials were collected from black flysch samples after treatment with HF and HCl acids.

IC was measured as the full width at half maximum (FWHM) of the ca. 1 nm XRD reflection (002) of the white mica (illite) phase. The width expressed in $^{\circ}\Delta 2\theta$ using CuKa radiation is known as the Kübler Index (Kübler 1964) and was calibrated based on a set of IC standards provided by Warr and Rice (1994). The IC boundaries for the anchizone are 0.25 and 0.42 $^{\circ}\Delta 2\theta$ and equivalent CC measurements were made using the FWHM of the chlorite (002) reflection (Árkai and Ghabrial 1997). Mixed-layer illite/smectite (I/S) phases were detected on the bases of the variations of the 1 nm "complex" reflection after glycolation, and heat treatment at 375 °C for an hour.

Determination of illite polytypes were performed by XRD method using random preparations measured over the diffraction range of $25-32^{\circ}2\theta$, where the diagnostic reflections for $2M_1$ and 1M polytype of illite could be identified. Decomposition procedures were used to separate the interference peaks overlapping the (112) reflection of 1M structure and the (025) reflection of the $2M_1$ structure of illite whereby all fitting reliabilities were below 3 %.

The b cell dimension of K-white micas was calculated from the relation $b = d_{(060, -331)} \times 6$ in which the $d_{(060, -331)}$ $_{-331}$ was measured using the quartz reflection (211) as an internal standard.



Fig. 2 Texture variation with depth. **a** Mudrock, single polar, 100 m, HW-511, no orientation was observed in clay matrix. **b** Shale, single polar, 358.4 m, HW-446, sedimentary lamination keeps well. **c** Slate, single polar, 4375.1 m, HW-589, new formed clay minerals grow approximately along bedding layer. **d** Phyllite, single polar, 7011.2 m, HW-734, phyllitic structure, penetrative schistosity with

For chlorite chemical geothermometry (Inoue et al. 2009), EMPA data from core samples collected from the high anchizone and anchi-epizone transition were used. Such HA and A-E rocks are assumed to have attained equilibrium and thus be suitable for mineral geothermometer application. For calcite geobarothermometry, the pressure condition is referred to about 3 kbar. See Sect. 4.6 for detail.

three deformation phases developed. **e** Mylonite, single polar, 6073.2 m, HW-732, augen structure. **f** Back-scattered electron scanning microscopy image, mircotexture of phyllite, 7011.2 m, HW-734, matrix is dominated by chlorite and muscovite; micro crenulation can be observed. Qtz quartz, Fs feldspar, Ms muscovite, *Chl* chlorite, *Ill* illite, *Rt* rutile

4 Results and discussions

4.1 Mineral assemblages

The main mineral phases recorded throughout borehole are quartz, feldspar, illite or muscovite and chlorite. Diagenetic minerals, namely mixed-layer illite/smectite (I/S) and chlorite/smectite (C/S) phases, and kaolinite occur between 0–3,042, 0–40 and 1,000 m respectively. The ordering type of I/S is $R \ge 1$ and the amount of smectite in I/S ranges from 12 to 23 %. C/S is a randomly ordering type. The metamorphic index mineral graphite was found in several segments below 5,038 m depth. EMPA composition data for calcite, illite, muscovite and chlorite is listed in Table 1.

4.2 Rock fabric

Figure 2 shows the changes in rock fabric with depth, which range from mudrocks and shales at the surface to slates, phyllites and even mylonites toward the bottom of the borehole. The various textural zones contain rocks with clay matrixes change from illite-smectite and chloritesmectite assemblages to more crystalline muscovite-chlorite assemblages at depth. Mudrocks (Fig. 2a, 100 m) are characterized by no preferred orientation in the matrix, whereas the shales (Fig. 2b, 358.4 m) contain a sedimentary fabric within the clay matrix forming a thin beds and lamination. Illite-chlorite bearing slates (Fig. 2c HW-589, 4.375.1 m) are characterized by new formed phyllosilicates orientating at low-angles to the sedimentary bedding. Muscovite-chlorite phyllites (Fig. 2d, 7,011.2 m) contain neocrystallized phyllosilicates forming a series of cleavages penetrating the rocks, with strain-induced segregation of quartz and feldspar forming syn-tectonic mineralization. Three deformation cleavages S1-S3 were observed. S1 is penetrative and comprises of chlorite and muscovite (previously referred to as sericite, Rieder et al. 1998). This cleavage was overprinted by the S2 cleavage at an angle of 68°. S3 is restricted to a localized area and has an angle of 40° to S2. Because it is not possible to locate all three fabrics in the cored rocks, the observed S1-3 deformation phases cannot be directly linked to other geological structures. Mylonites contain (Fig. 2e, 6,073.2 m) an elongated and mortar texture of corroded quartz porphyroclasts and feldspar that occasional contain pressure shadows filled with newly formed phyllosilicates. While most quartz porphyroclasts are elongated and rounded into to form augen like structures, some asymmetrical clasts indicate a sinistral shear sense (shearing direction is marked by a pair of arrows in Fig. 2e).

4.3 Illite "crystallinity" and chlorite "crystallinity"

IC values from well Hongcan 1 range between 0.234– 0.679° $\Delta 2\theta$ and CC values between 0.214–0.477° $\Delta 2\theta$. From the top to the bottom of the borehole, the IC Kübler index generally decreases from >0.60 to ca. 0.25° $\Delta 2\theta$ (Fig. 3). Adopting accepted anchizone boundaries at 0.42 for the lower limit and 0.25° $\Delta 2\theta$ for the upper limit (Kübler 1964; Merriman and Peacor 1999), the well can be



Fig. 3 Variation of IC with depth in well Hongcan 1

divided into the diagenetic zone (D, above 1,500 m), a transition from diagenetic zone to anchizone (D-LA, 1,500–3,270 m), the low anchizone (LA, 3,270–5,470 m), the high anchizone (HA, 5,470–6,000) and a transitional section from high-anchizone to epizone (HA-E, >6,000 m). A good correlation (Fig. 4) between IC and CC was derived as:

$$IC = 2.9714CC^{1.7101}$$
 ($R^2 = 0.857, N = 233$). (1)

Based on this correlation the boundaries of anchizone in terms of CC values are 0.314 and $0.242^{\circ}\Delta 2\theta$ for the lower and upper limits. If weathered near surface sample (HW-462) is excluded as well as sandstone and meta-sandstone lithologies, an even better correlation between IC and CC within those core samples is obtained as IC = $5.356CC^{2.17}$, $(R^2 = 0.912, N = 27)$. Weathering has likely oxidized the Fe⁺² in chlorite to Fe⁺³ causing changes in the chlorite structure and alterations to crystallinity. The lack of correlation for many surfaces samples was also noted by Wang et al. (1996). Due the narrow range of CC values across the anchizone (only $0.07^{\circ}\Delta 2\theta$) this zone was not further subdivided when based on CC measurement.

4.4 Illite polytypes

As pointed out by Frey (1987), the illite polytype transformation from $1M_d$ to $2M_1$ can be used as an indicator of the state of diagenesis and very low grade metamorphism. The illite polytype in well Hongcan 1 was investigated by XRD analyses of random powder preparations which uses the integrated intensity ratio $P = 2M_1(I_{025})/[1M(I_{112}) + 2M_1(I_{025})]$, see Fig. 5 for detail. The total range of P in the



Fig. 4 Correlation between IC and CC



Fig. 5 Measurement of illite polytype parameter $P = 2M_1(I_{025})/[1M(I_{112}) + 2M_1(I_{025})]$. There is a major difference between 1M and $2M_1$ structures of illite, that is, d_{112} (3.66 Å) of 1M illite and d_{025} (2.988Å) of $2M_1$ illite (according to ICDD 2005). Because d_{114} of $2M_1$ structure is often interfered by feldspar's major reflections specially by the main reflection (3.19 Å) of albite and d_{-113} is too weak, the amount of $2M_1$ in the mixture of $1M + 2M_1$ is measured and calculated using the integrated intensities of reflection (112) of 1M and (025) of $2M_1$ illite for the sake of simplification. When other reflection appears the deconvolution technique was used and this way the pure reflections of 025 and 112 can be obtained

Table 2 Geo-thermometric data from part core samples

well is 0.4–1 and from the surface to the bottom, a general increasing tendency of P exists from ca. 0.6–1. However, because of the presentation of detrital mica the P is enhanced and 0 values for P in diagenetic rocks is not to be expected. Below 3,000 m the P increases, on average, to 0.61 at 3,000 m, to 0.73 between 3,000–4,000 m, to 0.94 between 4,000–5,000 m, to 0.98 between 5,000–6,000 m and to 0.99 at depths >6,000 m. A poor power functional correlation between IC and P is derived as:

$$IC = 0.270P^{-0.97}$$
 (N = 232, R² = 0.718) (2)

4.5 Quartz fluid inclusions

Some quartz veins were collected from core samples which occur parallel and subparallel to bedding (S_0) . The homogenization temperature and composition of fluid inclusions were determined and assuming constant composition and volume since trapping (Mullis 1987; Mullis et al. 2002), the results could be used to determine the lower limit of formation temperatures. Three populations of homogenization temperatures (Table 2) could be recognized that could also be distinguished by features of quartz morphology (Mullis 1987). The diagenetic zone contained primary quartz inclusions with the lower homogenization temperatures and compositions relatively rich in HHC. The quartz fluid inclusions found in high anchizone show a broad temperature range typical for both diagenetic to metamorphism conditions but are notably rich in H₂O. This mixture of homogenization temperature within the quartz particle is considered to represent its long growth history. In these samples, the CH₄ and the H₂O Raman shifts were successfully detected at 2,914 and 3,000–3,300 cm^{-1} corresponding to LA and A-E zones respectively (see Fig. 6).

No.	Depth (m)	$T^{a}_{(Cc-Do)} (^{\circ}C)^{d}$	$T^{\mathrm{b}}_{(\mathrm{Ch})} (^{\circ}\mathrm{C})^{\mathrm{d}}$	$T_{\rm h}^{\rm c}$ (°C)
HW-462	0			184, 189, 188
HW-447	469.4			129, 118, 135, 138, 169, 179, 181, 157
HW-458	1949			154, 185
HW-589	4375.1	264		
HW-591	4945.2	316		
HW-698	5847.5	293		
HW-699	6006		213,237	
HW-732	6073.2			179, 159, 170, 150, 287, 163, 236, 235, 218, 239
HW-733	6543.7		328, 348, 317	133, 139, 152, 157, 177, 174, 174, 235, 270 , 273 , 230, 249, 156, 176, 161, 192, 166
HW-734	7011.2			232, 223, 235

^a Temperature evaluated from calcite geobarothermometer, 3 kbar pressure condition has been considered according to b cell geo-barometry of K-white mica and the erosion and depth of Triassic in the well, see text for detail

^b Temperature evaluated from chlorite chemical geothermometer (Inoue et al. 2009)

^c Homogenization temperature of fluid inclusion in quartz

^d Calculated from EMPA data



Fig. 6 Raman spectroscopy of fluid inclusion trapped in quartz. a Methane and b water

4.6 Metamorphic pressure evaluation

Statistical analyses and cumulative frequency patterns of the K-white mica b cell parameter has been well investigated in metamorphic terrains of different types ranging from low to high pressure facies (Sassi and Scolari 1974). Metamorphic pressure plays a role in affecting the composition of mica series, with substitutions in IV and VI sites, as well as in the interlayer (Guidotti and Sassia 2002). Structural analysis (based on ionic radii calculations, Shannon 1976) indicates that the substitutions with increasing pressure of $Fe^{2+}Mg{\leftrightarrow}Al^{3+}$ and $Fe^{3+}{\leftrightarrow}Al^{3+}$ within octahedrons plays a more important role in impacting mica structure than the $Si^{4+} \leftrightarrow Al^{3+}$ substitution in tetrahedrons. This is in agreement with the statistic results of K-white mica geobarometer. From this point of view, it is reasonable and reliable to use the K-white mica b cell geobarometer in the study of metamorphic pressure evaluation for very low grade metamorphism of clastic rocks.

Table 3 lists these describing substitutions in muscovite and chlorite and the exchange coefficient K_D of the Tschermak substitution between muscovite and chlorite. The meanings of the ratio of t, p and K_D are referred to Miyashiro and Shido (1985). It shows from Table 3 that t, p and K_D increase to a top (5,847–6,073 m) and then decrease consistently. This indicates that the amount of celadonite in muscovite and antigorite in chlorite increase and then decrease (Miyashiro and Shido 1985).

Being a species of the mica group, the illite b cell dimension has the same meaning as the muscovite b cell and has been widely used as a mica b cell geobarometer by many researchers (Padan et al. 1982; Yang and Hesse

Table 3 *t*, *b* cell and Na/(Na + K) of muscovite, *p* of chlorite and K_D of Tschermak substitution between muscovite and chlorite from core samples in HA and A-E

No.	Depth (m)	<i>b</i> cell (nm)	Na/ (Na + K)	t	K _D	р
HW-698	5847.5	0.9011	0.041	0.103	0.23	0.333
HW-699	6006	0.9005	0.087	0.128	0.281	0.343
HW-732	6073.2	0.9013	0.045	0.189	0.414	0.36
HW-733	6543.7	0.9013	0.036	0.145	0.345	0.33
HW-734	7011.2	0.8995	0.159	0.056	0.137	0.303

t = Si - 3 (formula of muscovite is calculated based on 11 oxygen); p = (Si/2 - 2)/2 (formula of chlorite is calculated based on 28 oxygen); $K_{\text{D}} = [t/(1 - t)]/[p/(1 - p)]$; see Miyashiro and Shido (1985)

1991; Wang et al. 1996; Gutierrez Alonso and Nieto 1996; Cruz and Jiménez 2002; Bozkaya and Yalçin 2005; Potel 2007; Brime et al. 2008; Kemp and Merriman 2009; Corrado et al. 2010; Offler et al. 2011). K-white mica *b* cell values of 52 samples were measured from the Triassic flysches in well Hongcan 1. The values range from 0.8992 to 0.9023 nm, with an average of 0.9008 nm. As derived from the cumulative frequency curves of the *b* cell values (Fig. 7), the pressure condition below 5,470 m (HA to A-E) is a little lower than the N. New Hampshire pressure type (low intermediate, Rumble 1973; Guidotti and Sassia 1986). According to Guidotti and Sassia (1986) the average *b* cell value of core samples (9.008 Å, close to the 9.010 Å line) corresponds to c. 3 kbar, for the high anchizone (HA)



Fig. 7 Cumulative frequency curves of K-white mica *b* cell dimension. Solid line 1 Bosos low pressure type, solid line 2 N. New Hampshire low intermediate pressure type, solid line 3 Otago intermediate high pressure type, solid line 4 Sanbagawa high pressure type, shaded line represents the cumulative frequency curves of K-white mica *b* cell dimensions from HA and A-E transition (5,470-7,000 m)

and anchi-epizonal (A-E) equivalent temperatures. The estimated erosion (>3.8 km) and depth (7 km) of Triassic in the well Hongcan-1 (Bureau of geology and mineral resources of Sichuan province 1991; Li et al. 2006) are also compatible with pressure condition around 3 kbar.

4.7 Temperature evaluation

The chlorite chemical geothermometer (Inoue et al. 2009), calcite-dolomite (Cc-Do) geobaro-thermometer (Goldsmith et al. 1955; Goldsmith and Newton 1969; Bickle and Powell 1977; Turner 1981) and homogenization temperature of quartz fluid inclusions were used to evaluate the metamorphic peak temperature of Triassic flysches in well Hongcan 1. All temperature data are listed in Table 2. Because application of mineral geothermometer requires equilibrium assemblages only flysch of the HA and A-E transition was used (Note in Fig. 3f the chlorite and muscovite in the A-E transition sample are in equilibrium). Chlorite is composed by two tetrahedral and two octahedral sheets, the temperature would impact on both of them. It is clear that chlorite Al IV site geothermometer (Cathelineau 1988) obtains temperature information only from empirical data about IV site while the chlorite chemical geothermometer (Inoue et al. 2009) calculates temperature, using a thermodynamic approach from both IV and VI sites. For this reason we have chosen the chlorite chemical geothermometer for temperature evaluation.

X-ray diffractometry is a more statistically valid approach as it measures countless small particles of minerals without limitations in dimension and it has been widely used in analyzing very low grade metamorphic rocks. It is well known that rocks of greenschist facies and higher metamorphic facies are well crystallized and when their minerals are in equilibrium those geothermometers and geobarometers can be applied. However, it should keep in mind that minerals in equilibrium should not be limited by the effective resolution of the microscope (2 µm) or EMPA (1 μ m). Minerals in equilibrium can rationally be less than 1-2 µm in size. The general temperatures variations with depth in the well Hongcan 1 based on all methods are shown in Fig. 8. All indicate increasing temperatures with decreasing depth in the Triassic flysch corresponding to the diagenetic to epizonal transition.

The tectono-thermal history can be summarized as follows. Following deposition in a deep sea environment of the Paleo-Tethys ocean, and accumulations of roughly 5–7.5 km thick turbidites in the Songpan basin during the Carnian stage (T_{2-3}) (p219, the Bureau of Geology and Mineral Resources of Sichuan Province 1991), collision between the south and the north China blocks caused a folding of Triassic flysches (see the geological sketch around the well in Fig. 1) and structural thickening of the sequence to over 7 km in the well Hongcan 1 or 10–15 km in the area near Zoigê (closed fold or intrafolial fold produced in the Triassic flysch strata an increase of, at least, 2 times in thickness, Zhao et al. 2004). Structural overloading in a foreland basin setting is suggested to have been responsible for the increasing temperature at depth (350 °C/10 km for a normal gradient 35 °C/km), inducing anchimetamorphism at the bottom of Triassic flysches. This temperature agrees well with 348 °C evaluated from the chlorite chemical geothermometer. With increasing depth, the decreasing of IC and CC, increasing of P, rock fabric evolution from no preferred orientation in the matrix to penetrating cleavages, fluid inclusion in quartz from HHC zone to CH₄ and to H₂O zone and the mineral assemblage from illite-I/S-C/S-chlorite to muscovitechlorite; all of them consistently indicate the increase in grade. "Fold overloading model" is therefore proposed to describe the anchimetamorphism of the Triassic flysches in the well. In the eastern Sichuan basin, the neighboring area, where the Triassic consists of about 1,800 m carbonaceous limestone of T_{1-2} and 1,500 clastic rocks of T_3 , the structural overloading was not able to cause very low grade metamorphism due to the thinner thickness of the Triassic strata. Post-metamorphic structural movements (shearing) produced a series of detachments within the Triassic flysches (mylonites) at different levels of the well, which were related to the development of S2-3 cleavages. The Xianshuihe fault produced a strike-slip movement in the early Tertiary and disturbed the distribution of metamorphic zones (Wang et al. 2011). Finally the Himalayas movement caused uplift and denudation of the Triassic flysch (>3.8 km erosion since Cretaceous, Bureau of geology and mineral resources of Sichuan province 1991, Li et al. 2006), but this final event had little influence on the distribution of the very-low grade metamorphic rocks.

5 Conclusions

The 7 km thick Triassic flysch sequence penetrated by well Hongcan 1 shows a continuous increase in metamorphic grade with depth ranging from late diagenesis in the upper 1,500 m to epizonal conditions at bottom of the borehole.

Fluid inclusions within quartz from core samples are consistent with the grade changes with a higher hydrocarbon zone corresponding to the diagenetic rocks, a methane zone within the diagenetic to anchizone rocks and a water zone (H_2O) corresponding to the anchizone-epizone transition.

The peak metamorphic pressure condition experienced by the Triassic flysch was slightly lower than the intermediate-low pressure conditions and peak temperature reached 348 °C. The diagenetic to epizonal metamorphism



Fig. 8 Comprehensive variations of all evolutionary parameters from diagenesis to very low grade metamorphism with depth of well Hongcan 1. *D* diagenetic zone, *D*-*A* transition between diagenetic zone and anchizone, *LA* low anchizone, *HA* high anchizone, *A*-*E* transition between anchizone and epizone, $T_{3z}hw$ Zhuwu formation of upper Triassic, $T_{3z}gn$ Zagunao formation of upper Triassic, $T_{2z}gsh$ Zagashan formation of middle Triassic, Qtz quartz, *Fs* feldspar, *Ill* illite, *Ms* muscovite, *Chl* chlorite, *I/S* illite/smectite mixed-layer phase, *C/S* chlorite/smectite mixed-layer phase, *Kln* kaolinite, *Cal* calcite, *Sd* siderite, *Dol* dolomite, *Ank* ankerite, *Stp* stilpnomelane, *Gr*

of the studied sequence reflects structural thickening of the Triassic sedimentary rocks.

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graphite, *IC* "illite crystallinity", *CC* "chlorite crystallinity", $P = 2M_{025}/(2M_{025} + 1M_{112})$, *HHC* higher hydrocarbons, *CH*₄ methane, *H*₂*O* water, *T* formation temperature. Numbers with a minus sign by the left of column indicate the depth down from the ground surface. *Legend 1* shale, *2* fine sandstone, *3* meta-sandstone, *4* slate, *5* phyllite, *6* marble, *7* detachment, *8* folding trace. *Plus sign* indicates homogenization temperature of fluid inclusion in quartz; *triangle* indicates temperature evaluated by Cc–Do geobarothermometer; *open circle* indicates temperature evaluated by chlorite chemical geothermometer (Inoue et al. 2009)

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