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Objektyp: **Article**

Zeitschrift: **Schweizerische mineralogische und petrographische Mitteilungen
= Bulletin suisse de minéralogie et pétrographie**

Band (Jahr): **75 (1995)**

Heft 2

PDF erstellt am: **28.04.2024**

Persistenter Link: <https://doi.org/10.5169/seals-57148>

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K–Ar dating of a Mesozoic hydrothermal activity in Carboniferous to Triassic clay minerals of northern Switzerland

by Urs Schaltegger^{1,2}, Horst Zwingmann¹, Norbert Clauer¹, Philippe Larqué¹ and Peter Stille¹

Abstract

Clay fractions of 0.2 μm up to 2–6 μm size from Upper Triassic (Keuper series at Frick) and Upper Carboniferous sediments (Stephanian strata at Weiach, NAGRA drillhole), both in northern Switzerland, were analyzed for their K–Ar ages in order to trace their post-depositional history and to date a hypothetical hydrothermal overprint. The latter had to be assumed because of published K–Ar and Rb–Sr data that are by up to 200 million years younger than the age of deposition in sediments or metamorphism in crystalline rocks, respectively, of the same region.

The K–Ar ages from an Upper Triassic marl, a sandstone and a shale are all younger than their depositional age. They do not indicate any hydrothermal overprint, but most likely indicate diffusive Ar loss from poorly organized sheet silicates.

Siltstones from the Weiach borehole (Upper Carboniferous from the North Swiss Permocarboniferous Trough, NPT) reflect old detrital components and a post-depositional Ar loss. Three tuff samples interlayered with the siltstones define an age of 183 ± 5 Ma for a penetrative hydrothermal overprint causing complete illitization of the tuffs and extensive cementation of secondary pore space of the siltstones, partly by replacement of precursor clays (kaolinite). The three siltstone samples were differentially overprinted by the fluids, according to their depth in the borehole: The deepest sample shows a nearly size-independent age distribution with a mean value around the proposed age of hydrothermal activity of 183 Ma. Samples higher up in the column are more strongly dominated by their detrital components, exhibiting the typical correlation between apparent age and grain size. Hump-shape type age patterns characterize samples that contain abundant aggregates of small sized particles in their coarse size fractions.

A model is proposed, which infers fluid migration in the deeper part of the NPT (1700 to 2050 meters) along subhorizontal shear zones, causing highly variable illite/kaolinite ratios depending on the fluid/rock ratio. These fluids may have introduced enough additional heat to create an impact on thermal indicators used for basin modelling, such as porosity, illite/smectite ratios, fluid inclusions and the degree of maturation of the organic material (vitrinite reflexion).

Keywords: K–Ar age determinations, clay minerals, Mesozoic, fluid migration, hydrothermal alteration, northern Switzerland.

Introduction

The post-depositional history of a sediment often includes thermal episodes of multiple origin, either as burial diagenetic processes or as hydrothermal overprints. These processes usually cause a differential overprint of the rocks, according to grain size and retentivity of the daugh-

ter isotopes in the rock components, resulting in a wide range of so-called "apparent ages" (see e.g. the case studies of HUNZIKER, 1986, and CLAUER et al., 1995; SCHALTEGGER et al., 1994). The K–Ar system of clay minerals is known to record even very weak hydrothermal to diagenetic events and is, therefore, best suited to investigate the hydrothermal history of any given re-

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gion (see review in CLAUER and CHAUDHURI, 1995). However, K–Ar ages are often difficult to interpret, because they are biased by the presence of detrital components more or less incompletely equilibrated during preceding (hydro-) thermal events, and authigenic mineral phases of one or more generations (AHRENDT et al., 1978; HUNZIKER, 1986; HUNZIKER et al., 1986; REUTER, 1987).

The European continental crust has been found to be repeatedly flushed by hydrothermal fluids since the end of Variscan orogeny. ZIEGLER (1990) and PLATT (1993) compiled K–Ar data from central and northern Europe and observed a clustering of K–Ar ages around 110, 130–150, 170 and 180–210 Ma. They consequently proposed the existence of a series of distinct hydrothermal pulses of these ages. This approach appears questionable in the light of the heterogeneity of the $< 2 \mu\text{m}$ clay fractions commonly used for K–Ar dating in sediments (CLAUER et al., 1992). Late-Variscan to Jurassic hydrothermal events are generally of high temperature throughout western Europe, and are responsible for the formation of ore deposits. The host rocks often contain coevally formed illite phases either

in gouges (BROCKAMP et al., 1987, 1994), or as pore cements in oil- and gas-bearing sandstones (GAUPP et al., 1993; LIEWIG et al., 1987; MOSSMANN et al., 1992), or within Pb–Zn or U ore deposits (BONHOMME et al., 1983; CLAUER et al., 1985; MENDEZ et al., 1991; PHILIPPE et al., 1993; TOULKERIDIS et al., 1993; TURPIN et al., 1991).

The region of northern Switzerland, the southern termination of the Rhinegraben rift and bordering uplifted Black Forest basement, is prone to hydrothermal activities, because it has continuously been the locus of tectonic movements through Mesozoic and Cenozoic times. Various dating attempts in the Black Forest and on drill-core material of the NAGRA (National Cooperative for the Storage of Radioactive Waste) from northern Switzerland, revealed that the post-Variscan hydrothermal activity is multi-episodic between 280 and 125 Ma: Late Variscan hydrothermal feldspar dissolution and illite growth was recorded by K–Ar illite ages and a Rb–Sr whole rock isochron age from granitoid rocks around 280–270 Ma (PETERS et al., 1987a; MATTER et al., 1987). Dispersed K–Ar ages between 270 and 230 Ma, and down to 120 Ma (Kai-sten well; PETERS et al., 1987b) suggest the pres-

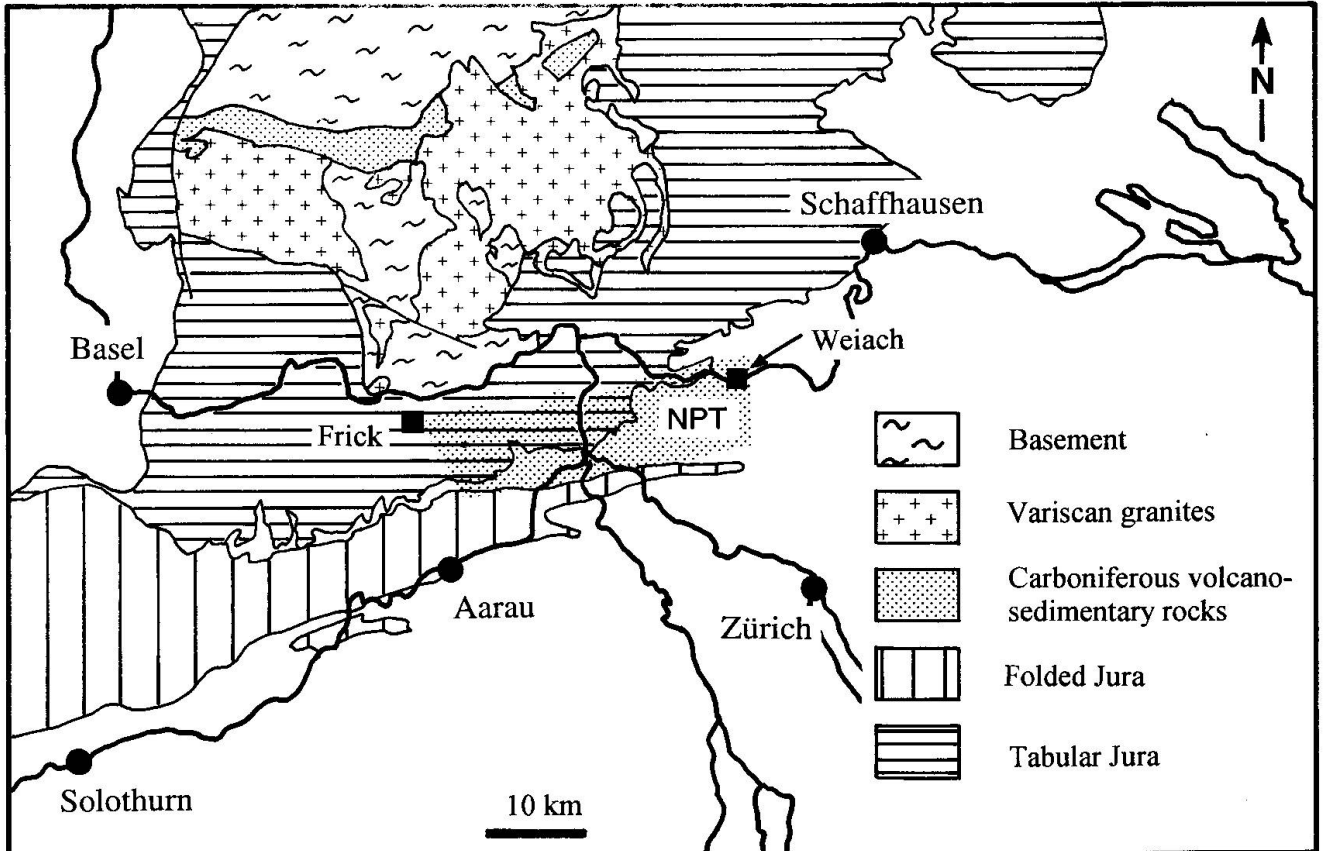


Fig. 1 Tectonic map of northern Switzerland and adjacent areas; from MATTER et al. (1988), modified. NPT = Northern Swiss Permian Trough, with approximate outlines (stippled).

ence of a poorly defined younger event of unknown age. K-Ar ages from the Black Forest range between 190 and 150 Ma, including illites from major fault systems (BROCKAMP et al., 1994) and from ore deposits (BONHOMME et al., 1983; BROCKAMP et al., 1987). Diagenetic formation of roscoelite in Permian red beds of the Riniken well was dated at 190–112 Ma, whereas chemical microprobe U-Pb pitchblende ages range from 160 to 135 Ma (HOFMANN, 1990). The K-Ar age range of 190 to 140 Ma seems to be restricted to illite growth in sedimentary host rocks, the crystalline rocks of the basement usually record higher dates between 300 and 230 Ma, except for illites from fault gouges. No synoptic review exists yet on these age determinations, and no precise indication has been provided for the exact age of any of these suspected hydrothermal events.

The present study was undertaken to substantiate the occurrence of hypothetical hydrothermal pulses in northern Switzerland, using a different approach than in the earlier investigations. We analyzed illite-type minerals in sediments having different lithologies, depositional ages, chemical compositions and burial histories, as well as associated tuffs. By separating individual grain-size fractions, we intended to eliminate the detrital component as much as possible and tried to obtain significant ages that are defined by size-independent "plateau age" patterns. Size fractionations in the very small particle sizes often allow to separate the detrital from newly formed material, which might be of hydrothermal origin in the present case.

Sample description

The investigated samples originate from two different localities in northwestern Switzerland (Fig. 1), and belong to two different stratigraphic units. Samples 3537 to 3539 were taken in a quarry near the village of Frick in the Tabular Jura, which represents a well exposed section through the Upper Keuper series. The mineralogical composition of the studied samples, their occurrence and stratigraphic positions are given in table 1 and figure 2a. The three samples are of different depositional lithologies and chemical compositions: a grey to green carbonate-rich marl (sample 3537), a red clay (3538) and a red sandstone (3539). The latter is expected to contain older detrital components as the two former ones, because it is correlated with the Nordic Keuper. The Triassic sedimentary pile was never buried in excess of a few hundred meters (PE-

TERS, 1964). Differences in clay mineralogy, therefore, can mirror different depositional environments, and/or different post-depositional overprint. Sample 3537 is virtually identical to sample 3 (F176), and sample 3539 is located four meters below sample 1 (F120), both investigated by HUNZIKER et al. (1986).

Samples 3540, 3544, 3545, and 3587 to 3589 were taken from NAGRA drilling site at Weiach (Fig. 1; MATTER et al., 1988). This drilling evidenced the presence of a large Permo-Carboniferous graben within the crystalline basement rocks that is buried below Mesozoic and Cenozoic sediments of the Alpine Molasse foreland basin. It was formed during Upper Carboniferous transtensional tectonics and extensional normal faults were partly reactivated during later transpressive stages. The sediments have been stratigraphically interpreted to be of Stephanian and Autunian ages (MATTER et al., 1988).

Samples 3540, 3544, and 3545 represent strongly illite-cemented siltstones with abundant microporosity of secondary origin, high contents of organic matter (see Tab. 1), and up to 1 cm large fragments of granitoid rocks and their mineral constituents (quartz, feldspars). MATTER et al. (1988) called these rocks crystal tuffs ("Kristalltuffite"), but thin section observations, the presence of organic material and U-Pb ages obtained on individual zircon grains 30 Ma in excess of the age of deposition (SCHALTEGGER and CORFU, 1994), indicate the clastic nature of these rocks without pyroclastic contribution. The samples were taken at drilling depths of 1348, 1781 and 1960 m and correlate with the stratigraphic range from Lower Autunian to Middle Stephanian (according to MATTER et al., 1988).

Samples 3587, 3588, and 3589 represent yellowish-grey tuffs recovered from the same NAGRA well at depths of 1432, 1443 and 1587 m. They consist of up to 90% clay minerals and rare volcanogenic phenocrysts (quartz, rutile, zircon). Preliminary U-Pb zircon ages suggest an age of 298 ± 1 Ma for the tuff sample 3587 (SCHALTEGGER and CORFU, 1994). These tuffs were included in the study, because they provide a unique opportunity to examine the K-Ar system of clay minerals devoid of any detrital memory or component.

The entire set of selected samples was subjected to burial depths ranging from at least 500 m at Frick with a geothermal gradient of about 30–40 °C/km, to 1800 m at the Weiach site with a gradient of about 110 °C/km at the time of deposition and subsequent rapid burial during the Early Permian (KEMPTER, 1987).

Tab. 1 Short description of the studied rock samples from Frick and Weiach, both northern Switzerland.

Sample number	Lithology, sedimentology, stratigraphy	Whole rock mineralogy
Quarry of Frick (Keuper/Triassic)		
3537	Grey carbonate-rich marl within a series of marine-estuarine mudstones; Top Keuper (Triassic), two meters below Liassic (Obere Mergelgruppe). Same lithology as sample 3 of HUNZIKER et al. (1986).	50% carb, 10% qtz, 2% kfs, 1% alb, 37% clay *
3538	Red marly clay, interlayered with sandy and dolomitic layers; lower part of the marine-estuarine deposits of the Obere Mergelgruppe. Adjacent to green clays of sample 2 of HUNZIKER et al. (1986).	no data
3539	Red sandstone; continental fluvial sediment, representing a phase of emersion after deposition of estuarine sediments. Top of Schilfsandsteingruppe; sample is situated 3 meters above sample 1 (red clay) of HUNZIKER et al. (1986).	55% qtz, 8% kfs, 11% alb, 26% clay **
Drillhole Weiach (Autunian/Permian and Stephanian/Carboniferous)		
3540 = WEI 1348.02	Black porous clay to siltstone with rock fragments (so-called "Kristalltuffit", crystal tuff), in a lacustrine series of Autunian age (Lakustrische Serie).	28% qtz, 20% kfs, 10% alb, 40% clay
3587 = WEI 1432.26	Yellowish-grey tuff, 20 cm thick, in a series of detrital sediments (sandstones, silt, clay); Grosszyklische Grobsandstein-Ton-Serie, Autunien. Depositional age 298 ± 1 Ma (U-Pb zircon age, SCHALTEGGER and CORFU, 1994).	9% qtz, 1% carb, 7% kfs, 83% clay
3588 = WEI 1443.35	Yellowish-grey tuff, 10 cm thick layer adjacent to thin coal bed; in shales that are situated 5 m above suggested Carboniferous/Permian boundary of MATTER et al. (1989) in the Grosszyklische Grobsandstein clay Ton-Serie, Autunian.	6% qtz, 1% kfs, 4% carb, 89%
3589 = WEI 1586.52	Yellowish-grey tuff, 70 cm thick, within a 6 m thick coal bed; tuff contains fracture fillings of cc, dol, ba; in a succession of fluvial to estuarine sediments (Kohle-Serie, Stephanian C+D).	4% qtz, 20% carb, 76% clay
3544 = WEI 1780.82	Black porous clay to siltstone with large fragments of kfs (so-called "Kristalltuffit", crystal tuff), in a series of fine-grained clastic sediments with coal beds (Mittlere Kleinzyklische Sandstein-Ton-Serie, Stephanian C+D).	no data
3545 = WEI 1959.87	Black porous clay to siltstone with rock fragments (so-called "Kristalltuffit", crystal tuff); 30 cm thick layer in coarse- to fine-grained sandstones of the Mittlere Kleinzyklische Sandstein-Ton-Serie, Stephanian C+D; sample is situated ca. 70 m above basement/sediment contact.	33% qtz, 1% kfs, 1% alb, 65% clay
Stratigraphy taken from PETERS (1964) for the Frick samples, and from MATTER (1987) and MATTER et al. (1989) for the Weiach samples, including whole rock mineralogy for the latter. * Sample 176; ** Sample 115 from PETERS (1964). Abbreviations: alb = albite, ba = baryte, carb = carbonate, cc = calcite, dol = dolomite, kfs = K-feldspar, qtz = quartz.		

Methods

The samples were prepared with maximum care to avoid artificial fragmentation of the original grain components. Samples 3538, and 3587 to 3589 were disaggregated in distilled water by shaking and stirring, whereas samples 3537 and 3539 were first crushed with a hammer and then

disaggregated during repeated freezing-thawing cycles in distilled water and closed containers over a period of two months. Samples 3540, 3544, and 3545 turned out to be very resistant and had to be crushed with a jaw crusher using maximum distance of the plates. They were subsequently disaggregated using freezing-thawing cycles during ten days. The $< 2 \mu\text{m}$ and $2\text{--}6 \mu\text{m}$ fractions

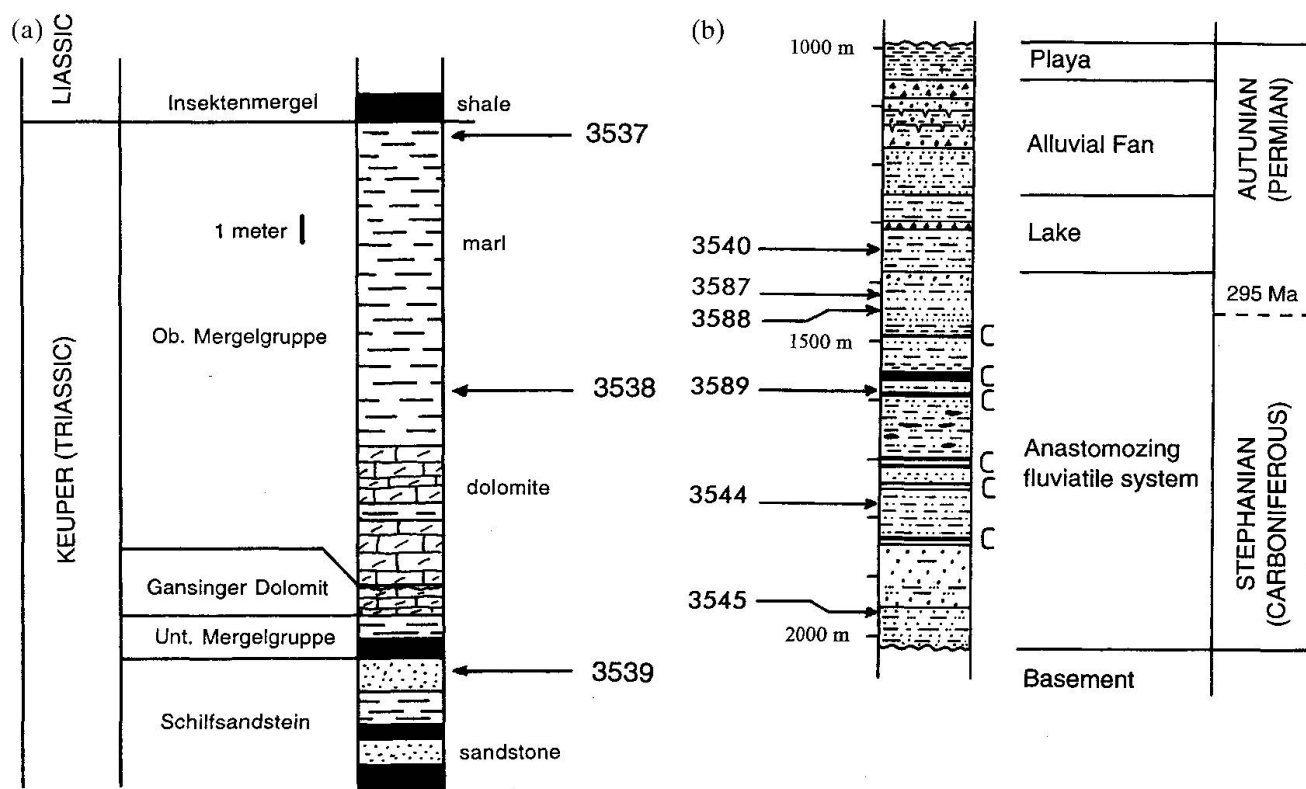


Fig. 2 Stratigraphic profiles from the investigated localities, (a) Upper Triassic Keuper series from the quarry near the village of Frick, Tabular Jura (from PETERS, 1964); (b) drilled sequence of Permocarboniferous sediments at Weiach, NAGRA drilling site (from MATTER et al., 1988). Age of the Carboniferous/Permian boundary after ODIN (1994).

were separated by settling in distilled water according to Stokes' law. Further subfractions (< 0.2 , $0.2-0.4$, $0.4-0.8$ and $0.8-2 \mu\text{m}$) were obtained by means of an overflow ultracentrifuge. Ultrasonic treatments before the separations were avoided not to break up the delicate smectite enriched mixed layer minerals.

Each clay fraction was studied for its mineralogical composition using standard X-ray diffraction techniques. The morphology of some of the investigated clay minerals was examined by transmission electron microscopy (TEM), and by scanning electron microscopy (SEM). For determination of the K concentration, ca. 50–60 mg of dry sample were heated at 850°C for 24 hours prior to digestion, to oxidize the organic matter. Dissolution was achieved in screwed Savillex vials containing HF and HNO_3 during five days. The dissolved samples were diluted with 2% HNO_3 and their K concentration was measured by atomic absorption spectrometry with an analytical accuracy of ca. $\pm 1\%$. The Ar isotopic composition was measured on ca. 50 mg of sample, which was previously dried overnight at 110°C , using an Ar extraction method close to that described by BONHOMME et al. (1975) and an upgraded AEI MS-20 mass spectrometer. The iso-

tope ratios are corrected for blank and mass discrimination. Repeated analyses of the GLO reference glauconite yielded a mean value of $24.93 \pm 0.28 \cdot 10^{-6} \text{ cm}^3/\text{g STP}$ ($n = 10$).

Results

MINERALOGICAL COMPOSITION

The results of the mineralogical investigation compiled in table 2 indicate that the clay fractions consisted of illite, illite/smectite (I/S) mixed-layers enriched in illite ($> 85\%$), chlorite, and kaolinite. The clay fractions chosen for K-Ar dating are generally rich in illite and I/S phases, ranging between 50 and 93 vol.%. Kaolinite is concentrated in the siltstones of Weiach drill hole and is rare in the Frick samples. Illite and kaolinite clearly behave antagonistic in samples 3540, 3544 and 3545, suggesting a possible secondary formation of illite at the expense of kaolinite. Chlorite is present in appreciable amounts of up to 35% in samples 3539, 3540 and 3545. While no feldspar and/or quartz grains can be detected by X-ray diffraction in the size fractions of the marl sample (3537), minor quantities of these minerals can be

Tab. 2 Mineralogical composition of the investigated clay fractions.

Sample	Size [μm]	Illite	I/S a)	% S in I/S b)	Chlorite	Kaolinite	Accessory minerals c)
3537	< 0.2	61	39	13			
	0.2–0.4	70	30	5			
	0.4–0.8	72	28				
	< 2	74	26				
3538	< 0.2	70	28			2	
	0.2–0.4	70	29			1	
	0.4–0.8	76	23	5		1	
	0.8–2	86	14				fsp + qtz
	< 2	80	20				
3539	< 0.2	53	32		15		
	0.2–0.4	55	28		17		
	0.4–0.8	55	17		24	4	fsp + qtz
	0.8–2	65	10		21	4	fsp + qtz
	< 2	60	18		18	4	
3540	< 0.2	43	35	15	15	7	ap, fsp?
	0.2–0.4	37	26		16	21	fsp
	0.4–0.8	35	19		17	29	fsp + qtz
	0.8–2	36	14	5	18	32	fsp + qtz
3544	< 0.2	75	(I + I/S)	15	20	5	
	0.2–0.4	53	18		19	10	
	0.4–0.8	37	18		30	15	fsp \pm qtz
	0.8–2	20	30	5	35	15	\pm fsp
3545	< 0.2	70	18	15		12	
	0.2–0.4	47	22		7	24	
	0.4–0.8	44	19		7	30	
	0.8–2	37	14	5	5	44	qtz + fsp ?
3587	< 0.2		93	< 5	2	5	
	0.2–0.4	80			6	14	
	0.4–2	80			10	10	
	< 2		83		7	10	
3588	< 2		64		4	32	qtz + fsp
3589	< 2		69		5	26	fsp

a) Interlayered illite/smectite
b) Percentage of 10–14 Å smectite in I/S
c) Abbreviations: ap = apatite; fsp = feldspar; qtz = quartz

detected in one or several fractions of the claystone and the sandstone of the Frick quarry, and of the siltstones and the tuffs of the Weiach borehole (Tab. 2).

TEM photographs of the Weiach samples show some lath-type illites in the least illite-cemented sample 3540, suggesting the presence of low-temperature illite minerals (Fig. 3a). The two other samples (3544 and 3545) are pervasively cemented by irregularly shaped illite-type material beside some chlorite and kaolinite. Observation of rock chips under a SEM revealed ill-defined booklet-shaped particles, which might

suggest pseudomorphic replacement of kaolinite by illite. TEM photographs also reveal that coarse particle cores are surrounded by fine irregularly shaped flakes (Fig. 3b). The latter are considered as a younger generation of illite. The tuff samples contain illite or illite-rich I/S mixed-layers of equal size with sharp edges, without indices of further growth of younger materials (Fig. 3c).

Some X-ray diagrams were computed using Reynold's code (1980, 1985) to evaluate the amounts of smectite layers in the I/S mixed-layers. The amounts range between 15% (< 0.2 μm)

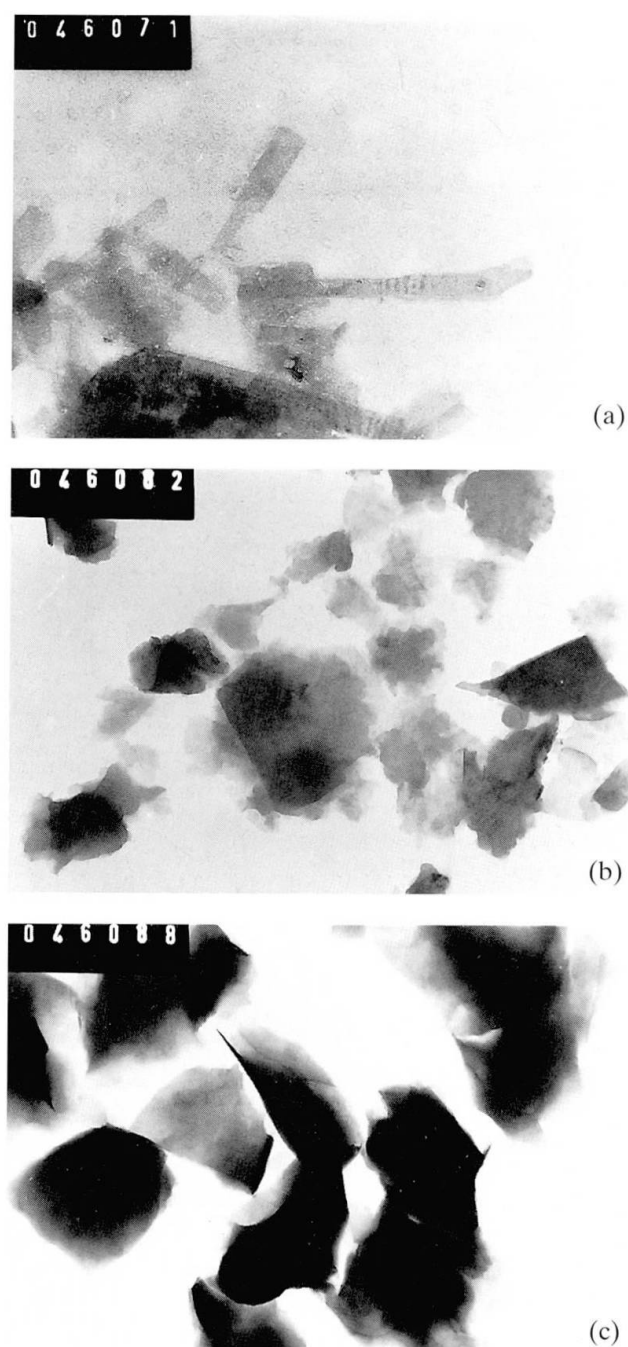


Fig. 3 TEM and SEM images of the investigated material from the North Swiss Permocarbiniferous Trough (NPT) at Weiach.

(a) Sample 3540 siltstone, $< 0.2 \mu\text{m}$: lath-type illite (magnification 110'000 \times).

(b) Sample 3545 siltstone, $0.2\text{--}0.4 \mu\text{m}$: irregularly shaped illite, I/S and some chlorite, overgrown by a new generation of illite (magnification 32'000 \times).

(c) Sample 3587 tuff, $0.2\text{--}0.4 \mu\text{m}$: flakes of well-ordered I/S with ca. 80% illite layers (magnification 32'000 \times).

and 5% (0.4 to $2 \mu\text{m}$; Tab. 2) in the siltstones. One determination on the $< 0.2 \mu\text{m}$ size fraction of sample 3587 indicates that the amount of smectite layers in the tuff sample is significantly

smaller ($< 5\%$), than that in the equivalent clay fractions of the sediments (13–15%). Obviously, the illite-type mixed-layers of the tuff samples are better crystallized than their sedimentary counterparts.

K-Ar ISOTOPIC RESULTS

The K-Ar age determinations (Tab. 3) show an overall relationship of increasing ages with increasing grain-sizes for the silt-, sand-, mud- and marlstones, which is a common finding for sediments and metasediments containing more or less detrital components (ARONSON and HOWER, 1976; CLAUER et al., 1995; HUNZIKER, 1986; REUTER, 1987). The apparent ages range from 267 to 145 Ma (Fig. 4). The tuffs of Weiach drill hole (samples 3587 to 3589), however, yield a consistent age pattern between 175 and 191 Ma. Figure 4 outlines three types of K-Ar age vs grain size patterns: (1) a hump type, (2) a slope type, and (3) a flat type. The hump type clearly belongs to the marlstone (3537) and the mudstone (3538) of Frick quarry, and to two of Weiach siltstones (3540 and 3544). It appears that grains larger than a given size in such rocks consist of aggregates of small and coarse particles, as convincingly demonstrated by REUTER (1987). This means, in turn, that the $> 0.8 \mu\text{m}$ fractions in the samples 3538 and 3540, and the $> 2 \mu\text{m}$ in the samples 3537 and 3544, consist of mixtures of young small, and old large mica-type particles. The slope-type pattern seems to be characteristic for the sandstone sample (3539) of Frick quarry and one siltstone sample (3545) of Weiach hole, suggesting that the adopted disaggregation technique of the samples was well suited for this lithology. The flat pattern of the tuff clay fractions (3587 to 3589) is the best proof that the fractions are isotopically homogeneous, and thus the K-Ar age is geologically meaningful.

Samples from Frick quarry (Fig. 4a)

The analyzed clay fractions span a maximum age range from 145 to 261 Ma. No "plateau age" could be detected, indicating that the data represent intermediate ages resulting from mixtures of at least two inhomogeneous components of different formation ages. The older component is assumingly of detrital nature and thus has a Variscan minimum age of > 290 Ma. No mineralogical differences could be assigned to the trends in the K-Ar data, as the fractions consist only of illite and I/S mixed-layer minerals, with some traces of kaolinite. Sample 3539 also contains sig-

Tab. 3 K–Ar isotopic results.

Sample	Size	%K	⁴⁰ Ar ccm/g [x1E-6]	⁴⁰ Ar rad. [%]	⁴⁰ Ar/ ³⁶ Ar	⁴⁰ K/ ³⁶ Ar [x1E6]	Age [Ma]
3537	< 0.1 µm	5.40	31.62	81.78	1621.83	0.151	145 ± 4
	< 0.2 µm	5.50	32.36	82.29	1668.28	0.156	146 ± 4
	0.2–0.4 µm	5.63	37.35	85.72	2069.93	0.178	163 ± 4
	0.4–2 µm	5.24	50.06	85.68	2063.36	0.123	231 ± 6
	2–6 µm	4.43	32.00	88.36	2538.38	0.207	177 ± 4
3538	< 0.2 µm	5.73	40.34	89.42	2793.84	0.237	173 ± 4
	0.2–0.4 µm	5.89	51.63	91.87	3633.41	0.254	213 ± 5
	0.4–0.8 µm	5.41	59.06	94.26	5148.23	0.297	261 ± 6
	0.8–2 µm	5.57	47.98	92.90	4161.36	0.299	209 ± 5
	2–6 µm	4.89	41.63	93.32	4426.08	0.324	207 ± 5
3539	< 0.2 µm	5.35	38.56	91.70	3560.79	0.303	177 ± 4
	0.2–0.4 µm	5.79	44.52	93.42	4493.48	0.364	188 ± 4
	0.4–0.8 µm	6.03	48.93	95.12	6054.60	0.478	196 ± 4
	0.8–2 µm	5.67	47.22	94.71	5588.77	0.424	203 ± 5
	2–6 µm	5.54	47.73	94.89	5778.65	0.424	209 ± 5
3540	< 0.2 µm	4.77	31.21	88.77	2630.93	0.238	161 ± 4
	0.2–0.4 µm	4.09	35.25	89.59	2838.99	0.197	209 ± 5
	0.4–0.8 µm	3.31	36.99	87.86	2434.75	0.128	267 ± 7
	0.8–2 µm	3.78	33.68	90.26	3034.63	0.205	216 ± 5
	2–6 µm	3.25	34.17	92.72	4060.32	0.239	253 ± 6
3544	< 0.2 µm	6.29	38.68	92.85	4132.51	0.416	152 ± 3
	0.2–0.4 µm	5.45	36.80	91.68	3550.36	0.322	166 ± 4
	0.4–0.8 µm	4.52	35.76	90.75	3196.27	0.245	193 ± 5
	0.8–2 µm	3.63	31.73	89.72	2874.09	0.197	212 ± 5
	2–6 µm	4.25	35.21	91.42	3445.53	0.254	202 ± 5
3545	< 0.2 µm	7.00	47.84	94.15	5048.21	0.464	168 ± 4
	0.2–0.4 µm	5.98	43.16	95.69	6849.47	0.605	177 ± 4
	0.4–0.8 µm	5.30	38.86	93.66	4657.59	0.397	180 ± 4
	0.8–2 µm	4.77	36.57	93.90	4847.32	0.396	187 ± 4
	2–6 µm	4.80	35.20	94.23	5118.45	0.438	180 ± 4
3587	< 0.2 µm	5.44	40.95	82.52	1690.08	0.124	184 ± 5
	0.2–0.4 µm	5.63	42.27	83.70	1813.41	0.135	184 ± 5
	< 2 µm	5.65	41.63	82.41	1679.59	0.125	181 ± 5
	2–6 µm	5.43	40.29	87.77	2416.48	0.191	182 ± 4
3588	< 2 µm	4.94	37.35	80.82	1540.77	0.110	185 ± 5
	2–6 µm	4.17	29.46	83.08	1746.86	0.137	174 ± 4
3589	< 2 µm	5.69	44.16	89.42	2792.81	0.215	190 ± 4
	2–6 µm	4.19	32.82	95.18	6133.54	0.486	191 ± 4

nificant amounts of chlorite that could have been formed together with the younger fine-grained illite. No detectable age difference could be attributed to the Vindelician Keuper samples (3537, 3538) relative to that of the Nordic Keuper sample (3539).

Diagenetic effects by burial were probably relatively unefficient in these rocks, as they were never buried to depths more than a few 100 m (PETERS, 1964). Despite of this shallow burial, the > 0.2 µm size fractions yield ages between 145 and 177 Ma. HUNZIKER et al. (1986) even found

an age as low as 118 ± 8 Ma for the < 2 µm fraction of a similar sample, which we may adopt as a maximum age for the hydrothermal event that caused the formation of very fine-grained illite in the investigated clay fractions. Alternatively, the fine-grained illites may have behaved as open systems with respect to the K–Ar system during long periods of time. This latter behavior has been critically examined by CLAUER and CHAUDHURI (1995), and it may only be considered when the ambient temperature remained close to the formation temperature of the illites.

Furthermore, this hypothesis does not explain the observed lath-type particles (Fig. 3a), which suggest at least two episodes of illite formation.

The data points do not plot along straight lines in the isochron $^{40}\text{Ar}/^{36}\text{Ar}$ vs $^{40}\text{K}/^{36}\text{Ar}$ and ^{40}Ar rad. vs ^{40}K diagrams. The smallest size fractions (< 0.1 and $< 0.2 \mu\text{m}$) tend to scatter along a line with a slope giving a reasonable age of 212 Ma but with a negative y-intercept of -350 (Fig. 5a) which is clearly indicative of a mixing line as discussed by CLAUER et al. (1995).

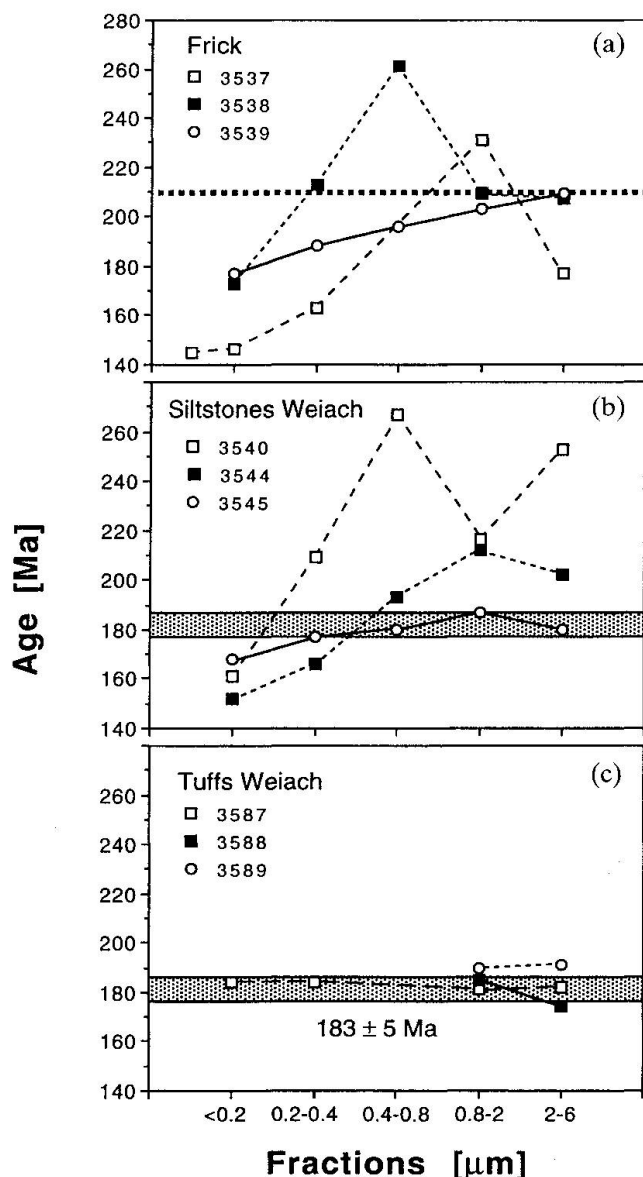


Fig. 4 Apparent K-Ar ages of the analyzed clay fractions: rocks from the quarry of Frick (top), and siltstones (center) and tuffs (bottom) from the Weiach borehole. The mean K-Ar age of is 183 ± 5 Ma for fractions $< 0.2 \mu\text{m}$ to $2-6 \mu\text{m}$ from the tuff sample 3587 (bottom) is taken as reference age for the proposed hydrothermal event. The broken line in the top diagram (Frick) approximates the age of sedimentation of the Keuper strata.

Siltstones from Weiach well (see Fig. 4b)

The K-Ar ages obtained on the different size fractions of the Weiach siltstone samples are significantly lower than the depositional age of 298 Ma (SCHALTEGGER and CORFU, 1994), and also lower than the first deep burial at about 260 Ma, according to the evolutionary model of KEMPTER (1987). The maximum age span between the finest and the coarsest fractions decreases towards deeper samples and may be interpreted with decreasing influence of a detrital component relative to the authigenic one. Sample 3540, buried at 1348.02 m, yields an age range of 267 to 161 Ma, compared to sample 3545 buried at 1959.87 m which yields a relatively consistent value of 181 ± 4 Ma for particle sizes $> 0.2 \mu\text{m}$. This latter age is very similar to that of the interlayered ash tuffs. The $< 0.2 \mu\text{m}$ fractions of the three siltstone samples range narrowly between 152 and 168 Ma, which might be considered as the maximum age for the latest hydrothermal overprint of these rocks.

The size fractions of the three siltstones yield striking linear relationships between K-Ar ages and K concentrations (Fig. 5b), favouring the idea of mixing old K-depleted sheet silicates with young K-enriched illite. The resulting linear arrays in isochron or Harper diagrams are, therefore, mixing lines. Sample 3545 yields the highest K concentrations, but has also high contents of kaolinite. The K-rich mineral phase is probably a well-crystallized illite with K contents clearly above 7%. The mixing of kaolinite and illite in sample 3545 does not affect the age (except for $< 0.2 \mu\text{m}$). On the other hand, the increasing content of kaolinite with increasing age and grain size in the samples 3540 and 3544 suggests the occurrence of an older generation of illite contemporaneous with kaolinite. These samples (3540 and 3544) do, furthermore, provide no evidence for a 180 Ma-old activity.

Tuffs from Weiach well (see Fig. 4c)

The three samples of yellowish ash tuffs recovered between 1432.26 m and 1586.52 m yield consistent ages of 174–191 Ma. Sample 3587 yields a mean age of 183 ± 5 Ma for the < 0.2 to $2-6 \mu\text{m}$ fractions, which is identical to that of the $< 2 \mu\text{m}$ fraction of sample 3588. The $2-6 \mu\text{m}$ fraction of this latter sample is lower in age, which could be due to aggregates consisting of very small and younger particles of $< 0.2 \mu\text{m}$ size. Sample 3589 is slightly older at 190 ± 4 Ma. The samples are min-

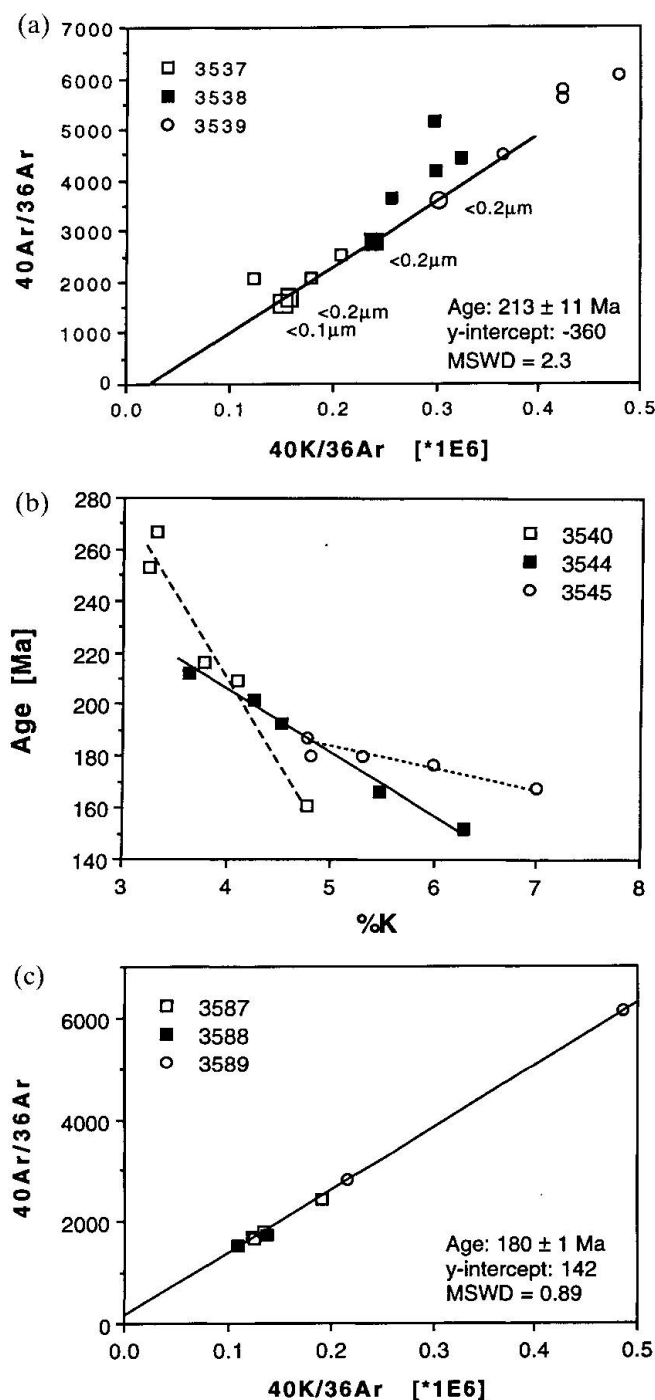


Fig. 5 (a) $^{40}\text{Ar}/^{36}\text{Ar}$ vs $^{40}\text{K}/^{36}\text{Ar}$ (isochron) diagram for the samples from the Frick quarry. Best-fit line of 212 Ma is defined by the < 0.1 and < 0.2 μm fractions of the three samples, has a highly negative y-intercept and is interpreted as a mixing line.

(b) Age vs % K diagram for the size fractions of three siltstone samples from the Weiach drillhole.

(c) Isochron diagram for sample 3587, tuff from the Weiach drilling.

erologically very homogenous, consisting of up to 93% I/S mixed layers with less than 5% smectite, and subordinate kaolinite (Tab. 2).

The K–Ar isotopic data of sample 3587 (together with 3589) show a linear array in an isochron diagram (Fig. 5c), yielding an age of 180 ± 1 Ma and an initial $^{40}\text{Ar}/^{36}\text{Ar}$ intercept close to the air value. This line is probably a mixing-line between air-derived and radiogenic argon, as the four fractions exhibit no variations in the K concentrations. We are, therefore, inclined to propose the mean K–Ar age of sample 3587 of 183 ± 5 Ma as the age of illite formation in the tuffs.

Discussion

Data from Frick quarry (3537 to 3539)

The K–Ar data suggest that radiogenic Ar was lost from at least 300 Ma old detrital micas. As partial resetting of the Ar system of mica-type minerals is generally induced by Ar loss due to the increase of the ambient temperature, the extent of the loss may on the other hand depend on the mineral restructuration during diagenesis (ARONSON and HOWER, 1976). The lath-type illites shown in figure 3a indicate that new mineral growth occurred during diagenesis of these sediments. The rocks were obviously never deeply buried, a result that is supported by mineralogical data of HUNZIKER et al. (1986), who found 1Md sheet silicates with ca. 25% expandable layers in similar samples of the same outcrop.

In conclusion, no evidence can be derived for the occurrence of an 180 Ma-old hydrothermal activity; it seems that only volume diffusion of radiogenic ^{40}Ar out of the detrital micas and possibly also the newly formed clay minerals occurred. This claim is supported by the fact that the linear array of the < 0.2 μm fractions in an isochron diagram is fortuitous (Fig. 5a), because the data points of the same samples do not exhibit a linear relationships in the ^{40}Ar rad.– ^{40}K diagram. At this point we can state that any K–Ar age derived from slopes of linear arrays or from individual model ages of the different size fractions of the Frick samples are purely fortuitous, due to the combination of inherited detrital components, new authigenic growth and volume diffusion. Authigenic growth of illite-type minerals may be assumed, but no argument in favour of a post-depositional hydrothermal overprint emerges presently from our data.

Data from Weiach tuffs (3587 to 3589)

Volcanic tuffs are known to bear no reworked detrital components and are, therefore, best suit-

ed for checking the geological significance of illite K-Ar ages of associated shales (REUTER, 1987). The single-generation mineral assemblage in these rocks is evidenced by TEM observations (Fig. 3c), and the occurrence of a grain-size independent age plateau around 183 Ma may be assigned to an episodic event imprinted in the tuffs. We assume that this 183 Ma-old event caused the formation of the illite-rich I/S mixed layers at the expenses of a K-poor predecessor phase, probably of smectite type. The pH- a_{K^+} conditions prevailing during burial diagenesis seem to have favoured the formation of kaolinite in the overlying sandstones of Permian and Triassic ages (BLÜM, 1987; RAMSEYER, 1987). The 183-Ma-old pulse of K-rich hydrothermal fluids might have caused almost quantitatively the replacement of kaolinite and/or smectite by illite. No evidence for younger thermal overprinting, recrystallization or post-formational volume diffusion of Ar can be deduced from the K-Ar results, as the finest fractions ($< 0.2 \mu\text{m}$) do not yield younger ages than the coarser ones.

Data from Weiach siltstones (3540, 3544, 3545)

As discussed above, the siltstones contain detrital material which could have been older than 300 Ma, as it is the case for the samples of Frick quarry. The age pattern of figure 4b, therefore, results from mixing of detrital micas and authigenic illite-type minerals with a probable age of 183 Ma. The low scatter of the K-Ar apparent ages of the 0.2 to 6 μm fractions of sample 3545 suggests that the components of these fractions were almost completely rejuvenated by the 183-Ma-old hydrothermal event. The thermal model of KEMPTER (1987) suggests maximum temperatures of ca 180–200 °C 265 million years ago for the base of the Carboniferous sediments. This temperature range is reasonable if compared to a theoretical 210 °C temperature given by the Ar diffusion code of HUON et al. (1993), if one assumes an age of 300 Ma for the detrital end member and an age of 180 Ma for the authigenic end member.

The degree of hydrothermal rejuvenation seems also to be dependent on burial depth: the K-Ar age trend of the deepest sample 3545 is almost flat at about 180 Ma, whereas that of the less buried samples is of a hump type. Fluid circulation along subhorizontal faults in the basal part of the NPT, or along the sediment-basement interface, may explain the present result. We can assume that intensive illitization along fluid migration pathways created extremely high il-

lite/kaolinite ratios in the clay fraction. This assumption is corroborated by highly variable illite/kaolinite ratios in the deeper part of the NPT, below 1700 meters depth (Fig. 6). Illitized zones may also be detected above 1700 meters, but their number and the extent of mineral transformation seems to be smaller.

The hydrothermal activity at 180 Ma is considered to be an important time-marker for the volume of the whole NPT fillings, because it overprinted different lithologies (siltstones and tuffs) at different depths. The thermal model of KEMPTER (1987) does not assume the occurrence of a thermal pulse at this time. Circulation of ca. 210 °C hot fluids at the base of the sediment pile certainly had an impact on parameters that are used for the thermal modelling of sedimentary basins, such as porosity, clay mineral composition (illite/smectite ratios) or fluid inclusion composition. It even may have influenced the degree of maturity of the organic matter with increasing depth, R_{max} values currently ranging between 0.7% (top Permian), and 1.4% (bottom Carboniferous; KEMPTER, 1987).

The fact that the smallest size fractions of the Weiach siltstones ($< 0.2 \mu\text{m}$) yield systematically apparent K-Ar ages below 183 Ma, suggests that the samples were subjected to some kind of post-formational volume diffusion.

CONTROL OF ILLITE FORMATION

SEM observations of whole-rock fragments emphasized that an extensive illite cementation phase filled almost completely the pre-existing macroporosity. Different results favor a secondary post-compaction formation of this illite: (1) the tuff age data indicate a complete and mono-episodic illitisation at 183 Ma, and (2) the findings of BLÜM (1987) and RAMSEYER (1987) evidenced diagenetic formation of kaolinite in overlying Permian and Triassic sandstones from which illite could have been derived (Tab. 2).

GAUPP et al. (1993) and PLATT (1993) invoked migration of acidic fluids to be responsible for the authigenic formation of primary kaolinite/dickite in Rotliegende sandstones of northern Germany. Such acidic fluids formed by the maturation of organic matter in tectonically juxtaposed Westphalian coal measures which released large amounts of humic acids. These fluids caused concomitant kaolinite/dickite precipitation and K-feldspar dissolution, the latter enhancing the K activity in the fluids, and illite formation farther away from the Westphalian/Rotliegende contact, inducing cementation of the pore space along distinct fluid

migration planes. The temperature of illite cementation in the Rotliegende sandstones was suggested to be 60–115 °C at burial depths of 1.5–4 km (PLATT, 1993). MOSSMANN *et al.* (1992), on the other hand, described well crystallized authigenic illite-rich I/S mixed-layer minerals from Paris Basin and assumed a formation temperature of at least 150 °C, which might have been as high as 230 ± 20 °C, as recently shown by oxygen isotope determinations of the authigenic illite and the associated quartz overgrowth (CLAUER *et al.*, in prep.). These high temperatures are confirmed by the fact that expelling hydrocarbons needs about 160 °C according to HUNT (1979). This might have occurred about 260 Ma ago during maximum burial, as well as about 185 Ma ago during the proposed hydrothermal episode.

Kaolinite formation, K-feldspar dissolution, and illite cementation are therefore concurrent processes, depending on the a_{H^+} vs a_{K^+} relationship, which may follow each other in space and time. In the case of the Weiach siltstones, fluid flushing at 180 Ma could have caused intense K-feldspar dissolution and illite cementation. The latter depends on burial depth (see Fig. 6):

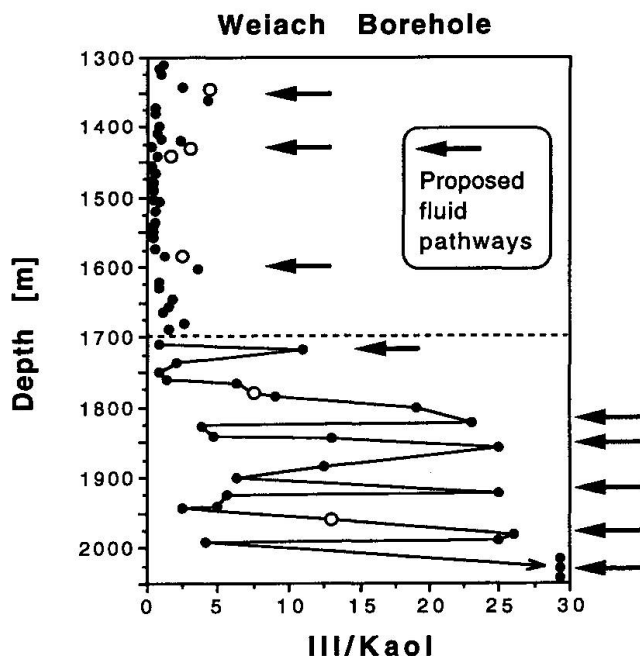


Fig. 6 Illite/kaolinite ratios of $< 2 \mu\text{m}$ clay fractions in Carboniferous and Permian strata of the NPT are shown in relation to borehole depth. The high-illite peaks are thought to indicate illitization of diagenetic kaolinite along distinct fluid migration pathways, mainly at depths below 1700 meters (data from MATTER *et al.*, 1988). Circles indicate samples analyzed for their K–Ar age.

sample 3545 from the lower part of the sediment series is most extensively illitized and shows the lowest porosity, the detrital memory being almost erased from framework components. Sample 3540, on the other hand, still exhibits lath-like low-temperature illites (Fig. 3a) and some preserved isotopic memory from detrital components in the fractions $> 0.2 \mu\text{m}$ (Fig. 4). The relationships in figure 6 suggest, moreover, the existence of subhorizontal, highly permeable discontinuities in the basal part of the NPT, along which the fluids migrated and caused illitization of the precursor clays.

The suggested occurrence of primary kaolinite is only corroborated by the observation of the questionable illite pseudomorphs after kaolinite booklets, mentioned earlier. The 300 Ma-old tuffs, however, originally consisted of volcanic glass that probably first altered to kaolinite and was then entirely illitized about 180 Ma ago. There is no question that the main illitization and cementation of (secondary) porosity in the investigated rocks took place at 180 Ma and not at 260 Ma during burial at maximum temperatures.

TRIASSIC-LIASSIC AGE DATA IN EUROPE

Many K–Ar age determinations in European sediments yielded ages of around 180–190 Ma (BONHOMME *et al.*, 1983; GAUPP *et al.*, 1993; LIEWIG *et al.*, 1987; MOSSMANN *et al.*, 1992; PLATT, 1993; ZWINGMANN *et al.*, 1994), whereas ages around 150 or 90–100 Ma only occur in some specific areas (Paris Basin, LIEWIG *et al.*, 1987; North Sea, LEE *et al.*, 1989). The period around 180–190 Ma is known to have been an important time of fault reactivation, which was probably linked to increased Kimmerian tectonic activity during opening of the Central Atlantic. It also marks the beginning of gas generation from Carboniferous coals in northern Germany and is a period of enhanced salt movement (Zechstein salt diapirs; discussion in GAUPP *et al.*, 1993). Fluid migration and hydrothermal activity were reported all the way between northern Germany and Morocco in sandstones (*op. cit.*), along faults (BROCKAMP *et al.*, 1987, 1994), and in ore deposits (BONESS, 1987; BONHOMME *et al.*, 1983; LANCELOT and VELLA, 1989; HAAK, 1993; LANCELOT and CLAUER, 1993; TOULKERIDIS *et al.*, 1993).

In the Helvetic domain of the Central Alps, the time from Upper Triassic to Upper Jurassic is characterized by lithospheric thinning along detachment faults, uplift of continental blocks and rifting in the Tethyan realm. During the Lower Jurassic, the shoulders of the incipient rift system

underwent a phase of strong uplift (LOUP, 1992; STAMPFLI and MARTHALER, 1990) and must have been characterized by an enhanced thermal gradient caused by the upwelling of hot fluids and by lithospheric detachment. These events correlate well in age with our 183 Ma-age of the Weiach tuffs.

Conclusions

No indications for a Mesozoic hydrothermal activity were found in Triassic strata (Keuper) from the Tabular Jura at Frick. The disturbed K-Ar isotope systematics can be assigned to diffusive loss of radiogenic argon out of poorly organized clay minerals.

Illitization processes in Stephanian tuffs and siltstones of the Northern Swiss Permo-Carboniferous Trough (NPT) at Weiach are not controlled by burial diagenesis in Upper Permian times, but by a hydrothermal alteration that occurred 120 Ma after sedimentation. A homogeneous generation of illites with an age of 183 ± 4 Ma was found in tuffs and is also present in the deepest siltstone sample. In two higher siltstone samples the analyzed fractions comprise old (diagenetic) illite beside I/S mixed-layers, kaolinite and some chlorite and yield intermediate apparent ages depending on grain size.

Hydrothermal fluids are shown to have preferably penetrated into permeable strata at the base of the NPT, creating narrow illitized zones. The 183 Ma fluid migration is suggested to be a pervasive event for the whole pile of sediments at Weiach and possibly affected critical parameters for the reconstruction of basin evolution. No evidences have been found for a younger (hydro-) thermal event; K-Ar ages younger than 180 Ma have, therefore, to be interpreted by post-formational Ar loss.

Acknowledgements

The technical staff of the Centre de Géochimie de la Surface contributed considerable work to this study. The help of J.L. Cézard, Ph. Karcher, G. Krempf, D. Million, G. Morvan, Rob. Wendling, R. Wendling and R. Winkler is kindly acknowledged. The National Cooperative for the Storage of Radioactive Waste (NAGRA, Wettingen) kindly provided sample material from the Weiach drill-cores. M. Mazurek and N. Waber, Bern, helped with sampling and with the identification of possible tuff layers. Help during sampling on a muddy day in the Frick quarry by M. Frey, and scientific contributions by W. Stern, both Basel, are highly appreciated. Comments of M. Frey, Basel, J.C. Hunziker,

Lausanne, and W. Winkler, Zürich, are highly appreciated.

This study was carried out while U.S. stayed at the Centre de Géochimie de la Surface in Strasbourg with a fellowship of the Schweizer Nationalfonds, whose financial support is kindly acknowledged.

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Manuscript received January 20, 1995; minor revision accepted May 3, 1995.